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EXPERIMENTAL AND NUMERICAL ANALYSIS OF VISCOELASTIC BEHAVIOR OF EPOXY RESIN WITH SILICA FILLER BASED ON MASTER CURVE CONCEPT

The viscoelastic behavior of polymers is normally studied by chemical engineers to monitor the progress of various molecular phenomena, such as: chain scission (driven by oxidative degradation and hydrolysis), viscous flow, as well as molecular relaxation. Mechanical engineers usually enter the arena of viscoelastic modeling when analyzing the damping properties of the materials, or when considering energy dissipation mechanisms. Available viscoelastic models however, allow for more detailed studies, which cover the response of polymers subjected to a complex load history, with different thermo-mechanical conditions. It is especially important when strains and stresses in real, industrial products of high quality must be investigated. In this paper, the experimental and numerical results of the complex viscoelastic behavior of the CY228 epoxy system are presented. The concepts of time-temperature superposition and the Master Curve, as well as the generalized Maxwell model and WLF equation are recalled, and applied to a stress-strain analysis of the composite under consideration. It was shown that detailed measurements of viscoelastic properties allow for very accurate modeling of the composite mechanical response.

Keywords: epoxy resin, viscoelasticity, Prony series, time-temperature superposition

EKSPERYMENTALNA I NUMERYCZNA ANALIZA PROCESÓW REOLOGICZNYCH W ŻYWICY EPOKSYDOWEJ Z WYPEŁNIACZEM MINERALNYM W OPARCIU O KRZYWĄ WIODĄCĄ

Reologia polimerów jest obszarem badań chemików zwykle, gdy zachodzi konieczność monitorowania szybkości różnych procesów molekularnych, np.: degradacji materiału (spowodowanej utlenianiem bądź hydrolizą), zmian lepkości, czy mobilności łańcuchów polimerowych. Mechanicy zwykle zajmują się wiskoelastyką materiałów, gdy mają do czynienia z tłumieniem wibracji bądź hałasu lub gdy studiują różne metody dyssypacji energii. Warto jednak zauważyć, że modele reologiczne pozwalają także na analizowanie zachowania się materiałów w przypadku obciążeń występujących w złożonych warunkach cieplno-mechanicznych o skomplikowanej historii obciążeń. Możliwość ta nabiera szczególnego znaczenia w przypadku rozpatrywania rzeczywistych produktów, od których wymaga się bardzo wysokiej jakości. W artykule przedstawiono eksperymentalne i numeryczne wyniki studiów nad reologią żywicy epoksydowej CY228. Przywołano superpozycję czasu i temperatury, koncepcję Krzywej Wiodącej oraz uogólniony model Maxwella. Modele te zastosowano w analizie odkształceń i naprężeń. Wskazano metodykę pozwalającą na bardzo dokładny opis zachowania się materiału kompozytowego.

Słowa kluczowe: żywica epoksydowa, reologia, szereg Prony, superpozycja czasu i temperatury

INTRODUCTION

Thermosetting materials are frequently used as insulation in various electrical apparatus, including voltage and current transformers, sensors and bushings. In these products, an electrical barrier is formed by an epoxy resin with a mineral, mostly silica, filler. Such composites offer not only very good electrical properties, but also superior mechanical and thermal performance. These materials however, exhibit very complex mechanical response to structural and thermal loads, driven mainly by their strong viscoelastic properties.

Components made of epoxy resins are normally processed by reactive molding technology, which exposes these products to various thermal and chemical conditions [1]. When a cast epoxy resin starts to polymerize during the production process, the internally developed loads tend to deform the product and give rise to residual strains. The restrained deformations generate internal stresses which may have a damaging effect on the product quality. For this reason, detailed knowledge about stress-strain behavior, especially for viscoelastic materials, is of great importance.

This work focuses on a study of the viscoelastic response of a composite based on Huntsman's CY228 epoxy system with a silica filler. The theoretical background for the mechanical behavior of such a polymer is first recalled. The concepts of time-temperature superposition and the Master Curve are given. They both have been applied practically in Dynamic Mechanical Analysis to define the parameters of the generalized Maxwell model. The influence of temperature was introduced by the WLF equation. Finally, the numerical example was calculated by means of analytical and FEM methods in order to present the applicability of the developed approach.

