

A New Procedure to Analyze Glass-Transition Peaks in Polymers

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SYNOPSIS

A new procedure for analyzing internal friction peaks as a function of temperature has been developed. The true and apparent energies of activation of the involved processes can be obtained independently from each other. The procedure is applied to internal friction peaks in poly(methyl methacrylate); the results for both energies agree with experimental values found in the literature. Finally, it is shown that the parameter that relates the true and apparent energies is a function of the halfwidth of the distribution function associated with the internal friction and therefore is associated with molecular movements. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Internal friction is, in contrast with the moduli or compliances, a magnitude that can be measured directly, that is, without calibration of the measurement system and is independent of the geometry of the sample. This is the main reason for which internal friction is usually used to obtain information about transition processes.

Some descriptions of internal friction as a function of frequency and/or temperature can be found in the literature.¹⁻³ A traditional methodology to determine the relevant parameters associated to this magnitude was proposed by Nowick and Berry,^{4,5} who used the lognormal distribution function to describe internal friction peaks to obtain the mean characteristic time τ_m , the halfwidth β , and the relaxation strength Δ .

Another way of describe internal friction peaks is through the so-called power law,^{1,6} which allows to separate the dependences with temperature and frequency. In particular, it can be mentioned the model proposed by Perez et al.,⁷ which describes the

relationship between the mechanical relaxation times τ_{mr} and the internal friction peak temperature by using a parameter related to the intensity of correlation effects in glass transition processes. A different approach was proposed by Hermida and Povoló,² who describe the individual internal friction curves by using the power law in the characteristic times.

The purpose of this work is to present a novel powerful technique for analyzing internal friction peaks as a function of temperature. Its main advantage is that both the true and apparent energy of activation are obtained independently from each other. The relationship between these magnitudes gives a physical interpretation of the parameters that characterize the distribution function associated with the internal friction peaks.

THEORETICAL BACKGROUND

The dynamic mechanical moduli (or compliances) of linear viscoelastic materials are generally related to a distribution function of relaxation (or retardation) times. In the same way, internal friction IF

can be described by another distribution, the tangent distribution function Ψ_t as⁸

$$IF(\omega) = \int_{-\alpha}^{\alpha} \Psi_t(\ln \tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d(\ln \tau) \quad (1)$$

where ω is the circular frequency. The importance of the tangent distribution function lies on the fact that, as it was demonstrated in another work,⁹ the relaxation and retardation spectra, and therefore the information about all dynamic mechanical magnitudes, can be derived from this distribution.

Equation (1) can be expressed in a different way, by using the integrated distribution τ_t ,⁸ which is more suitable when IF is studied as a function of temperature. Therefore, IF may be written as

$$IF(\omega) = \tilde{\alpha}(T) \frac{\omega \tau_t(\omega, T)}{1 + \omega^2 \tau_t^2(\omega, T)} \quad (2)$$

where $\tilde{\alpha}(T)$ is the envelope function.⁸ When each internal friction peak is a function of temperature, with the frequency as a parameter, the envelope function does not depend on the frequency, that is, is an unique function for all the peaks. This calculates $\tilde{\alpha}$ as a continuous function that contains all the peak maxima. Once this function is known, each integrated distribution τ_t can be obtained by a simple calculation from eq. (2). Therefore, τ_t is obtained as a function of temperature and the frequency as a parameter. These relaxation times, which are associated to the internal friction, are related to the energy of activation of the transition processes.

In the case that internal friction can be described by a Debye function, all the integrated distribution curves are parts of a single curve, which contains also the τ_{mr} versus T_p curve, where τ_{mr} is $1/\omega$ and T_p is the temperature at which IF takes its maximum value.⁸ For most materials, the distribution functions are wider than those associated to Debye processes. This leads to different integrated distribution curves for different peaks and also to a different τ_{mr} curve. However, the latter is always used to define the apparent activation energy E_a , as¹⁰

$$E_a = -k_B \frac{d(\ln \tau_{mr})}{d(1/T)} \quad (3)$$

where k_B is Boltzmann constant.

THEORY

Parameters of the Integrated Distribution Function

The integrated distribution is used to calculate the activation energy E , when the latter does not depend on temperature, as

$$\ln \tau_t = \ln \tau_0 + \frac{E}{k_B T} \quad (4)$$

E may be regarded as the true activation energy, because it contains all the information about the distribution function associated with the material.

On the other hand, the apparent energy is independent of the shape of the distribution function. It depends only on the peak temperature T_p . Therefore, it is impossible to reproduce internal friction peaks using only the apparent energy. The relationship between true and apparent energies should have a parameter that contains the information associated with the distribution function. We propose a power law to describe the integrated distribution, $\tau_t(T)$, where the involved energy is the apparent energy, E_a , that is,

$$\tau_t = [\tau_0^* \exp(E_a/k_B T)]^{w_s} \quad (5)$$

and w_s is the parameter associated with the distribution function width.

