Analysis of Temperature Dependence of Dynamic Loss Tangent ($\tan \delta$) Relating to Molecular Motion of Polymer Chain in Amorphous Region in Fiber and Fiber-forming Polymeric Materials

Part 1: Viscoelastic Body Composed of Single Relaxation Time

By Sei-ichi Manabe, Kenji Kamide and Chozo Nakayama, Member, TMSJ

Textile Research Laboratory, Asahi Chemical Industry Company Ltd., Hacchonawate 11-7, Takatsuki-shi, Osaka

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Abstract

A theoretical equation is derived to determine the $\tan \delta$ -temperature (T) curve of the system composed of a single relaxation time, and the curve is calculated. Comparison of the calculation with experimental results shows that: (1) The three-element model combining the Maxwell element with one spring parallelly is most suitable for a viscoelastic model having a peak in the $\tan \delta$ - T curve. (2) The peak temperature in the $\tan \delta$ - T curve, $T_{\max}(k)$, and the apparent activation energy ΔH_a , give the inherent half value width of $\tan \delta$ - T curve $\Delta T_{1/2(s)}$ by the equation $\Delta T_{1/2(s)} = 5.24 \times 10^{-3} T_{\max}^2 / \Delta H_a$. (3) The log $\tan \delta$ - T curve can be approximated by an equilateral triangle. (4) The parameter B_∞ , defined by the equation $B_\infty = 522 \Delta H_a / T_{\max}$, is convenient for determining the mechanism of viscoelastic absorption. (5) The average $\Delta T_{1/2(s)}$ of various polymers is 13 deg for the absorption (α_a) related to the microbrownian movement of segment in amorphous, and 20 deg for the absorption (β_a) related to the local movement of the main chain. Thus, the value of β_a absorption is larger than that of α_a absorption. (6) A method is presented to determine the relaxation time at the glass transition temperature T_g by ΔH_a and $T_{\max}$.

1. Introduction

For the purpose of establishing the correlation between the fine structure and the physical properties of polymers, it is of great importance to evaluate quantitatively the aggregated state of the molecular chains in the amorphous region of semi-crystalline polymer solids, especially of fibers and fiber-forming polymeric materials. In this series of the studies, we will deal with the fine structure of the amorphous region whose size is 10–1000 Å order of magnitude.

Studies on the fine structure of fibers reported so far have been mainly limited to the crystal region. However, the regions which govern the processability of fibers are not only the crystal region but also the amorphous region. For instance, the amorphous region greatly contributes to the dyability and the hygroscopicity of fibers. The change of the breaking elongation of unoriented fibers in the simultaneous draft/false-twist processing due to the lapse of time and the shrinkage phenomenon of polyamide fibers in the manufacturing process, are closely related to their amorphous regions.

The methods for determining the fine structure in the crystal region (e.g., crystallinity, crystal size, crystal defects, conformation of molecular chain) have already been established satisfactorily. On the other hand, no method has not yet been fully established, for analyzing the fine structure

in the amorphous region, although some tentative methods are proposed such as hygroscopicity (e.g., isothermal absorption curve^[1-4]), iodo-absorbability or phenol-absorbability (e.g., isothermal absorption curve^[5,6]), dyability (e.g., diffusion rate of dyestuff, equilibrium degree of exhaustion of dyestuff^[7-9]) and reactivity towards chemical agents (e.g., change in the amount of reacted-agent with time or its concentration^[10]). These methods are principally based on the difference in the chemical reactivity of both regions which relates only indirectly to the fine structure of fibers. Therefore, we can not compare between the fine structures of polymer solids differing their chemical compositions by these methods. Also, undesirable change in the fine structure of samples during the measurement is unavoidable.

In contrast to this, the dynamic loss tangent ($\tan \delta$) versus temperature (T) curve is expected to reflect sensibly the fine structure of the region, in which the dynamic absorption denoted by α_a absorption is originated by the microbrownian motion of polymer chains in the amorphous region. Fukuda & Ohmori^[11] and Kamide, et al.^[12], for example, demonstrated experimentally that the degree of exhaustion of disperse dyes is proportional to the integrated value of $\tan \delta$ over the temperature region from T_2 to T_1 ; $\int_{T_2}^{T_1} \tan \delta dT$.