CLASSICAL VISCOELASTIC MODELS

When analyzing the mechanical behavior of polymeric materials, their viscoelactic characteristics come to the front. To permit a study on creep and relaxation processes, spring and dashpot elements are frequently used [2, 3]. Both elements can be joined together to develop proper models of viscoelastic behavior. If placed in a series they form the Maxwell model (Fig. 1a), if combined in parallel - the Kelvin (or Voigt) model is arranged (Fig. 1b.)
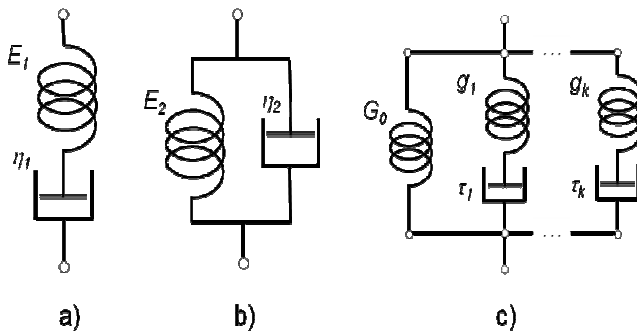

Fig. 1. a) Maxwell model, b) Kelvin model, c) generalized Maxwell model

Rys. 1. a) model Maxwella, b) model Kelvina, c) uogólniony model Maxwella

Since the Maxwell model is a combination of a spring and dashpot in a series, the total strain on the model is just the sum of the strains of its components. Based on that, one can easily describe the stress during a relaxation experiment as:

$$\sigma(t) = \varepsilon_0 E e^{-t/\tau_1} \qquad (1)$$

where τ_1 is the relaxation time, defined as the ratio between the dashpot viscosity, η_1 and the stress value, σ. On a molecular scale, the relaxation time of the polymer indicates the time required for a certain proportion of the polymer chains to respond to the external stress by thermal motion. The relaxation time can also be a measure of the time required for a chemical reaction to take place.

Based on (1), one can also state that because the stress is decreasing in the relaxation experiment under constant strain, the Young modulus must thus change over the time:

$$E_{REL}(t) = E_0 e^{-t/\tau_1} \qquad (2)$$

In many practical cases, it is more convenient to measure the shear motions of the body, $G_{REL}(t)$, as a response to the applied torque moment. In this case, eq. (2), the Kirchhoff modulus replaces the Young modulus, but relaxation time τ_1 remains the same (which is true for thermo-rheologically simple materials, TRS).

Similarly, when analyzing a creep experiment at constant stress, it can be shown that for the Kelvin element:

$$\varepsilon(t) = \frac{\sigma_0}{E}\left(1 - e^{-t/\tau_2}\right) \qquad (3)$$

where τ_2 is the retardation time, defined as η_2 / E.

The ratio of the time-varying strain to the constant stress is called (creep) compliance C:

$$C_{CRP}(t) = \frac{\varepsilon(t)}{\sigma_0} \qquad (4)$$

When comparing relaxation and creep experiments, one may find that they equally manifest the same molecular mechanisms, but in general $E_{REL}(t) \neq 1/C_{REL}(t)$. The relaxation response moves toward its equilibrium state more quickly than the creep response. Both times, the relaxation and the retardation can be used as the very first approximation of the time period needed to complete about a half of the analyzed phenomenon.

A real polymer however, does not relax (creep) with a single relaxation (retardation) time. Shorter molecular segments relax much faster than long ones. This leads to an extension of relaxation times, thus more complex models are required. Modern FEM packages take advantage of the generalized Maxwell model (known also as Wiechert model, Figure 1c), which is formed by a set of Maxwell elements and a spring added in parallel [4]. Mathematically, this configuration is described by the Prony series. The relaxation modulus of the material depicted by this model has the form of equation (5), and is schematically shown in Figure 2:

$$G(t) = G_0[1 - \sum_{i=1}^{N} g_i(1 - e^{-t/\tau_i})] \qquad (5)$$

where: G_0 is the value of the instantaneous modulus for the material (which corresponds to the glassy state for polymers), and G_∞ is the long-term modulus (which characterizes the rubbery state, as $t \to \infty$).
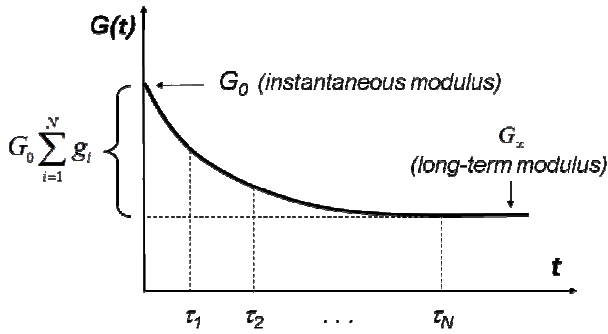
Fig. 2. Viscoelastic behavior as predicted by generalized Maxwell model in stress relaxation experiment

Rys. 2. Moduł sprężystości postaciowej podczas testu relaksacji naprężeń - zgodnie z uogólnionym modelem Maxwella

MEASURING VISCOELASTIC PROPERTIES

There are several methods to define the viscoelastic properties of polymers. In a stress relaxation experiment for example, the sample is rapidly stretched to the required length, and the stress is recorded as a function of time. It can be easily conducted on any displacement-controlled, tensile testing machine. The length of the sample remains constant, so there is no macroscopic movement of the body during the experiment. Creep experiments are conducted in the inverse manner. A constant stress is applied to a sample, and its dimensions are recorded as a function of time.

Normally, the temperature is also kept constant during a single measurement, but several different experiments can be conducted at various temperature levels. It was observed however, that the stress relaxation curves generated for TRS materials at diverse temperature levels have the same S-shape on a log-log scale, Figure 3. The curves are only shifted horizontally [5, 6], by the so-called shift factor, a_T.
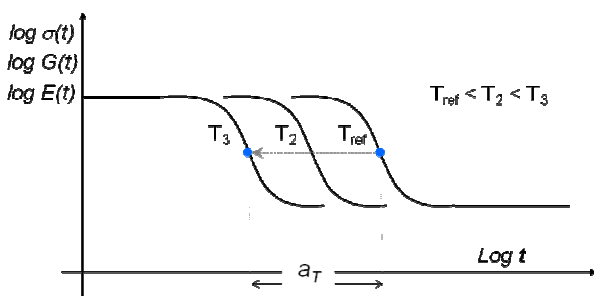

Fig. 3. Relaxation curves on log-log graph, for various temperatures

Rys. 3. Krzywe relaksacji w układzie podwójnie logarytmicznym dla różnych temperatur

This principle, known as the time-temperature superposition, simply states that the relaxation modulus at any given temperature, $G(T)$, can be derived if the relaxation modulus at the reference temperature, $G(T_{ref})$, and horizontal shift factor a_T, are known. The temperature shift factor may be expressed in the form of the commonly used Williams-Landell-Ferry (WLF) equation [7]:

$$\log a_T(T) = \frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}} \qquad (6)$$

where T is in Celsius, and C_1 and C_2 are material constants. If T_{ref} is chosen as the glass transition temperature, T_g, for many polymers $C_1 = 17.4$ 1/K and $C_2 = 51.6$ K. The original WLF paper [8] developed this relation empirically, but rationalized it in terms of the free-volume concept.

The time-temperature superposition also allows for splitting one, long-lasting experiment carried out at a single temperature, and conducting several much shorter tests at various temperatures. In this case, the Master Curve is created by shifting individual test result curves by means of the respective shift factors (Fig. 4).
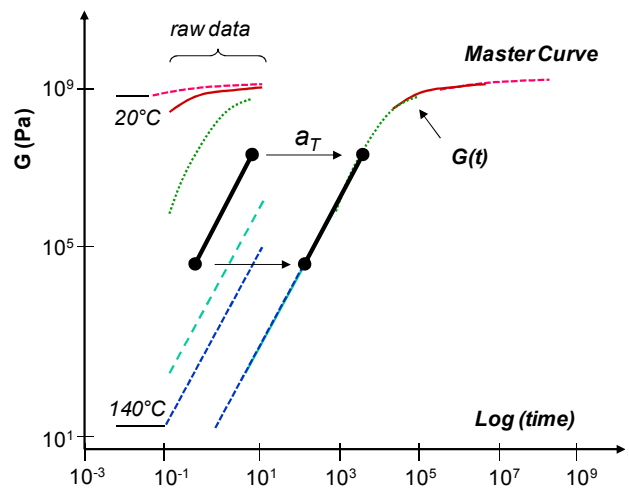

