

KINETIC VISCOELASTICITY MODELING APPLIED TO DEGRADATION DURING CARBON CARBON COMPOSITE PROCESSING

By

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Kinetic viscoelasticity modeling has been successfully utilized to describe phenomena during cure of thermoset based carbon fiber reinforced matrices. The basic difference from classic viscoelasticity is that the fundamental material descriptors change as a result of reaction kinetics. Accordingly, we can apply the same concept for different kinetic phenomena with simultaneous curing and degradation. The application of this concept can easily be utilized in processing and manufacturing of carbon-carbon composites, where phenolic resin matrices are cured degraded and reinfused in a carbon fiber bed. This work provides a major step towards understanding complex viscoelastic phenomena that go beyond simple thermomechanical descriptors.

Keywords: Kinetics, Carbon Carbon, Composites Degradation, Processing

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1. INTRODUCTION

1.1 Carbon Carbon Composites

Carbon Carbon Composites (“CCCs”) have been established as superior materials for extremely high temperature applications, because of their unique thermal, chemical and mechanical properties. Conventional carbon fiber reinforced polymeric composites that undergo high temperature pyrolytic processing produce the CCCs. A particular structure of matrix – interphase – fiber is developed during this processing that results in unique properties for the CCCs [7-9, 11 and 12].

The degradation step, which is required for CCC manufacturing, has a great influence on the properties and the final performance of CCCs [4-9, 11 and 12]. Particularly, the matrix conversion from organic polymer into inorganic carbon, with a carbon fiber reinforced phase, is one of the most important controlling factors in the processing and property investigation.

1.2 Phenolic Resins

Phenolic resins’ suitability for impregnation processes results from their low viscosity as well as high char yield, which are the main characteristics for utilizing phenolic resins as matrix precursors for CCCs. Nevertheless, it has been reported that a certain amount of shrinkage takes place (20% and 50% linear and bulk shrinkage, respectively), during the highly exothermic curing reaction of phenolic resin, which also generates water as a byproduct [6 and 10]. Hence, the lamination process of the carbon fiber reinforced phenolic resin system is considered as both difficult and significant in terms of conventional lamination process parameters (time, temperature, pressure, tooling, prepregging, layup, and debulking, etc).

In composite degradation methodologies such as polymer/ceramic composite debinding and CCC carbonization, polymer degradation is considered as a main manufacturing process. During those processes, gaseous by-products are evolved by degradation reactions, causing weight loss in the polymer matrix, resulting in the potential for explosive delamination of composites, non-uniform degradation, and internal stress build up, etc. Thus, polymer weight – loss kinetics characterization is one of the key elements in manufacturing processes of high performance composite materials [3 and 13].

2. BACKGROUND

2.1 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (“DMA”) and the properties measured by this technique are widely used to study the behavior of viscoelastic materials. DMA is a very useful method for quality control and for correlations between structure and properties of polymeric composite materials. Furthermore, testing polymeric composites with DMA is complex as their dynamic mechanical properties are sensitive to fiber orientation as well as inhomogeneities in matrix cross-linking [25]. Dynamic mechanical measurements are also able to detect the presence of the interphase in glass– and carbon–fiber reinforced polymers [14, 19, and 25]. Utilizing frequency multiplexing, it is possible to calculate apparent activation energies from relaxation spectra and to correlate with rheological models.

DMA shows high potential as an experimental technique for composite degradation studies due to its ability to show in situ viscoelastic characteristics of degrading composites over a wide range of temperatures and times or frequencies.

For viscoelastic materials, strain is not in phase with displacement stress, when a sinusoidal stress is applied. The dynamic modulus, M^* , is defined as the ratio of an applied sinusoidal stress, σ^* , to the resulting sinusoidal strain, ε^* . In the case that the sample is linearly viscoelastic, the strain’s frequency will be the same as the frequency of the applied stress, but will lag the stress by an angle δ , which is called the phase lag. At higher stress levels, in the non – linear viscoelastic region, the strain will be no longer sinusoidal and no longer proportional to the stress. The applied sinusoidal stress and the corresponding strain for a linear viscoelastic material may be expressed as [21, 22 and 24]

$$\sigma^* = \sigma_0 \exp(i\omega t) \quad (1)$$

$$\varepsilon^* = \varepsilon_0 \exp(i\omega t - i\delta) \quad (2)$$

Where:

σ_0 = sinusoidal stress amplitude

ω = stress angular frequency

t = time

ε_0 = sinusoidal strain amplitude

δ = phase lag between stress and strain

The dynamic mechanical modulus M^* is the one of the most common concepts to express dynamic mechanical data acquired during the experiment. It is defined as the ratio of an applied sinusoidal stress to the resulting sinusoidal strain in the material being tested. M^* can be expressed as follows:

$$M^* = \frac{\sigma^*}{\varepsilon^*} = |M^*|e^{i\delta} = M' + iM'' \quad (3.1)$$

$$|M^*|^2 = (M')^2 + (M'')^2 \quad (3.2)$$

$$\tan \delta = \frac{M''}{M'} \quad (3.3)$$

Where:

M' = storage modulus

M'' = loss modulus

$|M^*|$ = magnitude of dynamic mechanical modulus

δ = phase lag between the applied stress and the strain response

Dynamic mechanical data may also be expressed in the form of complex compliance, J^* defined as the reciprocal of complex modulus [24]:

$$J^* = J' - iJ'' = |J^*|e^{-i\delta} = \frac{1}{M^*} \quad (4.1)$$

$$J' = \frac{M'}{|M^*|^2} \quad (4.2)$$

$$J'' = \frac{M''}{|M^*|^2} \quad (4.3)$$

Where:

J' = storage compliance

J'' = loss modulus

$|J^*|$ = magnitude of complex compliance

Finally, dynamic mechanical data may also be expressed in the form of complex dynamic viscosity, μ^* , most commonly in the case of liquid systems:

$$\mu^* = \mu' - i\mu'' = |\mu^*|e^{i(\delta - \frac{\pi}{2})} = \frac{M^*}{i\omega} \quad (5.1)$$

$$\mu' = \frac{M''}{\omega} \quad (5.2)$$

$$\mu'' = \frac{M'}{\omega} \quad (5.3)$$

$$|\mu^*|^2 = \frac{|M^*|^2}{\omega^2} \quad (5.4)$$

Where:

μ' = viscous (or in-phase) component

μ'' = elastic (or out-of-phase) component

$|\mu^*|$ = magnitude of complex viscosity

The viscous parameter is in-phase when speaking for complex viscosity. However the material is not only viscous and it also tends to partly restore some of the obtained deformation (elastic parameter). This restoration occurs with retardation, and thus it is out-of-phase.

Nevertheless, it should be noted that all of these methods of reporting data are equivalent. Knowledge any two parameters, the rest can be defined by using the equations (1) through (5.4) [1-3, 13, and 15].

In the transition zones of a polymer during the experiment, the dynamic modulus is strongly dependent on temperature, and frequency, ω . Studying E' (Storage Modulus) (or G' (Shear Storage Modulus)) and $\tan\delta$ by changing frequency at constant temperature, and by changing temperature at constant frequency, is of high interest. DMA investigations by studying E^* (or G^*) versus T and ω can give information about relaxation processes: main chain relaxation (conventionally noted as α) from glass to rubber associated with the glass-transition process, and secondary transition (conventionally noted $\beta, \gamma...$) related to movements of side chains or to motions of small parts of the main chain [25]. In addition, dynamic mechanical properties associated with structural changes due to chemical reactions may also be studied, for instance, during thermoset crosslinking reactions and during phase transformation from an organic to an inorganic material system, because of the degradation process.

2.2 Time-Temperature Equivalence Principle and Master Curve

When external parameters (e.g. temperature, pressure, mechanical, electrical or magnetic fields ...) affect the internal parameters of a system (volume, strain, electrical or magnetic polarization), the polymeric system then passes from the

equilibrium state into a stable “excited” state. The process of spontaneous return of a microscopic system into a thermodynamically stable state is termed relaxation [27].

In order to describe the viscoelasticity temperature dependence in terms of relaxation time, Ferry introduced a coefficient, α_T [26]:

$$\alpha_T = \frac{\tau(T)}{\tau(T_g)} \quad (6)$$

Where:

α_T = shift factor

$\tau(T)$ and $\tau(T_g)$ are the relaxation times at T_g and T temperature respectively. Obviously $\alpha_T = 1$ at T_g .