Here T_1 is defined as the lower limit of α_a absorption. T_2 is decided experimentally, and depends on the molecular size of dyestuff and the exhaustion time and temperature. However, it should be pointed out that the physical meaning of the quantity $\int_{T_1}^{T_2} \tan \delta dT$ is not clear, and no theoretical background has not yet been given for integrating $\tan \delta$ with temperature. The lack of the fundamental theory on the $\tan \delta$ - T curve is mainly due to the following reasons:

(1) As is clear from the theory of linear viscoelasticity, $\tan \delta$ does not play an important role in the viscoelastic functions of the system in a strict sense, because $\tan \delta$ is only a parameter representing the loss component in the complex modulus and can not be reduced to any other fundamental function such as relaxation spectrum $H(\ln \tau)$. Therefore, when we put strain as excitation and stress as response, it is theoretically recommended to use storage modulus and loss modulus (E'') for describing the viscoelastic properties.

(2) When the system is composed of many components with different relaxation times, we can not calculate theoretically the $\tan \delta$ value of the whole system, even if we know each $\tan \delta$. In contrast to this, other fundamental functions (e.g., E' , E'' , $H(\ln \tau)$) are able to be calculated easily under the suitable assumptions such as the stress additivity or strain additivity from the corresponding values of components.

As $\tan \delta$ is principally independent of the sectional area of the sample, it can be more accurately measured than E' and E'' as far as the commercially available measuring apparatus of viscoelasticity concerns. So, $\tan \delta$ is widely adopted in order to deduce qualitatively the heterogeneity of amorphous regions in fibrous or irregularly-shaped samples despite of its ambiguity of physical meaning.

This series of papers intends to show both the basic theoretical equation for the $\tan \delta$ - T curve and the result of numerical calculation by this equation and also to present a new method for evaluating the fine structure in amorphous regions from the observed $\tan \delta$ - T curve.

In this paper, the theoretical equation and subsequent numerical calculation by it will be given for the viscoelastic body having only one relaxation time.

2. Theory

In Fig. 1 all the possible three-element models with a single relaxation time τ are shown. E_{1a} and E_{2a} are elastic moduli of springs, η_{2a} the viscosity of the dashpot, in model (a). Hereafter, suffixes *b*, *c*, and *d* denote models (b), (c), and (d), respectively. So, when the following equations hold, models (a) and (b) are completely equivalent to each other:

$$E_{1b} = E_{1a} + E_{2a} \quad \dots\dots\dots(1)$$

$$E_{2b} = E_{1a}(E_{1a} + E_{2a})/E_{2a} \quad \dots\dots\dots(2)$$

$$\eta_{2b} = \{(E_{1a} + E_{2a})/E_{2a}\}^2 \eta_{2a} \quad \dots\dots\dots(3)$$

Model (c) is also equivalent to model (d) if E_{1c} , E_{2c} and η_{2c}

Fig. 1 Three element models with a single relaxation time: E ; elastic modulus of spring, η ; viscosity coefficient of dashpot

are given by equations analogous to (1)–(3) (not shown here). Consequently, models (a) and (c) are regarded as the basic model among any three element model with a single relaxation time. After simple calculation we know that the $\tan \delta$ - T curve for model (c) has no maximum (peak) but a minimum. Since the system is composed of such elements as having only one relaxation time, τ_{1c} should be proportional to η_{2c} .

For a polymer solid many kinds of dynamic absorption have been observed in the $\tan \delta$ - T curve. For simplicity, we will discuss here the case in which three mechanical absorptions, α_1 , α_2 , and α_3 from higher temperature side, are observed in this curve and their temperature locations are apart sufficiently from each other. One Maxwell element may be assigned to each of these three absorptions, and three elements thus assigned are assumed to be connected in parallel like the generalized Maxwell model. τ_1 , τ_2 , and τ_3 are denoted as relaxation times of α_1 , α_2 , and α_3 absorptions, respectively. When the measured temperature is near $T_{\max}$ of α_2 absorption, $\omega\tau_1 \gg 1$ and $\omega\tau_3 \ll 1$ hold. This condition deduces that the Maxwell element representing α_1 absorption can be approximated by one spring, and the element of α_3 absorption can be ignored because the viscosity of dashpot of this element becomes nearly zero: The viscoelastic properties of the sample can be expressed by model (a) in Fig. 1.

We adopt model (a) in this study for the following four reasons: (1) This model is suitable for describing the viscoelastic properties of the polymer solid having many mechanical absorptions as mentioned above. (2) It is composed of the minimum mechanical elements which give a peak on

the $\tan \delta$ - T curve. (3) It is easily developed to the generalized Maxwell model when strain is excitation. (4) We can estimate three parameters (E_{1a} , E_{2a} , and η_{2a}) by flash inspection of the experimental E'' - T curve.