Fig. 4. Concept of Master Curve creation

Rys. 4. Zasada tworzenia Krzywej Wiodącej

For practical reasons, it is often more convenient to measure the modulus of thermosetting material as a function of frequency (and temperature), instead of time (and temperature) [9]. Using Dynamic Mechanical Analysis (DMA), storage $G'(\omega)$ and loss moduli $G''(\omega)$ can be approximated by a sum of the Maxwell elements:

$$G'(\omega) = G_0\left[1 - \sum_{i=1}^{N} g_i\right] + G_0 \sum_{i=1}^{N} \frac{g_i \omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \qquad (7)$$

$$G''(\omega) = G_0 \sum_{i=1}^{N} \frac{g_i \omega \tau_i}{1 + \omega^2 \tau_i^2} \qquad (8)$$

where ω is the radian frequency; τ_i and g_i are the same factors as in equation (5), and they describe the ith relaxation time and relaxation factor, respectively. Based on this statement, the viscoelastic parameters defined by the DMA experiment in the frequency domain (7)-(8) may be used in the definition of the time domain viscoelastic model (5).

Having the viscoelastic material characterized by the τ_i and g_i factors, one can illustrate the constitutive behavior of the material by considering a relaxation test, in which a strain, γ, is suddenly applied at time s to a specimen, and then is held constant for a long time. If the beginning of the experiment is taken as zero time, and the strain is maintained ($\gamma' = 0$), the responding shear stress $\sigma(t)$ is:

$$\sigma(t) = \int_0^t G(t-s)\dot{\gamma}(s)ds = G(t-s)\gamma \qquad (9)$$

One may notice, that the Kirchhoff modulus used in (9) is the function of two times: t - the actual (wall-clock) time and s - the reduced time (also called material time), at which the load was applied. Generally, these two times do not have to run at the same speed. Since the temperature affects the "material time", thus at higher temperatures the material relaxes faster in the wall-clock time. The relation between the actual (t) and reduced (s) times is defined through the horizontal shift factor:

$$\frac{ds}{dt} = \frac{1}{a_T(T)} \qquad (10)$$

The introduction of the Master Curve and the time-temperature superposition concepts into the DMA measures allow for complete characterization of the viscoelastic properties of the polymer under study.

VISCOELASTIC PROPERTIES OF CY228 EPOXY RESIN

The material investigated in this paper is a commercially available epoxy resin with a silica filler, CY228, supplied by the HUNTSMAN company. To obtain the viscoelastic behavior of the fully-cured epoxy resin, small material samples were cured at 120ºC for 4 hours. Next, the DMA measurements were made in the shear mode with use of an ARES instrument (by Rheometric Scientific). As many as 16 temperatures - ranging from –60 to 160°C, and 12 radial frequencies - between 0,01 and 50 rad/s, have been set in the performed experiments.

The dynamic moduli (storage and loss) for the tests conducted at various temperatures are depicted in Figure 5 (limited data is shown only, for clarity).

Based on the achieved DMA results, the Master Curve has been constructed by shifting the curves in Figure 5 by means of shift factors. Two reduced curves for respective moduli were created according to (7)-(8), using 80°C as the reference temperature. The values of shift factors a_T, as well as relaxation times and relaxation weights, τ_i and g_i were found by the optimization algorithm aiming to minimize an error between the measured and modeled curves. A set of 24 parameters of τ_i and g_i was used in order to obtain data best suited