The shift factor, α_T , has been determined by using the time-temperature superposition principle, which is essentially an empirical principle, but it has been verified by extensive experimental and theoretical studies. Among various analytical expressions of α_T , the expression proposed by Williams, Landel and Ferry is the most well-known equation [29].

The simplest application of time-temperature superposition is to produce master curve by selecting a particular temperature and applying only a horizontal shift on a logarithmic time scale to make the curve for other temperatures join as smooth as possible to the curve at this particular temperature. Mathematically, a modulus may be expressed as:

$$M(T_1, t) = M(T_2, t/\alpha_T) \quad (7.1)$$

$$M(T_1, t) = M(T_2, \omega\alpha_T) \quad (7.2)$$

Even though the success and the general application to amorphous polymers of this superposition principle have been proven, one additional correction is required. The molecular theories of viscoelasticity suggest that there should be an additional small vertical shift factor changing from the actual temperature T (at a density ρ) to the reference temperature T_0 (at a density ρ_0). The mathematical expression for the correction becomes:

$$\frac{M(T_1, t)}{\rho(T_1)T_1} = \frac{M(T_2, t/\alpha_T)}{\rho(T_2)T_2} \quad (8.1)$$

$$\frac{M(T_1, \omega)}{\rho(T_1)T_1} = \frac{M(T_2, \omega\alpha_T)}{\rho(T_2)T_2} \quad (8.2)$$

The above method gives the modulus or compliance as a function of time (or frequency) over a very wide range. Hence, it is possible to calculate the relaxation (or retardation) time spectrum, and to compare results with theoretical models. One equation that describes the relaxation time is the Williams, Landel and Ferry equation known as “WLF equation” [29]:

$$\log \alpha_T = \frac{C_1(T - T_R)}{C_2 + (T - T_R)} \quad (9)$$

Where C_1 and C_2 are constants and T_R is a reference temperature. The WLF equation covers the temperature range $T = T_R \pm 50$ °C for most of the amorphous polymers.

It is significant for the shift time to shorten in order to simulate (at the reference temperature T_R) a low-temperature property, while for the relative time to lengthen in order to simulate (at the T_R) a high-temperature property [13].

Furthermore, it is possible to express the activation energy (E) dependence based on kinetic theory. Using the activation energy, the Arrhenius shift factor can also be expressed as:

$$\log \alpha_T = \frac{E}{2.303R} \left[\frac{1}{T} - \frac{1}{T_R} \right] \quad (10)$$

For the glass transition process, the activation energy is in the range of 400-1000 KJ/mol. In the WLF equation, the activation energy at the reference temperature can be expressed by the constants C_1 and C_2 as:

$$E = 2.303R T_R^2 C_1 / C_2 \quad (11)$$

According to the form of shift factors, the relaxation time can be described as a function of temperature in two forms: WLF equation and Arrhenius-type equation. The Arrhenius-type equation is mostly used below T_g while the WLF equation is usually used above the T_g [2, 3 and 13].

2.3 Viscoelastic Behavior

Generally, the composite materials are assumed to be invariant during viscoelastic analysis of polymers. Nevertheless, for the situations that viscoelastic

characterization is of the most use, the structure is likely to be changing while the experiment. For those systems where the materials undergo significant chemical or physical change, the retardation time or relaxation time increases during the experiment [26]. Seferis, et al. analyzed Viscoelasticity of epoxy curing reactions, where the reaction kinetics was successfully described by the changing retardation time [15 and 20].

During carbonization processing of carbon carbon composites, the viscoelastic properties change due to degradation reactions which affect the final structure and performance of the composite. In such systems, a polymer matrix pre-form is degraded in an inert gaseous atmosphere, converting the organic part of the composite to a carbon matrix. Accordingly, it is very possible that a viscoelastic polymeric matrix composite may be transitioning to an elastic carbon matrix composite. Having been coupled with shrinkage and gasification during degradation, this transition is considered important processing stage because it can be related to beginning of micro-cracking and delamination of the laminate in the manufacturing processing of CCCs [16]. Moreover, the polymer matrix modulus may begin to increase due to further crosslinking reactions at high temperatures. Also, chain – scission reactions, which consist of typical degradation reactions for thermosetting polymers, can take place simultaneously having as a result modulus decrease. These coupled structural changes have to be understood in order to control the final performance of the CCCs.

Additionally, the thermo-oxidative stability (TOS) of composite materials is of primary technological concern in such programs as supersonic transport airplane development and in aircraft engine applications. In these load bearing applications at high temperatures, the viscoelastic properties of degrading composites reflect the stiffness variation as a function of time and temperature. For the specification of quality assurance and control tests in high temperature applications, viscoelastic characteristics of degrading composites should be identified in the form of modulus and/or compliance. Consequently, those viscoelastic properties may be correlated with other conventional TOS techniques such as oven aging and weight-loss measurements.

In this study, a dynamic mechanical time – temperature multiplexing technique was utilized to research the glass transition temperature and the initial degradation processes of a phenolic resin / carbon fiber composite system, which have

been used as a pre-form of CCCs. Modulus master curves for the two processes, were created by a horizontal and vertical shift method. Based on those results, the generalized standard linear solid model extensively utilized by Seferis and co-workers, was developed in order to describe the dynamic mechanical properties of the model composite systems as a function of frequency and temperature during degradation [3 and 13].

2.3.1 Generalized Standard Linear Solid Model

The general form of linear viscoelasticity is generally described by the equation [30]:

$$\alpha_0\sigma + \alpha_1\frac{d\sigma}{dt} + \alpha_2\frac{d^2\sigma}{dt^2} + \dots = b_0\varepsilon + b_1\frac{d\varepsilon}{dt} + b_2\frac{d^2\varepsilon}{dt^2} + \dots \quad (12)$$

Assuming non-zero constants in equation (12), four non-zero constants can describe the characteristic features of both stress relaxation and creep. Then, the model equation will be formed as:

$$\alpha_0\sigma + \alpha_1\frac{d\sigma}{dt} = b_0\varepsilon + b_1\frac{d\varepsilon}{dt} \quad (13)$$

The mechanical model, which is a composite of two elastic springs and one viscous dashpot in a series-parallel sequence, has this form of differential equation:

$$\sigma + \tau\frac{d\sigma}{dt} = G_r\varepsilon + G_u\tau\frac{d\varepsilon}{dt} \quad (14)$$

Where G_r is the relaxed modulus, G_u is the unrelaxed modulus and τ is the relaxation time defined as:

$$\tau = \frac{\mu}{G_u - G_r} \quad (15)$$

This model is known as Standard linear Solid (“SLS”) model [23].

In dynamic mechanical experiments with an oscillating induced stress of frequency ω , the complex modulus can be derived as:

$$G^* = G' + G'' = G_u - \frac{G_u - G_r}{1 + i\tau\omega} \quad (16)$$

The complex modulus G^* consists of the storage modulus G' and the loss modulus G''

Successful efforts to monitor the dynamic behavior of polymers have also been made in dielectric study. The analogy to dielectric analysis has been

demonstrated and utilized for the analysis of dynamic mechanical experiments [15, 17, 18 and 28]. Based on this analogy, a generalized standard linear solid model proposed by Dillman and Seferis was defined as [15]:

$$G^* = G' + G'' = G_u - \frac{G_u - G_r}{[1 + i\tau\omega^\beta]^\alpha} \quad (17)$$

Where α and β are parameters ranging from 0 to 1 which account for an asymmetric relaxation time distribution.

The real and imaginary components of the complex modulus can be derived by equations (14) through (17) as it is clearly described in the Dillman – Seferis model [15]. According to the same model, the compliance form of the model J^* can also be described [3, 13, 15].

The characteristic feature of α and β in the model has been investigated in terms of J' and J'' in the $\tau\omega$ axis [16]. The empirical parameters α and β account for the non-ideality of the system by considering the distribution of the relaxation time. As utilized in this study, the relaxation time may be described by the Arrhenius-type equation as:

$$\tau = \tau_0 \exp \left[\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (18)$$

Subsequently, the model consists of four parameters that need to be determined: τ_0 , E , α and β . The effect of these parameters on the normalized G' and G'' curves in the temperature axis can be derived by curves that have been expressed in the Dillman – Seferis model [3, 13, 15]. It is important to note that α may be accounted by the combined effects of β and τ_0 . The activation energy, E , of the relaxation time is considered as a unique value that represents the characteristics of the nature of a polymer in the same way that the universal constants represent in the WLF equation. In this study, the activation energy will be determined by the superposition principle, resulting in a temperature – dependent relaxation time. The other parameters of τ_0 and β will be appropriately determined to fit the experimental data, which will be analyzed in the following paragraphs.