E_{1a} corresponds to the elastic modulus of the sample after relaxation of specific absorption in question, and is not always consistent with the equilibrium elastic modulus E_e as generally observed in a cross-linked polymer. E_{2a} equals to the relaxation intensity, and η_{2a}/E_{2a} is approximated to the relaxation time.

With regard to model (a), the calculation of $\tan \delta$ will be done by setting $E_{1a} = E_1$, $E_{2a} = E_2$, $\eta_{2a} = \eta_2$ for simplicity, and

$$\tan \delta = a_s \chi / \{(1 + a_s) \chi^2 + 1\} \quad \dots\dots\dots(4)$$

where ω is measured angular frequency, $\tau = \eta_2/E_2$, $\chi = \omega\tau$, and elastic modulus ratio $a_s = E_2/E_1$. As shown in Appendix 1, eq. (5) holds:

$$\left. \begin{aligned} (\tan \delta)_{\max} &= a_s (1 + a_s)^{-1/2/2} \\ \Delta T_{1/2(s)} &= 5.24 \times 10^{-3} T_{\max}^2 / \Delta Ha \end{aligned} \right\} \quad \dots\dots\dots(5)$$

where suffix s denotes the value of the system composing of a single relaxation time, and ΔHa means apparent activation energy (Kcal/mol). In deriving eq. (5), temperature dependence of τ is assumed to be expressed by either Arrhenius (eq. (6)) or WLF type equation (eq. (7))^[16]:

$$\tau = \tau_{\infty} \exp (\Delta Ha / RT) \quad \dots\dots\dots(6),$$

$$\log \tau = \log \tau_g - C_1^g (T - T_g) / \{C_2^g + (T - T_g)\} \quad \dots\dots\dots(7),$$

where τ_{∞} and τ_g are relaxation times at $T = \infty$ and $T = T_g$, respectively. T_g is glass transition temperature, C_1^g , C_2^g are constants appearing WLF equation, and $C_1^g = 17$ and $C_2^g = 51.6$ are employed in practical calculation. Hereafter we attempt to calculate the $\tan \delta$ - T curve in two cases; Arrhenius and WLF type.

2.1 Case when the temperature-dependence of τ obeys Arrhenius type equation.

Eq. (8) is derived by putting τ of eq. (6) into eqs. (4) and (5):

$$\tan \delta = 2 (\tan \delta)_{\max} \frac{\exp \{(\Delta Ha / R)(1/T - 1/T_{\max})\}}{1 + \exp \{(2 \Delta Ha / R)(1/T - 1/T_{\max})\}} \quad \dots\dots\dots(8)$$

The influence of ω on shape and temperature location of the $\tan \delta$ - T curve is equivalent to that of $T_{\max}$ on them. $T_{\max}$ is given by eq. (9) which is derived from eq. (8) as shown in Appendix 2:

$$T_{\max} = -(\Delta Ha / R) / \{\ln(1 + a_s)^{1/2} + \ln \omega \tau_{\infty}\} \quad \dots\dots\dots(9)$$

Equation (9) indicates that $T_{\max}$ is proportional to ΔHa when τ_{∞} , ω , and a_s are kept constant, since the value of the denominator is always negative. τ_{∞} and a_s are regarded as the function dependent only on absorption mechanism and absorption intensity, respectively. From experimental results it is evident that the relation of $|\ln(1 + a_s)^{1/2}| \ll |\ln \omega \tau_{\infty}|$ holds, and therefore, $T_{\max}$ values of $\tan \delta$ - T curves

concerning to the identical absorption mechanism for various polymer species should be proportional to ΔHa as far as the viscoelasticity of the sample can be described by the Maxwell element with a single relaxation time and eq. (6) holds.

2.2 Case when the temperature dependence of τ obeys WLF type equation

By combining eqs. (4), (5) and (7), we obtain

$$\tan \delta = 2 (\tan \delta)_{\max} \frac{\exp \{(\Delta Ha^w \cdot \Delta Ha, m^w)^{1/2} (1/T_{\max} - 1/T)/R\}}{1 + \exp 2 \{(\Delta Ha^w \cdot \Delta Ha, m^w)^{1/2} (1/T_{\max} - 1/T)/R\}} \quad \dots\dots\dots(10)$$

where ΔHa^w means the apparent activation energy calculated by the equation derived from WLF equation (see eq. (A. 1-14), and $\Delta Ha, m^w$ is ΔHa^w at $T = T_{\max}$.