to the given model (not provided in this paper for space limitation reasons).
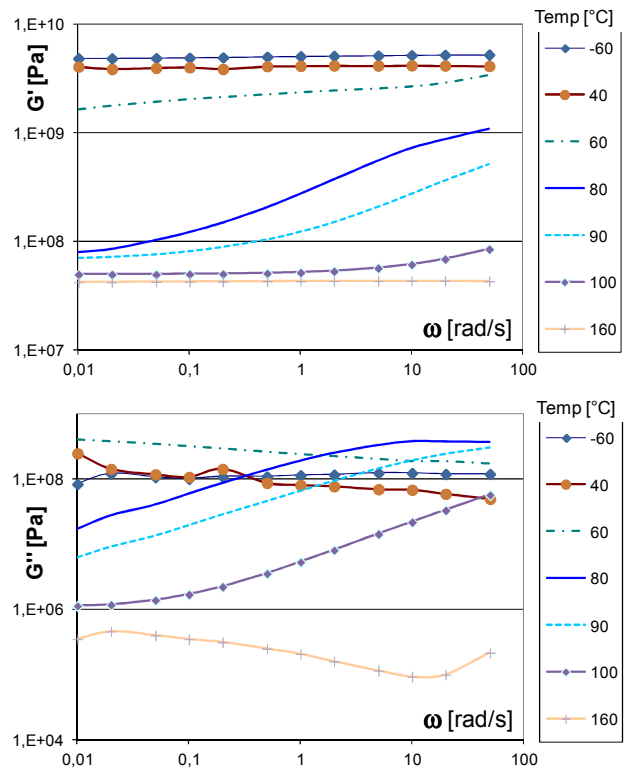

Fig. 5. Characteristic of storage $G'(\omega)$ and loss moduli $G''(\omega)$ vs. frequencies, for different temperatures [°C]

Rys. 5. Charakterystyki modułów zachowaczego $G'(\omega)$ i stratności $G''(\omega)$ dla różnych temperatur [°C]
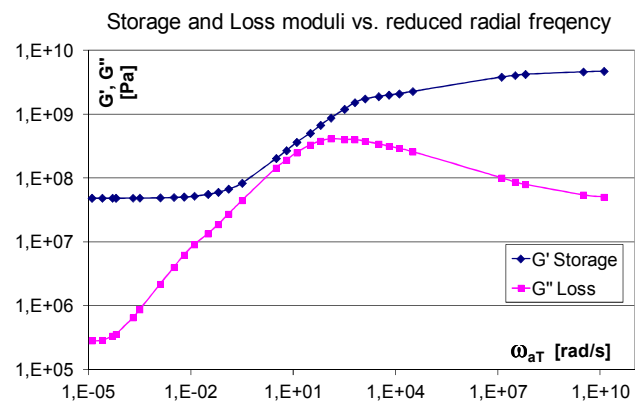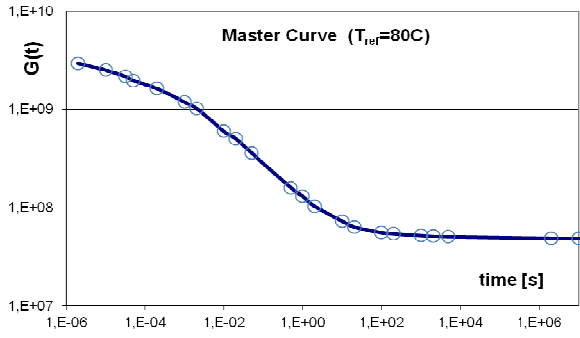

Fig. 6. Master curves in frequency domain

Rys. 6. Krzywe wiodące w dziedzinie częstotliwości

Finally, the Master Curve in the time domain, as characterized by equation (5), is given in Figure 7.

In a glassy state (or at the lowest temperatures) the Kirchhoff modulus shows instantaneous behavior, and reaches the level of $G_0 = 4.77E9$ Pa. As the testing temperature is increased (or time passes) the modulus drops, and in a rubbery state it is found to be around $G_\infty = 4.9E7$ Pa. The drop in the modulus between the glassy and rubbery states by about two orders of magnitude is very typical for many epoxy based systems.

Fig. 7. Master relaxation curve in time domain, T_{ref} = 80°C.
Rys. 7. Krzywa wiodąca w dziedzinie czasu, T_{ref} = 80°C.

The parameters of the WLF model were estimated to be C_1 = 15.74 1/K, C_2 = 97.67 K. One can notice that about 100 (1E2) seconds at the temperature of 80°C is enough to relax the material almost fully. However, if the temperature is lowered, to for example 60°C, this time elongates to about 1E6 seconds (since shift factor a_T moves the Master Curve about 4 decades).

