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Temperature-frequency-dependent mechanical properties model of epoxy resin and its composites

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ABSTRACT

Temperature-frequency-dependent dynamic mechanical properties of epoxy resin and glass/epoxy composites were studied at different loading modes by dynamic mechanical analysis. An improved temperature-dependent storage modulus model was developed to describe the storage modulus of the epoxy resin and glass/epoxy composites. A new and simple loss modulus model including two specific physical parameters was also developed. In addition, a model that can describe the temperature-frequency-dependent mechanical properties was established by combining the storage modulus model or loss modulus model with the Arrhenius equation. All of the model predictions showed very good agreements with the experimental results.

1. Introduction

Polymer matrix composites (PMCs) are widely used in aerospace, automotive, and civil engineering structures due to their outstanding mechanical properties [1]. One disadvantage of these materials is that their stiffness and strength decrease significantly in the range of the glass transition temperature [2]. To design PMCs, determining the relationship between temperature and mechanical properties in the full range of transition temperatures is important.

Many researchers have investigated the relationship between temperature and dynamic storage modulus [3–10]. Havriliak and Negami [3] modeled the dynamic mechanical behaviors of polymers in the frequency domain (named as HN model). Some studies [4,5] used the HN model to describe the temperature-dependent storage modulus by introducing an Arrhenius-type relationship between relaxation time and temperature. Bai et al. [6] modeled the temperature-dependent modulus using an Arrhenius-type equation. Mahieux and Reifsnider [7,8] suggested Weibull-type functions to describe the change in modulus over the full range of transition temperatures. Gibson et al. [9] presented a semi-empirical model that could describe the properties over the transition from the glass to rubber state. Recently, Guo et al. [10] proposed a simple temperature-dependent model that could be used to describe dynamic storage modulus and static flexural modulus. Among these models, some employing complicated expressions [3–6] could predict the dynamic storage modulus in the full temperature range, while others with simple forms [7–10] showed excellent agreement with experimental data for the glass transition region and rubber state.

Some researchers have also studied changes in the loss modulus of a polymer with changing temperature [4,11–13]. Szabo and Keough [4] used the HN model and Arrhenius relationship to describe the temperature-dependent loss modulus at a fixed frequency. Some researchers [12,13] studied the dynamic mechanical properties of polymers or composites by the semi-empirical FK model [11]. Nevertheless, these two models predict a vanishing value of loss modulus in the glass and rubber states, resulting in differences between the model predictions and experimental results in the two states.

In this paper, new models were developed to describe the progressive changes in the storage modulus and loss modulus of epoxy resin and glass/epoxy composites under elevated temperatures at a fixed frequency. By combining them with the Arrhenius equation, the new models were extended to describe the temperature-frequency- dependent dynamic modulus. The

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theoretical results were compared with corresponding experimental results.

2. Theory of dynamic mechanical analysis

2.1. Basic principles of dynamic mechanical analysis

Dynamic mechanical analysis (DMA) [14] can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force. The modulus measured in DMA is, however, not exactly the same as the Young's modulus of the classic stress–strain curve shown in Fig. 1. Young's modulus is the slope of a stress–strain curve in the initial linear region. In DMA, the complex modulus (E^*), storage modulus (E'), and loss modulus (E'') are calculated from the material response to the sine wave shown in Fig. 2.

The complex modulus E^* is the ratio of the stress amplitude to the strain amplitude and represents the stiffness of the material:

$$E^* = \frac{\sigma}{\varepsilon} = E' + E''i. \quad (1)$$

The real part of the complex modulus is the storage modulus E' which is determined by equation (2):

$$E' = |E^*| \cdot \cos\delta \quad (2)$$

The loss modulus E'' which is the imaginary part of the complex modulus is defined as being proportional to the energy dissipated during one loading cycle:

$$E'' = |E^*| \cdot \sin\delta \quad (3)$$

The phase angle δ is the phase difference between the dynamic stress and the dynamic strain in a viscoelastic material subjected to a sinusoidal oscillation. The loss factor $tan\delta$ is the ratio of loss modulus to storage modulus expressed in equation (4):