In order to simplify the numerical calculation, we employ eq. (4) and eq. (11) in place of eq. (10), since eq. (10) include ΔHa^w which depends on temperature in the complicated manner as shown in eq. (A. 1-13).

$$\log \chi = \log \omega \tau_g - C_1^g (T - T_g) / \{C_2^g + (T - T_g)\} \quad \dots\dots\dots(11)$$

Eq. (12) is derived from eq. (9) according to the procedure in Appendix 2.

$$T_{\max} = - \left(\frac{C_2^g \cdot \Delta Ha}{2.303 R C_1^g} \right)^{1/2} \{ \ln(1 + a_s)^{1/2} + \ln \omega \tau_g - 2.303 C_1^g \} \quad \dots\dots\dots(12)$$

$T_{\max}$ is proportional to $\Delta Ha^{1/2}$ under the conditions that a_s , ω , and τ_g are kept constant.

Comparison of the linearity of the plots of $T_{\max}$ vs. $\Delta Ha^{1/2}$ (c.f., eq. (12)) with that of $T_{\max}$ vs. ΔHa (c. f. eq. (9)) enables us to determine which type, Arrhenius or WLF, is preferable in order to express the temperature dependence of relaxation time.

3. Results of Numerical Calculation

3.1 Calculated $\tan \delta$ - $\omega\tau$ curve

In Fig. 2 is shown $\tan \delta$ - $\omega\tau$ ($= \chi$) curves calculated by eq. (4) for a constant a_s . Numbers in the figure indicate the a_s value. With the increase in a_s , $(\tan \delta)_{\max}$ increases as is expected from eq. (5). It has been widely believed from analogy to E'' - T curve that the $\tan \delta$ peak is located at $\chi (= \chi_{\max}) = 1$, but this is not true in the strict sense. The value of $\chi_{\max}$, corresponding to $(\tan \delta)_{\max}$, decreases with the increase of a_s as is shown by

$$(\tan \delta)_{\max} = (1 - \chi_{\max}^2) / \chi_{\max} \quad \dots\dots\dots(13)$$

Equation (13) is derived from eqs. (5) and (A. 1-1), and indicates $\chi_{\max} \leq 1$, that is, $\omega\tau_m \leq 1$.

The $\tan \delta$ value in Fig. 2 approaches to zero at larger value of χ . When $a_s \geq 3.2$, the $\tan \delta$ - T curve is fairly symmetrical with respect to the peak. But when a_s decreases, this symmetry becomes poor. The $\tan \delta$ versus frequency (ω) curve is analogous to that in Fig. 2. at a fixed temperature, since

τ is constant at constant temperature. So, the abscissa ($\omega\tau$ axis) of Fig. 2 is changeable to the frequency axis by multiplying a factor of τ . Naturally, the $\tan \delta$ - ω curve is independent of ΔH_a as seen in eq. (4).

Fig. 2 Theoretical $\tan \delta$ - $\omega\tau$ curves of the model (a) in Fig. 1

Fig. 3 Theoretical $\tan \delta$ -T curve calculated by eq. (8): Numbers denote $T_{\max}$ in K. $a_s = 0.1$, $\Delta H_a = 40$ kcal/mol

3.2 Calculated $\tan \delta$ -T curve when the temperature dependence of τ obeys the Arrhenius

Some examples of $\tan \delta$ -T curves calculated by eq. (8) are demonstrated in Fig. 3 when $(\tan \delta)_{\max} = 0.0477$ (i.e., $a_s = 0.1$, see eq. (5)), $\Delta H_a = 40$ Kcal/mol. Numbers in this figure denote $T_{\max}$, 350, 400, and 450 K. By eq. (5), a_s can be determined from the observed $(\tan \delta)_{\max}$ value. Since $1/\ln(1+a_s)^{1/2}$ is negligibly small compared with $1/\ln \omega\tau_{\infty}$ and ω is obtainable experimentally, $\ln \tau_{\infty}$ can be determined from experimental value of $\Delta H_a/T_{\max}$ by eq. (9).

The higher the $T_{\max}$ of $\log \tan \delta$ -T curve, the broader its shape is as is illustrated in Fig. 3. The curve can be reasonably approximated to a triangle. Here, we define T_l and T_h ($T_l < T_h$) as the temperatures at which the relation of $\log \tan \delta = \log (\tan \delta)_{\max} - 1$ holds. Then, $\Delta T_l = T_{\max} - T_l$ and $\Delta T_h = T_h - T_{\max}$ are calculated. In Fig. 4, $T_{\max}$ and ΔH_a dependence on ΔT_l (full line) and ΔT_h (broken line) are graphed. As $\Delta T_l \cong \Delta T_h$ holds, the $\log \tan \delta$ -T curve can be represented by an equilateral triangle with high accuracy.