3. EXPERIMENTAL

3.1 Materials

Phenolic resin (SC-1008), which is commercially available, was impregnated into the 8H woven fabric of T-300 carbon fiber provided by Toray. The materials were cured by heating to 135°C using controlled heating rates and postcured at 250°C for 5 hours. This thermal treatment fully cured the phenolic resin [31]. Also, during the curing process the laminates were pressurized at 250psi in the autoclave, after having been laid up under vacuum first. Depending on the debulking process, the fiber volume of a void-free composite was controlled to 74% measured by the acid digestion method.

3.2 Analysis

A TA Instruments DMA 2980 was used for carrying out the dynamic mechanical experiments. The DMA measurements were performed in regular serrated clamps, which were utilized in the horizontal set-up. The rectangular – shape composite sample dimension was 23.93x11.83x1.5mm. The oscillation amplitude was 0.2mm. For the thermal degradation study without oxidation, the experiment was conducted in nitrogen atmosphere with a flow rate of 300ml/min. nine frequencies were used: 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1, 3, 5 Hz. The temperature increase was set in 2.5°C steps from 100°C to 450°C and the heating rate between steps was about 1°C /min.

4. RESULTS & DISCUSSIONS

Figure 1 presents the storage modulus of the composite at nine different frequencies as a function of temperature. The higher modulus at higher frequencies shows typical viscoelastic behavior, as it was expected. The glass transition process was observed between 220°C and 300°C, identified by the decreasing modulus. Following the glass transition, modulus increase is observed between 320°C and 350°C because of the thermal degradation process and the high temperature crosslinking reactions. Above 350°C the modulus decreases and its dependence on frequency disappears, demonstrating a transition from viscoelastic to elastic behavior. Additionally, the increasing and decreasing modulus between 320°C and 400°C may

be ascribed to the coupled structural changes by random chain scission and additional crosslinking reactions.

Figure 1: Measured DMA storage modulus of phenolic resin/carbon fiber composite as a function of temperature at nine different frequencies: 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1, 3, and 5, in nitrogen atmosphere at 300 ml/min.

4.1 Master Curves for Glass Transition and Degradation Processes

By analyzing the master curve of glass transition, the high modulus portion is given by low-temperature experiments and the low modulus portion by high-temperature experiments. The storage modulus dependence on temperature and frequency is presented in Figure 2 for the glass transition between 230 and 295⁰C. As it can be observed, there is an overall change in the shape of the modulus-frequency curve as the temperature varies.

Figure 2: Storage modulus of phenolic resin/carbon fiber composite for glass transition as a function of inverse frequency at different temperatures as indicated

Figure 3: Shift factors compared with Arrhenius type equation using $E=790.4\text{KJ/mol}$ and $T_0=277.50\text{C}$ for the glass transition

Note that the time dependent modulus is quite similar in form to the storage modulus plotted versus inverse frequency. Dynamic results found in the literature are sometimes plotted versus frequency and sometimes versus inverse frequency [32].

Moreover, in Figure 3 the shift factors temperature dependence, which was empirically constructed, is compared to the Arrhenius-type equation (10) with $E=2766.2\text{ KJ/mol}$ and $T_0=277.5^0\text{C}$. This equation accurately fits the shift factor up to 290⁰C (End of glass transition region), but beyond 290⁰C, it seemingly deflects from the equation because degradation begins to occur.

Figure 4: Storage modulus of phenolic resin/carbon fiber composite for degradation processes as a function of inverse frequency at different temperatures as indicated

As far as the degradation process is concerned, the storage modulus dependence on temperature and frequency is presented in Figure 4 between 320 and 370⁰C. It can be observed that there is an overall change in the shape of the modulus-frequency curve as the temperature varies. At low temperatures the frequency-dependent viscoelastic modulus rapidly changes with respect to frequency. At high temperatures, however, the modulus is approximately constant with respect to frequency.

Figure 5: Horizontal shift factor for degradation process obtained by the DMA modulus maximum plotted as inverse maximum temperature vs. inverse frequency

Figure 6: Vertical shift factor for degradation process obtained from DMA modulus maximum plotted as inverse maximum temperature vs. maximum modulus

Furthermore, the modulus and frequency logarithmic values at the maximum peaks due to the high frequency dependence of the modulus in those areas are presented in Figures 5 and 6, as a function of maximum temperature (T_{max}). Logarithmic values of frequency and G'_{max} exhibited linear relations with respect $1/T_{max}$, giving activation energies for the shift factors as -2461.3 KJ/mol and 8.782 KJ/mole in the horizontal and vertical directions, respectively, with a reference temperature of 342.5⁰C.

Figure 7: DMA storage modulus master curves for glass transition and degradation processes

Finally, by utilizing these shift factors, the degradation master curve can be constructed as presented in Figure 7. A considerable result is that at specific time and temperature, the polymer property during degradation is comparable with the polymer property before degradation. In terms of polymer modulus, the degradation process may provide a favorably comparable material property, revealing the possibility to improve or change the polymer property by controlled degradation processing. Considering the degradation process from a CCC point of view, the initial degradation step, which has been investigated in this study up to 400⁰C, is an outstanding processing stage because there is a considerable change of modulus value from rubbery state to an elastic state.

4.2 Modeling Approach

From equation (17) the real and imaginary components of the complex modulus can be derived as:

$$G' = G_u - \frac{(G_u - G_r) \cos(\alpha\theta)}{[1 + 2(\tau\omega)^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\tau\omega)^{2\beta}]^{\frac{\alpha}{2}}} \quad (19)$$

$$G'' = \frac{(G_u - G_r) \sin(\alpha\theta)}{[1 + 2(\tau\omega)^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\tau\omega)^{2\beta}]^{\frac{\alpha}{2}}} \quad (20)$$

$$\tan \theta = \frac{(\tau\omega)^\beta \sin\left(\frac{\beta\pi}{2}\right)}{1 + (\tau\omega)^\beta \cos\left(\frac{\beta\pi}{2}\right)} \quad (21)$$

By equations (18) through (21) the relaxation times as well as the activation energies can be extracted for both the glass transition and the degradation processes independently through equations (22) and (23):

For the glass transition, v is equal to 1.7611 and this value is taken from master curve in Figure 7. Consequently, the relaxation time can be expressed as a function of temperature via:

$$\tau_g = 10^{1.7611} \exp\left[\frac{E_g}{R} \left(\frac{1}{T} - \frac{1}{T_g}\right)\right] \quad (22)$$

Where $E_g=766.2$ KJ/mol and $T_g=277.5^0$ C. The same procedure was performed for the degradation process, providing the following relaxation time:

$$\tau_d = 10^{6.492} \exp\left[\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{T_d}\right)\right] \quad (23)$$

Where $E_d=-2461.3$ KJ/mol and $T_d=342.5^0$ C.

The relaxed and unrelaxed moduli in the degradation processes were also derived by the master curve. Since the relaxation time was already determined, the other two parameters of G_u and G_r could be determined by rearranging equation (19):

$$G' = G_u - (G_u - G_r)h(\alpha_T\omega, \beta) \quad (24)$$

Where

$$h(\alpha_T \omega, \beta) = \frac{\cos(\alpha\theta)}{[1 + 2(\alpha_T \omega)^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\alpha_T \omega)^{2\beta}]^{\frac{\alpha}{2}}}$$

According to these equations, when master curve G' is plotted as a function of $h(\alpha_T \omega, \beta)$ for a certain value of β , G_u , G_r can be determined by the intercept and slope of the line, respectively.

The relaxed and unrelaxed moduli for the degradation process may be described by the temperature-dependent shift factor in the vertical direction, as:

$$G_u = G_u^0 \exp\left[\frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{T_d}\right)\right] \quad (25)$$

$$G_r = G_r^0 \exp\left[\frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{T_d}\right)\right] \quad (26)$$

Where $E_v = 8.782$ KJ/mol, $T_d = 342.5^\circ\text{C}$, and G_u^0 and G_r^0 are 16.02 and 9.313 GPa, respectively.