It must be noticed that eq. (5) establishes a relation between the integrated distribution τ_t and τ_{mr} , through the apparent energy. This leads to

$$\ln \tau_t(T) = C - \frac{w_s}{T} \frac{d(\ln \tau_{mr})}{d(1/T)} \quad (6)$$

where $C = w_s \ln \tau_0^*$ does not depend on temperature. Because τ_t depends on the internal friction spectrum, whereas τ_{mr} is only related to the peak maxima, it is clear that the parameter w_s is associated with the width of this spectrum.

According to eqs. (4) and (5), it results that

$$E = w_s E_a \quad (7)$$

In summary, eq. (7) shows that there is a linear relationship between the true and apparent energies, even in the case that these magnitudes depend on frequency. Moreover, the factor w_s is a parameter related to the distribution function.

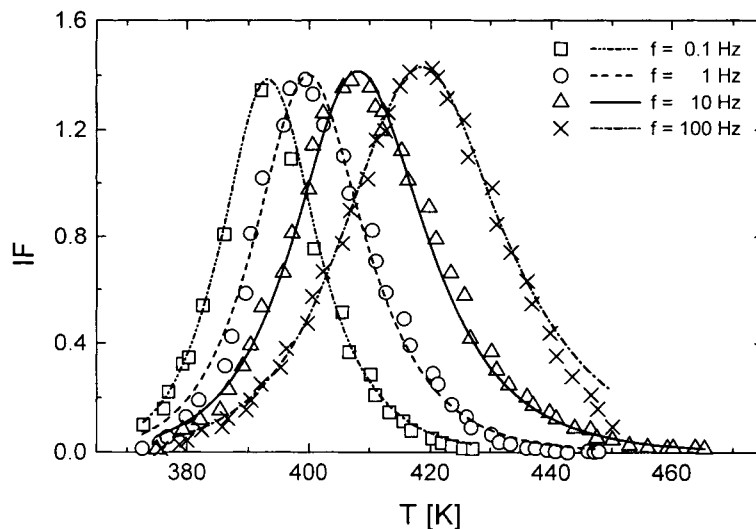


Figure 1 Comparison of experimental IF peaks³ and fitted curves by eq. (2) for PMMA at four frequencies.

APPLICATIONS

The concepts developed in this work were applied to internal friction data for a commercial injection-moulded sample of poly(methyl methacrylate) (PMMA), measured by Almond et al.³ The experimental data are peaks as a function of temperature at different frequencies, that is, 0.1, 1, 10, and 100 Hz (Fig. 1).

As it may be seen from Figure 1, the IF peak maxima, IF_p , seem to depend on the peak temperatures in a linear way. Therefore, the envelope function $\tilde{\alpha}$ can be calculated by a linear regression between IF_p and T_p . It can be expressed as

$$\tilde{\alpha}(T) = 0.003T + 1.599 \quad (8)$$

where T is in degrees Kelvin. It should be noted that $\tilde{\alpha}$ is an envelope function; therefore, it is calculated from the IF values in T_p , but it is a function of temperatures. This function allows to calculate the integrated distribution, for each experimental peak, by using eq. (2). The resulting curves, τ_i versus T , are shown in Figure 2.

As it can be seen from Figure 2, the $\ln \tau_i$ versus $1/T$ curves are straight lines, but they have different slopes. The fact that these curves are not part of a single one, i.e., that τ_i is function of both temperature and frequency, leads to the conclusion that the IF peaks do not correspond to a Debye process. Besides, the linear relationship between $\ln \tau_i$ and $1/T$ uses eq. (2) to describe the temperature dependence.

Therefore, the true energy of each peak is not a function of temperature and can be obtained from the $\ln \tau_i$ versus $1/T$ slope.

However, the different slopes indicate that E is a function of frequency, i.e., $E = E(\omega)$, or equivalently, $E = E(T_p)$, because for each excitation frequency there is only one peak temperature. It should be pointed out that E values decrease monotonously with frequency. Table I shows the values of the true energies at the different frequencies. The full curves of Figure 1 show the fitting obtained by using eqs. (2) and (8) and the values of τ_0 and E from Table I.