Fig. 5 shows the $\log \tan \delta$ -T curve calculated for various ΔH_a values in the region from 20 to 150 Kcal/mol. The increase of ΔH_a narrows the shape of the curve.

Fig. 6 shows the dependence of the $\tan \delta$ -T curve on a_s , ($\Delta H_a = 50$ Kcal/mol, $\ln \tau_{\infty} = -46.06$ sec). The increase in

Fig. 4 ΔH_a dependence of ΔT_l and ΔT_h : Full line; ΔT_l , broken line; ΔT_h

Fig. 5 Change of theoretical $\tan \delta$ -T curves with ΔH_a : Numbers in the figure denote values of ΔH_a in Kcal/mol. $a_s = 0.1$, $T_{\max} = 350$ K

Fig. 6 a_s dependence of theoretical $\tan \delta$ - T curve: ΔH_a is 50 Kcal/mol, and $\ln \tau_\infty$ is -46.06 sec.

Fig. 7 Theoretical $\tan \delta$ -($T-T_g$) curve: Numbers in this figure indicate values of $\log \tau_g$ in sec. a_s is 0.2

a_s makes $(\tan \delta)_{\max}$ large monotonously resulting in the slight shift of $T_{\max}$ to the higher temperature side. This kind of $T_{\max}$ shift is of the order of only 3 deg., even if a_s changes from 0.1 to 1.5.

3.3 Calculated $\tan \delta$ - T curve when the temperature dependence of τ obeys the WLF

As is obvious from eq. (11), $\tan \delta$ is a function of a_s , ω ,

τ_g , and $(T-T_g)$. Therefore it is recommended to use the $\tan \delta$ -($T-T_g$) curve instead of the $\tan \delta$ - T curve in order to determine the quantitative relationships between $\tan \delta$ and the characteristic values such as a_s , ω , and τ_g of a viscoelastic body. Here, we will discuss only the case where ω is constant (690.8 rad/sec). It should be stressed that the limitation of this constancy is not important, since the $\tan \delta$ - T curve at other frequency can be easily calculated from the $\tan \delta$ - T curve at $\omega = 690.8$ rad/sec by using eq. (11), if it is needed. Change in ω corresponds to the change in τ_g from the point of view of numerical calculation of $\tan \delta$ - T curves.

In Fig. 7, $\log \tan \delta$ -($T-T_g$) curves are shown in the $\log \tau_g$ range from 2 to 8 (sec) at fixed a_s (0.2). The curve can be approximated to a triangle. Therefore in the case where temperature dependence of τ is expressed by either Arrhenius or WLF type, the $\log \tan \delta$ - T curve can be approximated by a triangle of $\Delta T_h/\Delta T_l = 1.3$.

In the case where τ obeys the WLF type, the $\tan \delta$ -($T-T_g$) curve is independent of T_g , although Arrhenius-type $\tan \delta$ - T curves with different $T_{\max}$ and constant values of ω , a_s and ΔH_a are not superimposable with each other by shifting the curve along T axis. With the increase of a_s , $(\tan \delta)_{\max}$ increases (see eq. (2)), yielding a slight shift of $T_{\max}$ to the higher temperature side similarly to the case of Arrhenius type.

In Fig. 8 is shown τ_g dependence of $(T_{\max}-T_g)$ at two a_s values. The value of $(T_{\max}-T_g)$ is predominantly determined by τ_g value, almost independent of a_s . Relationships among these parameters are given in eq. (A. 2-3). Here, the value of $(T_{\max}-T_g)$ for $a_s = 0$ is the extrapolated value because of no peak on the $\tan \delta$ - T curve at $a_s = 0$.

Fig. 8 $\log \tau_g$ dependence of $(T_{\max}-T_g)$: Measured frequency is 690.8 rad/sec.