Extracting the relaxation times, the activation energies and the relaxed and unrelaxed moduli from equations (18) through (21) leads to results, illustrated from Figure 8 to 11, which fit the experimental results.

Figure 8: DMA storage modulus for the glass transition compared to the model (solid line), as a function of temperature, at three different frequencies: 0.01, 0.1 and 1 Hz

Figure 8 presents the comparison between the experimental modulus data and the model prediction in the glass transition as a function of temperature for three different frequencies: 0.01, 0.1, 1 Hz. The model is in excellent agreement with the experiment up to 290°C .

Figure 9: DMA storage modulus during degradation compared to the model (solid line), as a function of temperature, at three different frequencies: 0.01, 0.1 and 1.0 Hz

Moreover, Figure 9 compares the DMA storage modulus with the model prediction in the degradation process between 290°C and 360°C for three frequencies of 0.01, 0.1, 1 Hz. They are in good agreement as well and they demonstrate the

validity of the viscoelastic analysis methodology for the degradation process. Relaxation time and relaxed/unrelaxed modulus are the two temperature – dependent parameters involved in this model.

Figure 10: DMA storage modulus for both glass transition and degradation processes, compared to the model (solid line), as a function of temperature, at three different frequencies: 0.01, 0.1 and 1.0 Hz

Figure 11: Comparison of $\tan\delta$ with the model (solid line), as a function of temperature, at two different frequencies: A 1.0 Hz and B 0.01 Hz

Finally, as presented in Figure 10, this empirical equation describes the intermediate region between glass transition and degradation processes very well for different frequencies. Additionally, Figure 11 presents $\tan\delta$ value predicted by the model. Two peaks of $\tan\delta$ for 0.01 Hz and one broad peak for 1 Hz are predicted by the model.

5. CONCLUSIONS

A DMA time - temperature multiplexing technique to 400⁰C in a nitrogen atmosphere was used to analyze phenolic resin/carbon fiber composites. The glass transition and degradation processes were clearly detected by the changing DMA modulus with respect to temperature. In addition to the typical glass transition exhibited by a model system, during the degradation stage, the storage modulus initially increased and then passed through a maximum value, followed by a decrease.

A master curve for the glass transition was successfully constructed through horizontal shifting, however, a vertical shift as well as a horizontal shift was required to construct the master curve for the degradation process. The shift factors in the two directions were derived by the frequency- and temperature- dependent modulus maxima, which were detected by the DMA data in the temperature region between 340⁰C and 350⁰C. A degradation master curve was constructed from these factors in the horizontal and vertical directions, in order to demonstrate the validity of the analytical methodology.

The superposition procedure provided a basis for a phenomenological description of the glass transition and degradation processes in terms of the

temperature-dependent relaxation time. The Dillman – Seferis model was extended to describe the viscoelastic dynamic mechanical properties of the two processes. The characteristic feature of the model parameters was researched, and afterwards, the parameters were appropriately determined from the master curves. Finally, it was demonstrated that the model successfully described the dynamic mechanical properties, validating this expanding viscoelastic modeling methodology that couples relaxation phenomena to cure and degradation processes.

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8. VITAE

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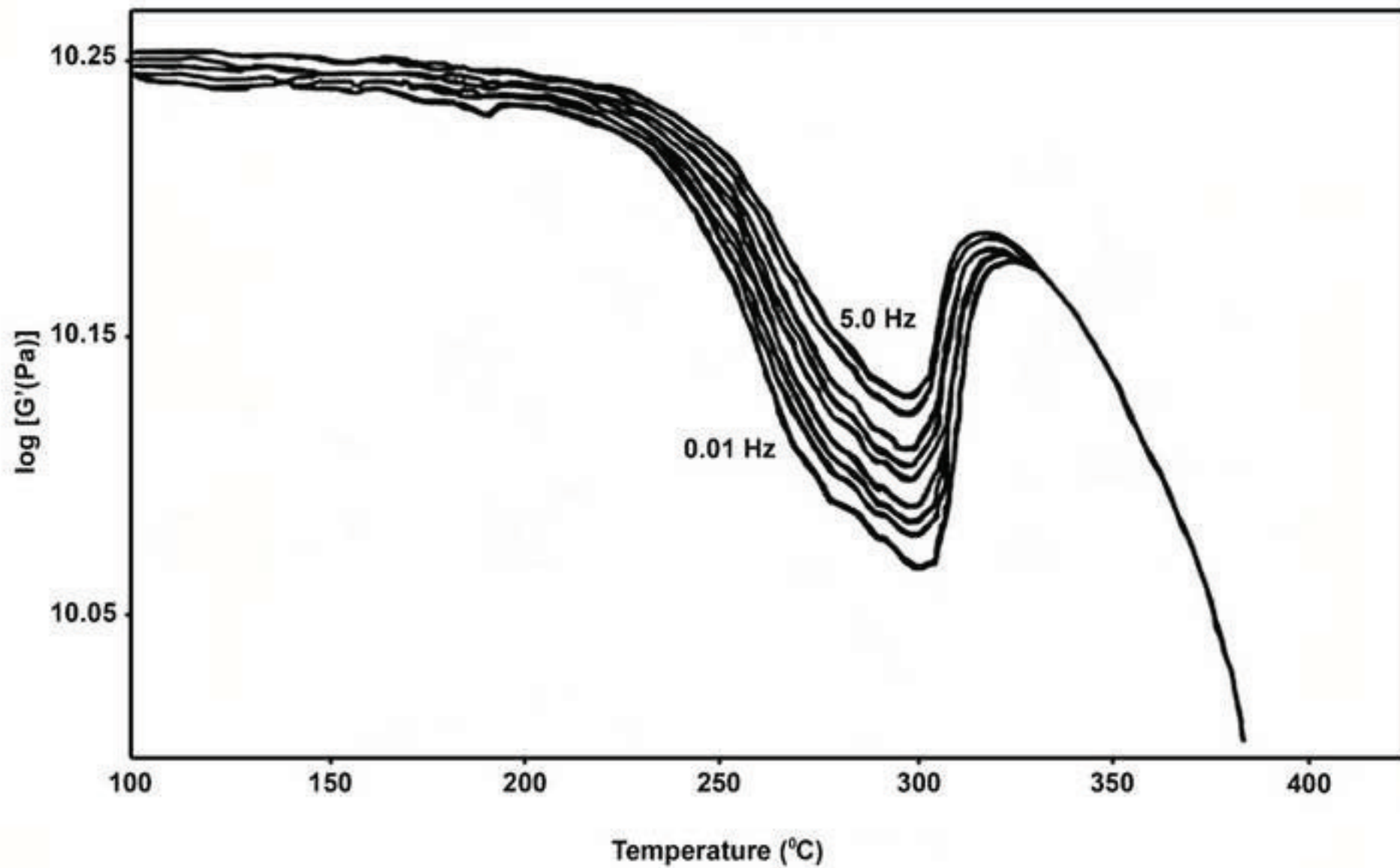