On the other hand, the apparent energies can be obtained, according eq. (3), from the local slopes of

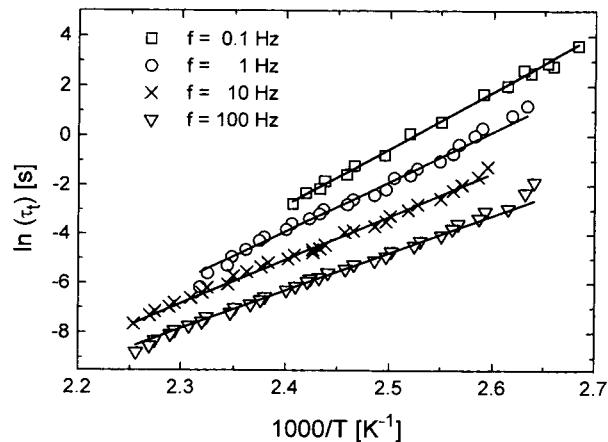


Figure 2 Integrated distribution curves for each IF peak of Figure 1.

Table I True and Apparent Energies for PMMA

f (Hz)	E_a (kJ/mol)	E (kJ/mol)	τ_0 (s)
0.1	455.7	190.0	$9 \cdot 10^{-26}$
1	406.8	168.4	$1 \cdot 10^{-23}$
10	324.7	147.2	$2 \cdot 10^{-21}$
100	291.6	127.2	$2 \cdot 10^{-19}$

a $\ln \tau_{mr}$ versus $1/T_p$ curve. Figure 3 shows that the relationship between $\ln \tau_{mr}$ and $1/T_p$ is not linear, and therefore, E_a takes different values for each frequency (see Table I).

Figure 4 shows the linear relationship between E and E_a . It should be remarked that the corresponding plot passes through the origin. This result lends support to the analytical expression, eq. (7), derived from the model proposed in this work. Therefore, the parameter w_s can be obtained from the slope of the E versus E_a curve. The result for this set of data is $w_s = 0.426$.

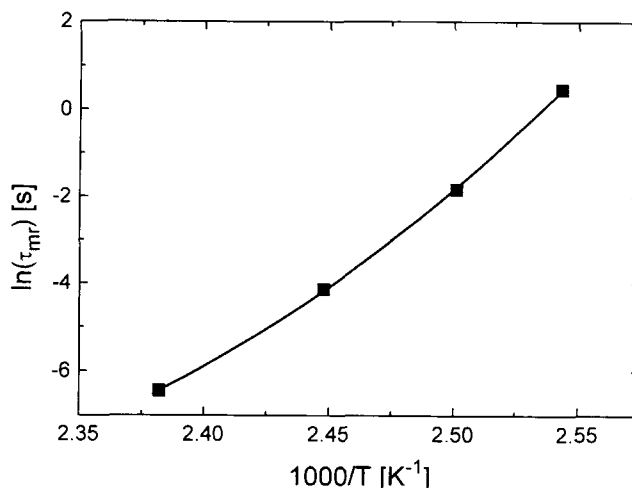
DISCUSSION

Values of Energy

According to the proposed method in this work, two energy values are obtained for each IF peak, characterized by its frequency. These values result from different procedures, in contrast with the proposed methodologies in other works,^{7,11} in which one energy is obtained from the data fitting and the other results as a correction from the first energy.

Bauwens-Crowet¹² calculated the activation energy for PMMA, making horizontal shifts in compression yield versus strain-rate curves, at different temperatures. Therefore, the obtained energy is the apparent energy. The resulting value is 411 kJ/mol, which is similar to the E_a obtained in this work for low frequency. Analogously, Thompson,¹¹ making horizontal shifts in shear creep curves, obtained an energy value of 442 kJ/mol. These values cannot be the true activation energies, because they are similar to the dissociation energies of components of the PMMA macromolecule. For example, the C—H bond is 414 kJ/mol.

On the other hand, Thompson¹¹ corrects his energy value by normalizing the creep curves. The resulting value is 178 kJ/mol, which is of the order of the true energy obtained in this work for low frequency. The E value obtained for 100 Hz (127.2 kJ/

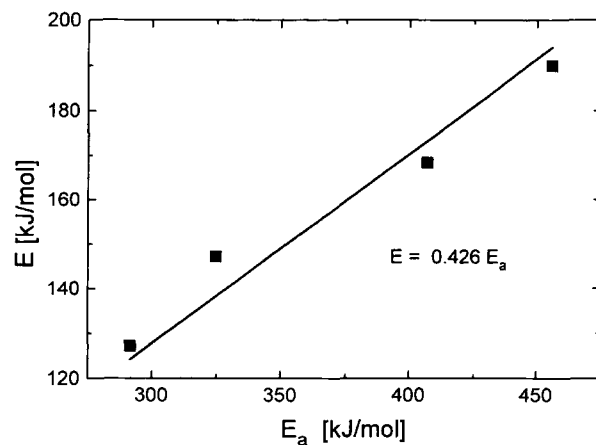
**Figure 3** Variation of τ_{mr} with temperature.

mol; see Table I) can be compared with the one reported by Povolo and Goyanes¹³ at 50 kHz (114 kJ/mol).