4. Application to Experimental Data

As far as the time-temperature transformation is applicable, temperature rise narrows the distribution of relaxation

time, and consequently, the distribution function can be approximated by a δ function at the temperature near $T_{\max}$. Therefore, various relationships (eqs. (5), (9), and (12) etc.), derived theoretically for a single relaxation time, are also satisfied by the $\tan \delta$ - T curve of real polymer systems. For example, $T_{\max}$ of α_a absorption shifts to the higher temperature side with the increase of ΔHa , and is nearly proportional to ΔHa (eq. (9)) or $\Delta Ha^{1/2}$ (eq. (12)). Furthermore, the observed half value width of the $\tan \delta$ - T curve of α_a is always larger than $\Delta T_{1/2(s)}$ obtained from eq. (5): the latter is the minimum $\Delta T_{1/2}$ and may be named as intrinsic half value width of the $\tan \delta$ - T curve.

A few examples of the application of some relationships derived in section 2 to experimental data will be given below.

4.1 Comparison between Arrhenius and WLF type

In the above theory, we assumed that the temperature dependence of ΔHa was known in advance. Thus, when we apply any relationship to the experimental $\tan \delta$ - T curves observed for real polymers, the temperature dependence of ΔHa for the system should be determined experimentally in any case. To do so, it is necessary to measure the temperature dependence of τ in the wide range of temperature. In practice, ΔHa is calculated by,

$$\Delta Ha = R \ln a_T / d(1/T) \quad \dots\dots\dots(14)$$

where a_T is a shift factor obtained by superimposing the $\tan \delta$ - ω curve at various fixed temperature. More conveniently, ΔHa can be estimated by putting the data of ω dependence of $T_{\max}$ into

$$\Delta Ha = R \ln f / d(1/T_{\max}). \quad \dots\dots\dots(14')$$

Equation (14') is derived by replacing T and a_T in eq. (14) with $T_{\max}$ and f , respectively. When ΔHa is known, it is possible to judge by using the data of $T_{\max}$ and ΔHa values which type, Arrhenius or WLF, is more preferable for representing the temperature dependence of τ .

By plotting experimental $T_{\max}$ values against ΔHa values obtained from literatures for amorphous and semi-crystalline polymers, we obtained the relation of $T_{\max} = 450 \Delta Ha^{1/2}$ for α_a absorption and $T_{\max} = 77 \Delta Ha$ for β_a absorption. This β_a is originated by local twisting vibration of polymer chains. The number of data were 33 for α_a and 22 for β_a absorption.

Comparing these experimental relations of $T_{\max}$ and ΔHa with eqs. (9) and (12), it may be concluded that the temperature dependence of τ obeys the WLF for α_a absorption, and the Arrhenius type equation for β_a absorption.

4.2 Method for determining the absorption mechanism by the $\tan \delta$ - T curve

The first step in the analysis of the $\tan \delta$ - T curve is to study whether the $\tan \delta$ - T curve consists of only one absorption or not. Since $\log \tan \delta$ - $1/T$ and $\log \tan \delta$ - T curves can be approximated by equilateral triangles in case of a single re-

laxation time, the asymmetry of these curves indicates the possibility of coexisting two or more absorptions. When the sample consists of a single relaxation time, its $\tan \delta$ - T curve becomes narrower with decreasing ω as is easily speculated from the result in Fig. 3. So, it may be concluded that the $\tan \delta$ - T curve consists of two or more absorptions, when the curve becomes broad with decreasing ω .

The crystallinity dependence of the absorption intensity makes it clear that the given absorption is originated either by the motion of molecular chains in amorphous regions or by that in crystal regions. When the absorption is originated by the molecular motion in amorphous regions, let us propose a new method by which the absorption is distinguished between α_a and β_a . Here we define a new parameter B_∞ which is given by $522 \Delta Ha / T_{\max}$. The absorption in question can be classified into α_a or β_a by this B_∞ . The coefficient of 522 is derived from the numerical calculation^[14,15] of the $\tan \delta$ - T curve by Rouse theory, by which the relation of $B_\infty = \ln a_0^2 \epsilon_\infty / 6\pi^2 k = -\ln \tau_\infty - 1$ holds. Here, a_0 is the end to end distance of the segment, ϵ_∞ the viscosity coefficient of segmental motion at $T \rightarrow \infty$, and k Boltzmann constant.

In Table 1 are listed the observed values of ΔHa and $T_{\max}/T_m$ (T_m is melting temperature) and calculated values of B_∞ for α_a and β_a absorptions. Since amorphous polymer does not show melting, the judgement of absorption mechanism by $T_{\max}/T_m$ is greatly restricted in practice.