$$\tan\delta = \frac{E''}{E'}. \quad (4)$$

2.2. Transition regions

Fig. 3 shows the typical variations of dynamic mechanical properties of a polymer with temperatures. As the temperature of a polymer is raised, it passes from a glass state to a rubber state. The transition from the glass to the rubber state is called glass transition or α transition which is accompanied by a rapid fall in storage modulus, and a peak in loss modulus and loss factor of the material. The glass transition is associated with large-scale motions of the polymer chains [15]. When the temperature continues to go down in the glass state, another peak appears in loss modulus and loss factor [16,17]. This transition is called β transition which is thought to be due to small scale motions of side chains [18]. Blow the β transition, a peak in loss modulus and loss factor at even lower temperatures can be found [19] and this is often referred to as the γ transition which is due to local motions of polymer segments involving at least four carbon atoms [20].

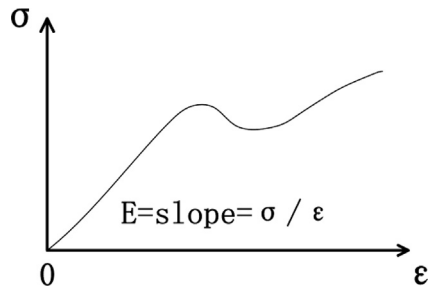

Fig. 1. Stress–strain curve.

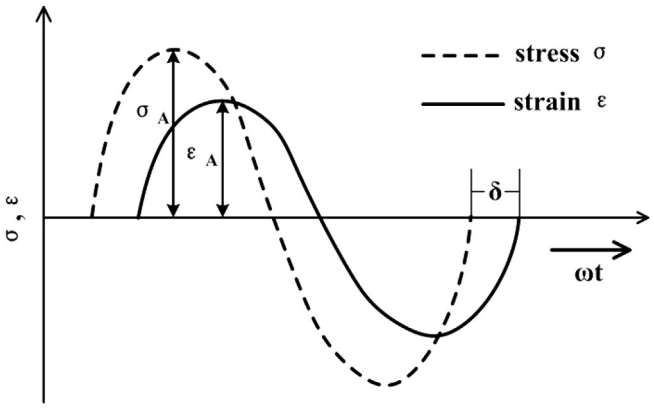

Fig. 2. Sinusoidal oscillation and response of a linear-viscoelastic material.

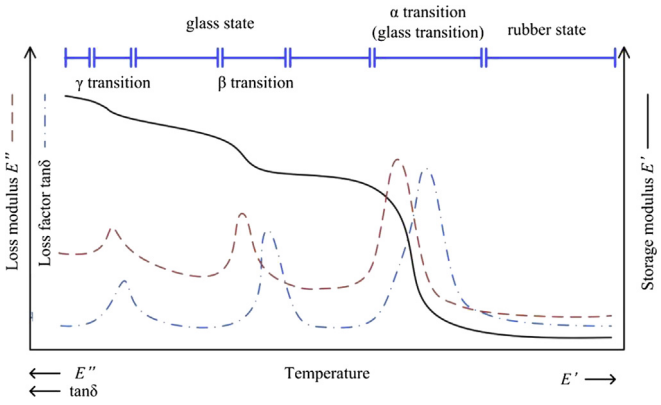

Fig. 3. Typical variations of dynamic mechanical properties with temperatures.

2.3. Methods of determining the glass transition temperature

Fig. 4 shows the different methods for determining T_g. The use of the storage modulus step to determine T_g is based on the standardized DSC method [21] and involves ascertaining the onset, end, and midpoint temperatures. Tangents are applied to the sections of the curve above and below the glass transition step. An inflectional tangent is applied to the step intersections with both these tangents at the extrapolated onset temperature T_{eig} and the extrapolated end temperature T_{efg}. The midpoint temperature T_{mg} is determined from the half-step height. T_g may also be defined as the temperature of the maximum loss modulus (E''_{max}) or maximum loss factor ($tan\delta_{max}$) [22]. These curves are easier to evaluate than the storage modulus step curves.

T_{eig} is the lowest, while T_g ($tan\delta_{max}$) is the highest among these T_gs demonstrated in Fig. 4. Thus in this paper, we focus on T_{eig}, T_{mg}, T_g (E''_{max}), and T_g ($tan\delta_{max}$), which represent the beginning (T_{eig}), middle (T_{mg} and T_g (E''_{max})), and the end (T_g ($tan\delta_{max}$)) of the glass transition region.