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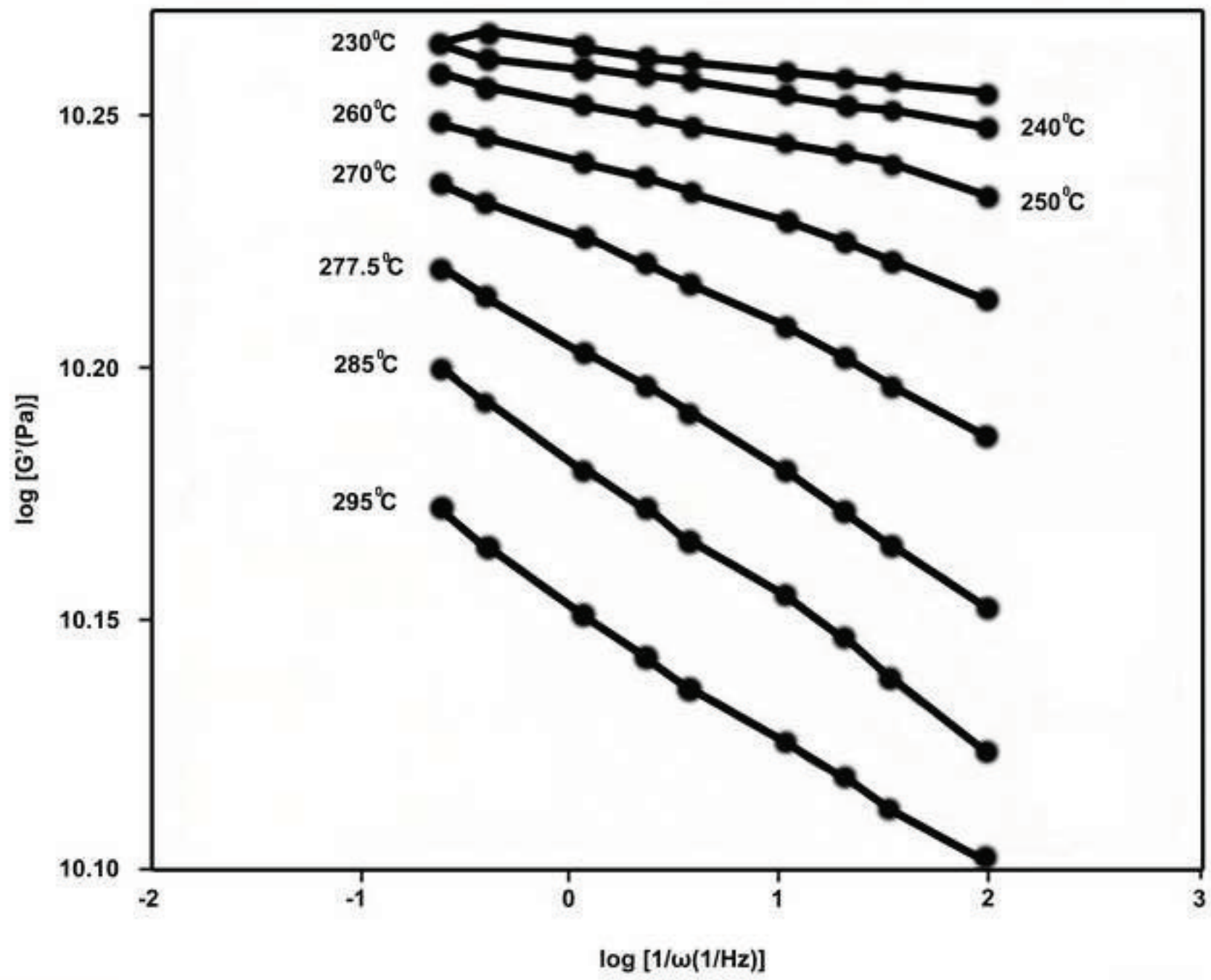


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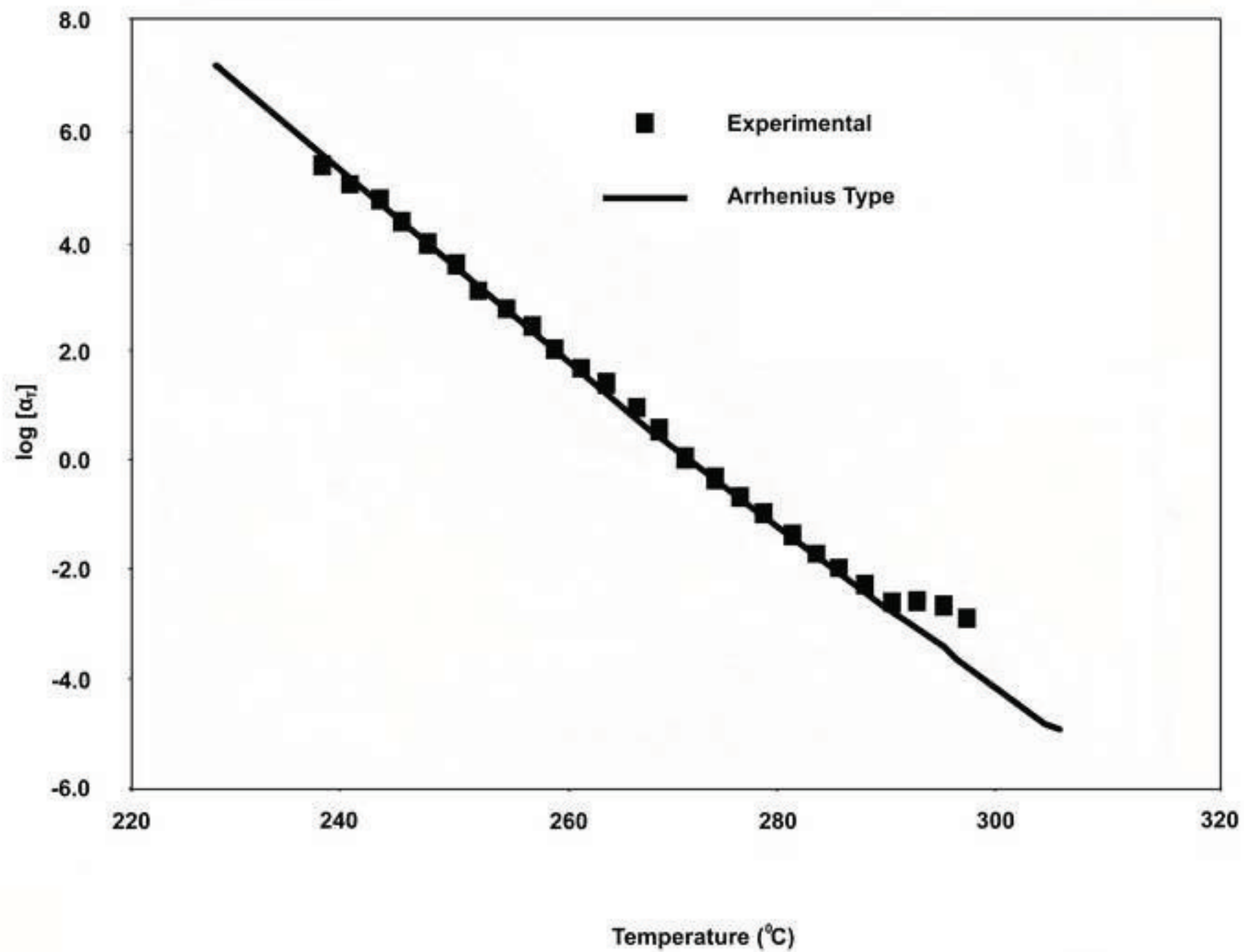


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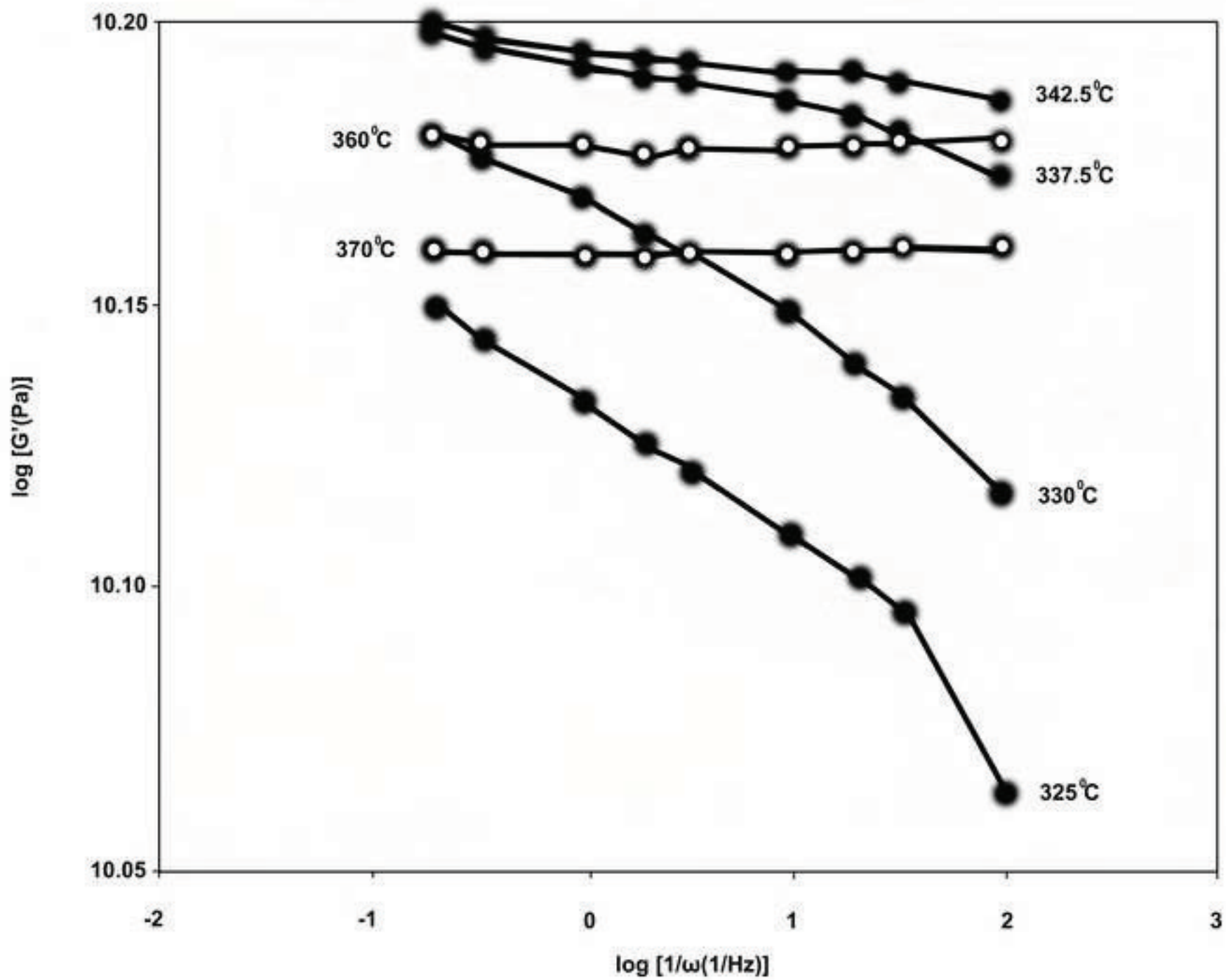