Table 1 Experimental values of ΔHa , $T_{\max}/T_m$, and calculated values of B_∞ for α_a and β_a absorptions

Absorption	ΔHa (Kcal/mol)	$T_{\max}/T_m$	B_∞ (Kcal/mol.K)
α_a	0-150	0.2-0.9	15-200
β_a	0-35	0.2-0.7	0-65

Figs. 9(a) and 9(b) show the normalized frequency distribution curves of ΔHa and B_∞ of α_a and β_a absorptions, which are obtained by employing 33 data for α_a absorption and 22 data for β_a absorption about polymer materials cited in literatures.

The probability to find from ΔHa value whether it belongs to α_a or β_a is about 25%. The corresponding probability to find it from B_∞ is 33%. So, the method by B_∞ is more reliable than the method by ΔHa . From Fig. 9 we can conclude that (1) when $\Delta Ha \geq 35$ Kcal/mol, the absorption can be attributed to α_a , (2) when $B_\infty \geq 63$, the absorption is α_a , and (3) when $B_\infty \leq 31$, the absorption is β_a .

4.3 Application to α_a and β_a absorptions

$T_{\max}$ shifts slightly to the higher temperature side with the increase of $(\tan \delta)_{\max}$ in both cases of Arrhenius and WLF type dependence of τ . Accordingly, with the increase of the crystallinity χ_c (that corresponds to the decrease of a_s , it is expected theoretically that $(\tan \delta)_{\max}$ for α_a and β_a ab-

Fig. 9 Distribution curves of ΔH_a and B_∞ for α_a and β_a absorptions observed for various polymers:

Table 2 Comparison of theoretical values of $\Delta T_{1/2(s)}$ with experimental values of $\Delta T_{1/2}$ in α_a and β_a absorptions for various polymers (110 Hz)

Polymer	α_a absorption				β_a absorption			
	$T_{\max}^{*1}$	ΔH_a^{*2}	$\Delta T_{1/2(s)}^{*3}$	$\Delta T_{1/2}^{*3}$	$T_{\max}$	ΔH_a	$\Delta T_{1/2(s)}$	$\Delta T_{1/2}$
Polyethylene	265	43	8.5	50–	162	13	10.6	50–75
Polypropylene	296	46	10.5	35–	233	14	20.2	110–
Polyethyleneterephthalate ^{*5}	400	67	12.5	20–	220	18	14.1	86.8
Polyvinylchloride	380	68	11.1	40–	285	18	23.6	150–
Polymethylmethacrylate	370	57	12.6	25	340	21	28.8	100–
Polystyrene	404	129	6.8	14–	350	30	21.4	—
Polyvinylacetate	330	40	14.3	45–	— ^{*4}	—	—	—

^{*1} absolute temperature (K), ^{*2} Kcal/mol, ^{*3} deg, ^{*4} unseparable from α_a absorption, ^{*5} crystallinity by X-ray method is 0%

sorptions decreases and $T_{\max}$ shifts to the lower temperature side.

Actually $(\tan \delta)_{\max}$ decreases with the increase in χ_c as is theoretically expected, but $T_{\max}$ shifts either to the higher temperature side^[17] or to the lower temperature side.^[18] The contradiction to the theory may be arisen from the fine structural change in amorphous regions accompanied by the change of χ_c . The fine structural change may induce the changes in ΔH_a and τ_∞ (or τ_g and T_g) at the same time.

The value of $\Delta T_{1/2(s)}$ was calculated by putting the experimental ΔH_a and $T_{\max}$ data into eq. (5), and is the half value width inherent to the $\tan \delta$ - T curve as mentioned above. When the experimental $\Delta T_{1/2}$ value is smaller than $\Delta T_{1/2(s)}$, the absorption may be induced by the resonance vibration in which the sample mass plays an important role.

In Table 2 are listed experimental $T_{\max}$, ΔH_a , $\Delta T_{1/2}$ for α_a and β_a absorptions, and calculated $\Delta T_{1/2(s)}$. $\Delta T_{1/2(s)}$ for β_a absorption (10–30 deg) is larger than that of α_a (5–20 deg). The experimental $\tan \delta$ - T curves relating to β_a absorption are known to be broad. This broadness has been interpreted to be due to the small size of the moving-unit of β_a absorption^[19]; the motion of this unit is affected by the local heterogeneity in the fine structure and therefore gives rise to the broad distribution of relaxation time, resulting in the broad $\tan \delta$ - T curve for β_a absorption. However, the large $\Delta T_{1/2(s)}$ value of β_a absorption may be another reason for broadening the curve. This effect of broadening the inherent half value width is evident (20–30 deg) in the case of polystyrene and polymethylmethacrylate in Table 2.