NUMERICAL EXAMPLE

To present how the viscoelastic properties can be used practically in numerical calculations, one can analyze a simple creep experiment in which the tensile stress, σ of 30 MPa is applied to the sample, maintained for t_1 = 100 s, and finally released. The total strain, $\varepsilon(t)$, can be calculated based on (3)-(4), and compliance $C(t)$ is defined by the author as:

$$C(t) = \begin{cases} \dfrac{1}{E_0}\left(1 - \dfrac{\sum\limits_{i=1}^{N} g_i}{1 - \sum\limits_{i=1}^{N} g_i}\right)\left(1 - e^{-t/\tau_c}\right) & \text{for } t \leq t_1 \\[2em] \dfrac{1}{E_0}\dfrac{\sum\limits_{i=1}^{N} g_i}{1 - \sum\limits_{i=1}^{N} g_i}\left(e^{-(t-t_1)/\tau_c} - e^{-t/\tau_c}\right) & \text{for } t > t_1 \end{cases} \quad (11)$$

where retardation time τ_c is given by:

$$\tau_c = \sum_{i=1}^{N} \tau_i \frac{1}{1 - \sum\limits_{i=1}^{N} g_i} \quad (12)$$

and the viscoelastic strain component ε_{CE} is simply specified as:

$$\varepsilon_{CE} = \varepsilon(t) - \sigma_0 / E_0 \quad (13)$$

Assuming exemplary material data (E_0 = 3 GPa, τ_1 = 10s, g_1 = 0.5), the total strain is derived as: 0.019179 after 50 s; 0.019932 after 99.99 s, and 0.000815 after 150 s. Exactly the same values were achieved using the FEM method in the ABAQUS software package (Fig. 8) [4].
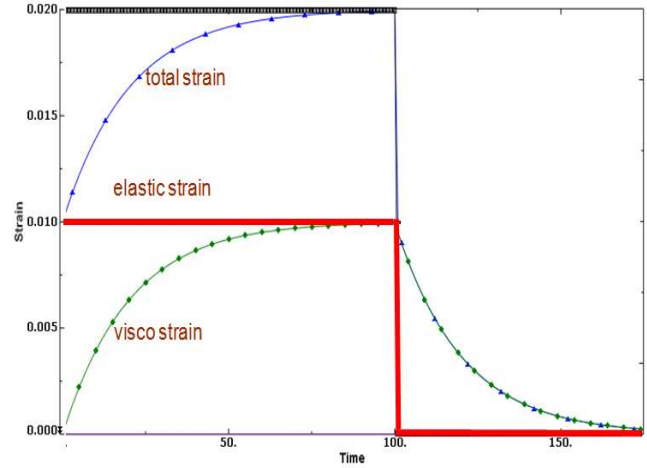

Fig. 8. Results of numerical simulations - strains
Rys. 8. Wyniki symulacji numerycznych - odkształcenia

One may also prove that the provided viscoelastic model works correctly for rate-dependent loads, and in the case of a simple Wiechert model consisting of one Maxwell arm, it is equivalent to the first-order ordinary differential equation:

$$\tau_1 \dot{\sigma} + \sigma = \tau_1\left(E_0 + g_1\right)\dot{\varepsilon} + E_0 \varepsilon \quad (14)$$

Introducing more Maxwell arms into the model leads to the n-order differential equation.

CONCLUSIONS

Analysis of the mechanical behavior of an epoxy based product during its manufacturing process is a complex task, since the viscoelastic properties of the analyzed composite play an important role. The load history, as well as the temperature profile during the production stages have an influence on the final 4 product quality. However, contemporary measurement techniques, such as DMA, and developed modeling concepts (Master Curves, Prony series) allow for very accurate analysis. The methodology presented in the paper confirmed, that the thermo-mechanical behavior of compound composites can be successfully predicted, if the numerical models are supported by an appropriate measurement program. The performed experiments should basically cover the dynamic mechanical analysis conducted at the near glass temperature, and within the recommended range of ± 50°C. Based on these results, the Master Curve can be generated in the frequency domain and recalculated into the time domain. This serves as a basis for a constitutive stress-strain relation, which also includes stress- and strain-dependent effects. The temperature dependence can be easily introduced by the WLF equation. The other dependencies (moisture content, or UV, for example) can also be considered if a modified relation for the shift factor is established.

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