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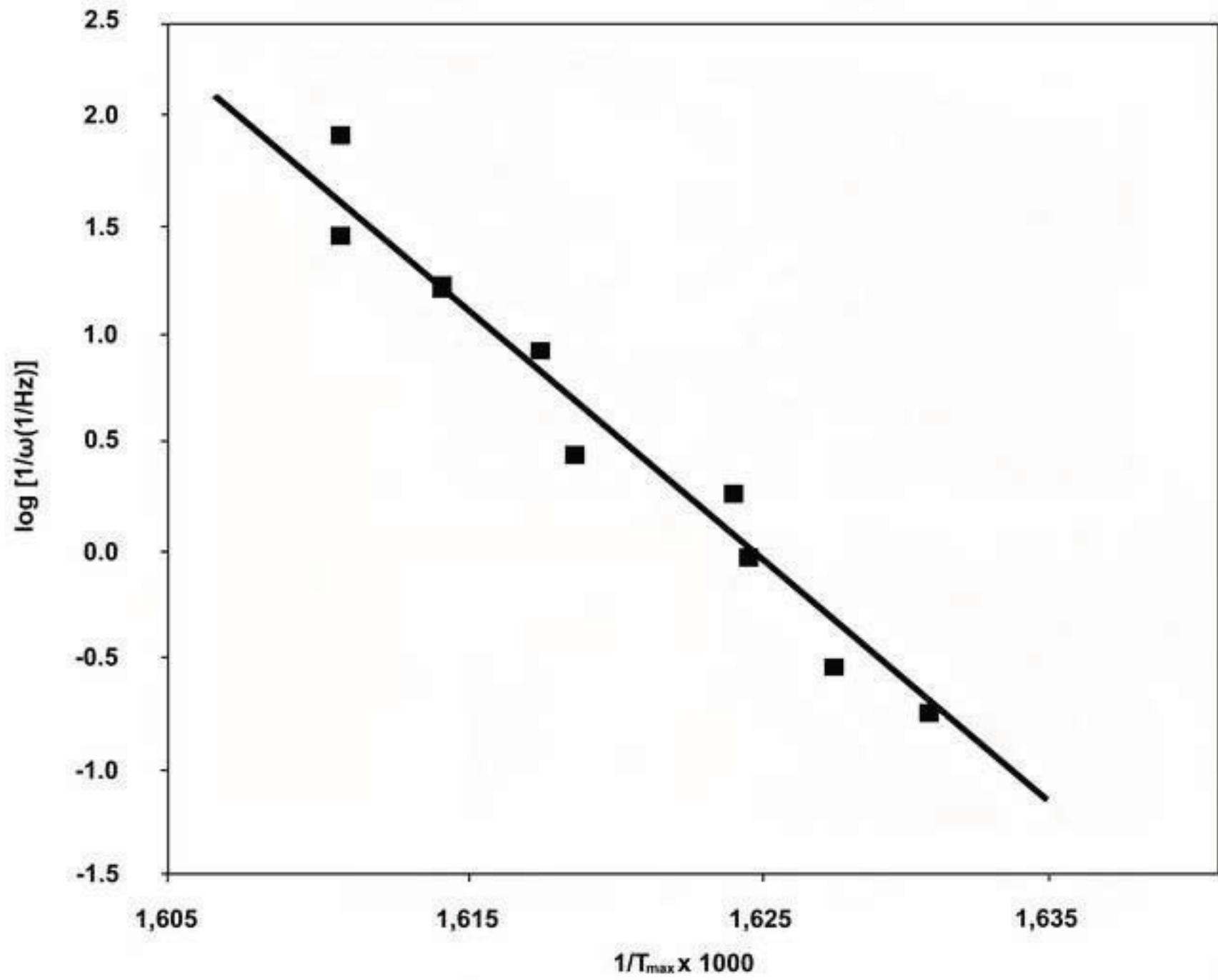


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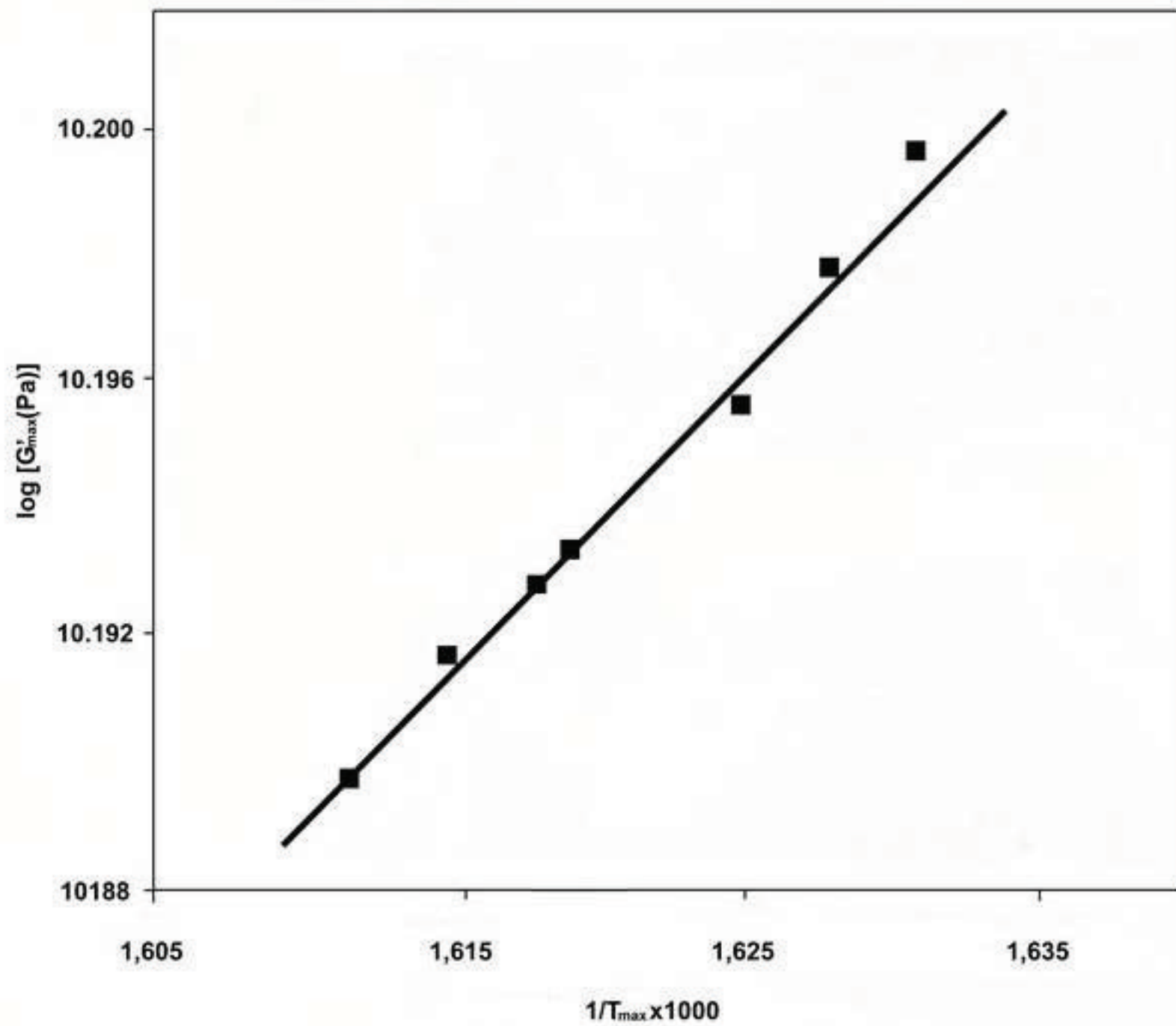