Interpretation of the Relationship Between the Energies

If IF peaks were Debye peaks, the true energy should be equal to the apparent energy. The presence of a nonsingular distribution function of relaxation times makes these values different. Therefore, it is possible that some of the parameters of the distribution function may be associated with the parameters which relate both energies.

One of the most used distribution function is the lognormal spectrum. Figure 5 shows the fitting of this distribution to the experimental data of Figure

**Figure 4** Relationship between the true and apparent energies.

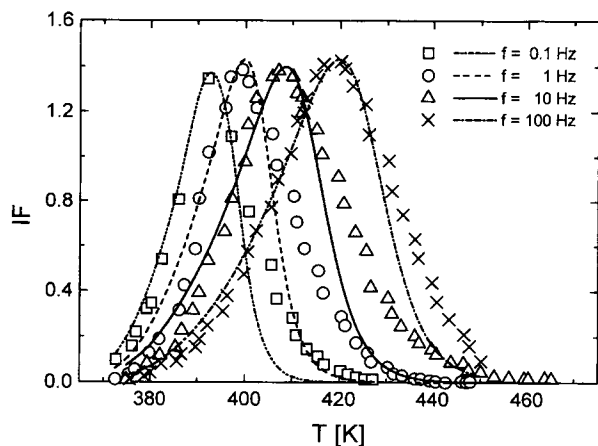


Figure 5 Comparison of experimental IF peaks of Figure 1 and fitted curves by using a lognormal distribution of halfwidth $\beta = 3$.

1. The parameters were obtained by using a standard nonlinear computational method, given a value of $\beta = 3$ in the distribution halfwidth for all peaks. As it can be noted from Figure 5, the fitting is not as good as the one in Figure 1, especially on the right tails of the peaks. However, the fitting on the peak zones and on the left side of the peaks are acceptable.

In a previous work, Hermida and Povoló² related the halfwidth of a log-normal distribution to the exponent of a power law. In fact, they have proposed a power law for the characteristic times (integrated distribution) to describe IF peaks, that is,

$$\tau_t(T, \omega)\omega = (\tau(T)\omega)^\gamma \quad (9)$$

and they related this exponent γ to β , both for the case of IF peaks at constant temperature or when $\tau(T)$ follows an Arrhenius dependence. According to this relationship, a value of $\beta = 3$ corresponds to a value of $\gamma \approx 0.44$. This value is quite similar to the one obtained for w_s in the previous section ($w_s = 0.426$). This result can be explained by the fact that in the model proposed in this work, besides the linear parameter that relates the apparent and true energies, w_s is also an exponent [eqs. (5) and (7)] and, therefore, it may be possible to identify γ as w_s .

On the other hand, Perez et al.⁷ proposed that for temperatures below the glass transition temperature, the mechanical relaxation times τ_{mr} are related to the temperature through the true energy E and a parameter k , which indicates the effectiveness of correlation effects existing during molecular movements in the viscoelastic behavior region. The au-

thors indicate that this parameter k relates the apparent and true energies as

$$E_a = \frac{E}{k} \quad (10)$$

Taking into account eqs. (7) and (10), it is clear that

$$k = w_s \quad (11)$$

It should be pointed out that the parameter γ of eq. (9) is only dependent of the individual IF peaks, that is, γ is related to τ_t , whereas the correlation parameter k is obtained from the mechanical relaxation times, defined as the reciprocal of the peak frequency. The model proposed in this work shows that both approaches are not independent and are related with each other [see eq. (6)].

Finally, it is possible to give a physical interpretation of the parameters associated with the distribution width. In fact, taking into account eq. (11), w_s gets the meaning of k given by Perez et al.⁷ Moreover, the exponent in the power law γ [eq. (9)] may also be considered as equivalent to w_s and k .

CONCLUSIONS

In this work, a new procedure for analyzing internal friction peaks as a function of temperature has been developed. Its main advantage is that both the true and apparent energy of activation are obtained independently from each other. It is shown that the parameter that relates these energies is a function of the halfwidth of the distribution function associated with the internal friction and therefore is associated with molecular movements. This method allows to bond different ways of analyzing internal friction peaks. In fact, it is possible to relate the mechanical relaxation times, associated with the maxima of IF peaks, to the integrated distribution, associated with the characteristic times of the individual internal friction curves.

The proposed method was applied to PMMA data, with a satisfactory fitting. The energy values obtained agree with results reported in the literature.

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