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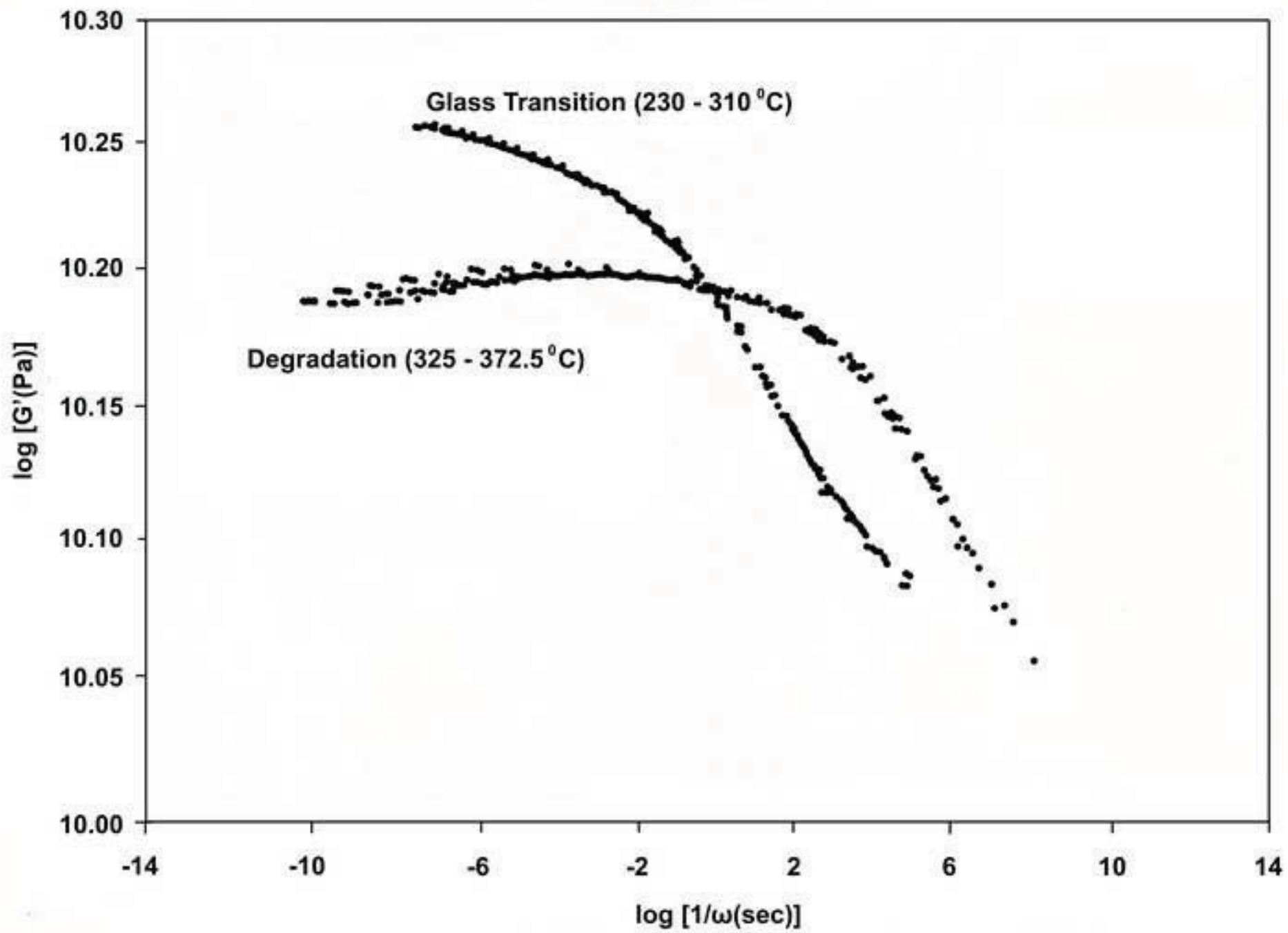


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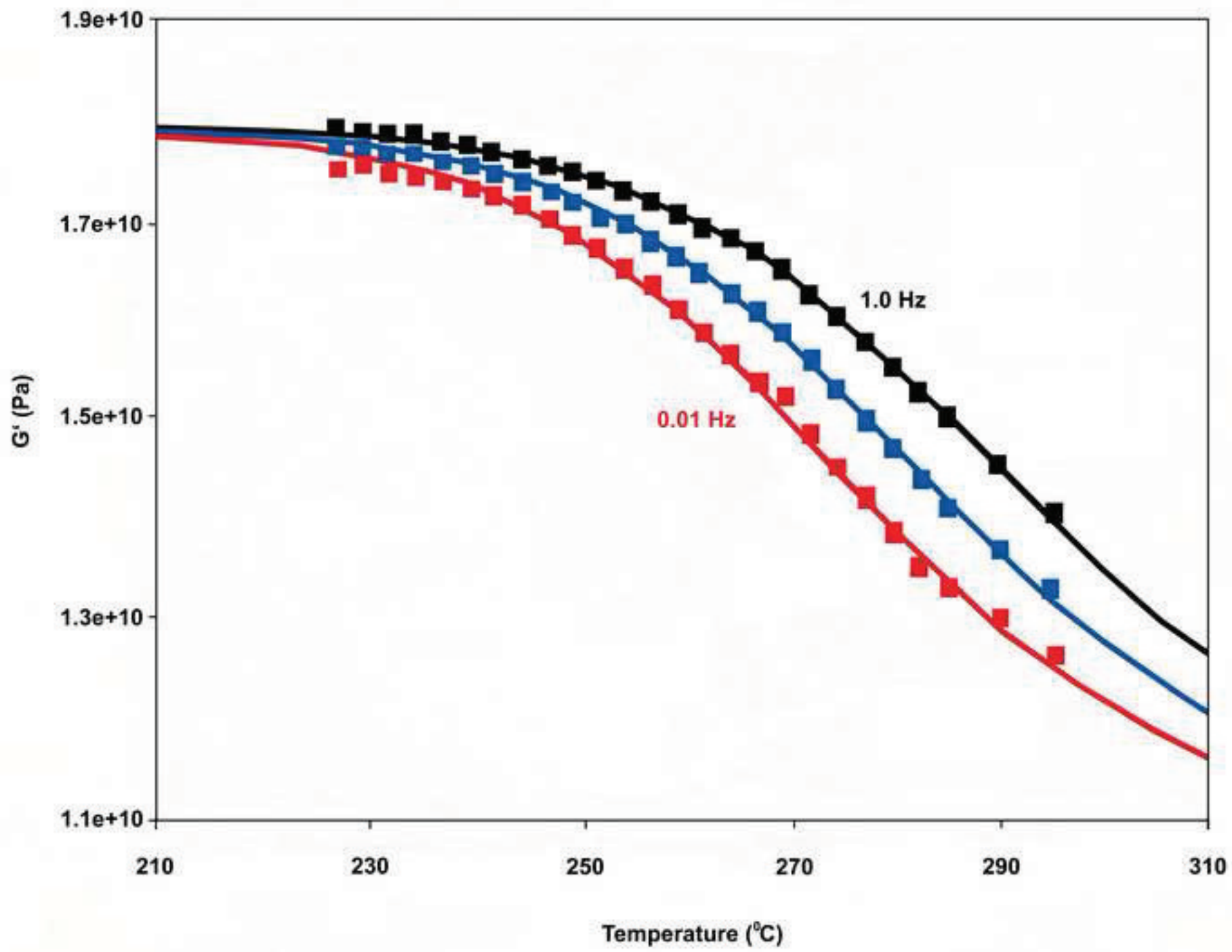


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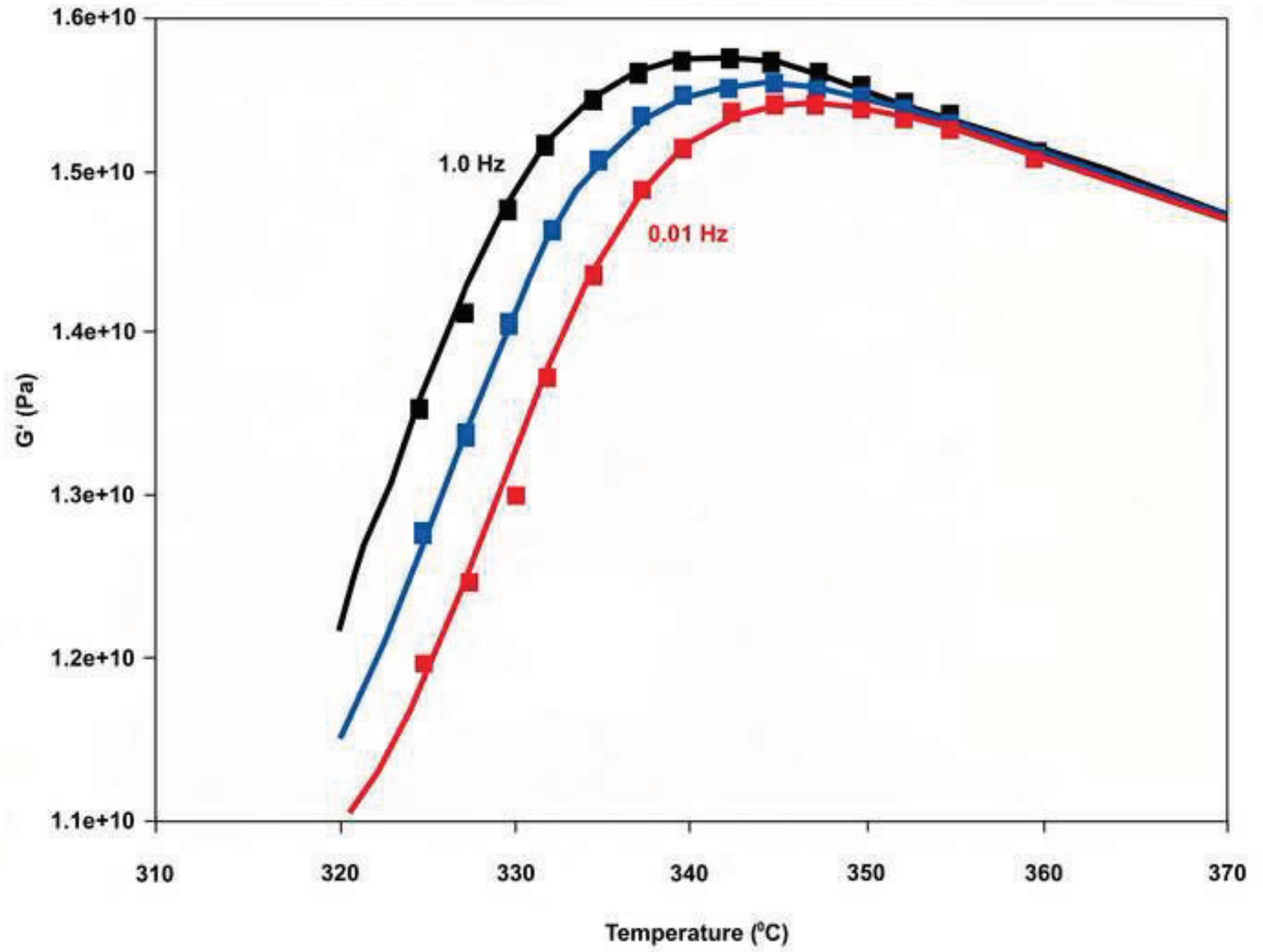


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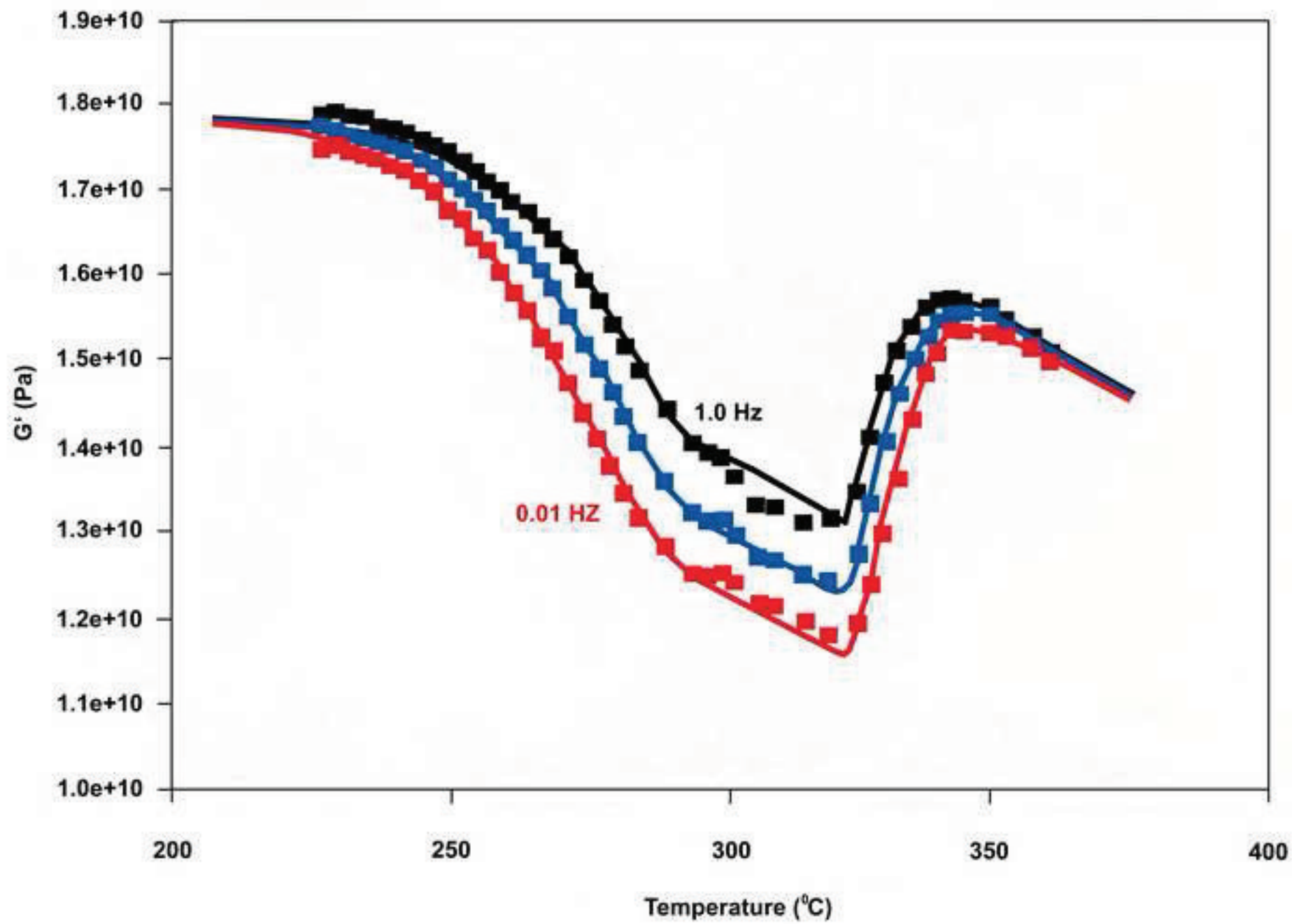


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