The values of $(T_{\max} - T_g)$ for α_a absorption obtained by putting experimental $T_{\max}$ and ΔH_a into eq. (A. 1-14) are rather in the narrow range of 20–60 deg, and concentrated around 50 deg. Accordingly, $T_{\max}$ is higher than T_g by about 50 deg.

When $(T_{\max} - T_g)$ is obtained by the above procedure, τ_g can be known from this value in Fig. 8. For example, $\log \tau_g \doteq 5.3$ (sec) in the case of $T_{\max} - T_g = 50$ deg. The τ_g value has not yet been extensively measured so far.^[20] This is due to the complicated analytical procedure adopted. For

example, it is in need to measure T_g in addition to E' , E'' - ω curve or relaxation modulus-time curve, and then to estimate the χ value at temperature T from above curves, and finally to calculate $\omega\tau_g$ by eq. (11). The method proposed here for estimating τ_g value has the merit to be able to decide it with simple analyzing procedure without knowing T_g from $T_{\max}$ and ΔHa .

5. Conclusion

Model (a) in Fig. 1 is most suitable to represent the $\tan \delta$ - T curve for the system in which more than two viscoelastic absorptions are observed. Theoretically, those $(\tan \delta)_{\max}$, $T_{\max}$, and ΔHa are the most important experimental values which characterize the $\tan \delta$ - T curve. The experimental value of $\Delta T_{1/2}$ is larger than $\Delta T_{1/2(s)}$ because of a rough approximation that the distribution of relaxation time of the system can be represented by a single relaxation time. Therefore, quantitative discussion by considering that distribution is still left to open.

Appendix 1 Relationships between a_s and $(\tan \delta)_{\max}$, $T_{\max}$, $\Delta T_{1/2(s)}$ in model (a) in Fig. 1

By applying to eq. (4) the relation of $d \tan \delta / d \chi = 0$ at $\chi = \chi_{\max}$, we obtain

$$\chi_{\max} = (1 + a_s)^{-1/2}. \quad \text{.....(A. 1-1)}$$

By substituting eq. (A. 1-1) into eq. (4), we derive

$$(\tan \delta)_{\max} = a_s / \{2(1 + a_s)^{1/2}\} \quad \text{.....(A. 1-2)}$$

The values of χ which satisfy the equation $(\tan \delta)_{\max} = 2 \tan \delta$ are given by

$$a_s / \{4(1 + a_s)^{1/2}\} = a_s \chi / \{(1 + a_s) \chi^2 + 1\}. \quad \text{.....(A. 1-3)}$$

Equation (A. 1-3) is derived by eqs. (4) and (A. 1-2). Two values of χ (χ_1 and χ_2) obtained from eq. (A. 1-3) are given

$$\begin{aligned} \chi_1 / \chi_{\max} &= (2 - \sqrt{3})/2 \\ \chi_2 / \chi_{\max} &= (2 + \sqrt{3})/2 \end{aligned} \quad \text{.....(A. 1-4)}$$

Thus, we have

$$\ln(\chi_2 / \chi_1) = \ln \{(2 + \sqrt{3}) / (2 - \sqrt{3})\} \quad \text{.....(A. 1-5)}$$

From eq. (6),

$$\begin{aligned} \chi_1 &= \omega\tau_{\infty} \exp(\Delta Ha / RT_1) \\ \chi_2 &= \omega\tau_{\infty} \exp(\Delta Ha / RT_2) \end{aligned} \quad \text{.....(A. 1-6)}$$

Substituting eq. (A. 1-6) into eq. (A. 1-5), T_1 and T_2 can be expressed as

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{R}{\Delta Ha} \ln \frac{2 + \sqrt{3}}{2 - \sqrt{3}} \quad \text{.....(A. 1-7)}$$

when the approximation $T_1 \cdot T_2 \doteq T_{\max}^2$ (A. 1-8) is adopted, eq. (5) holds. On the other hand, when τ is given by eq. (7), we have

$$\begin{aligned} \log \chi_1 &= \log \omega\tau_g + C_1^g(T_1 - T_g) / \{C_2^g + (T_1 - T_g)\} \\ \log \chi_2 &= \log \omega\tau_g + C_1^g(T_2 - T_g) / \{C_2^g + (T_2 - T_g)\} \end{aligned} \quad \text{.....(A. 1-9)}$$

By substituting eq. (A. 1-9) into (A. 1-5), it goes.

$$\frac{C_1^g(T_2 - T_g)}{C_2^g + (T_2 - T_g)} - \frac{C_1^g(T_1 - T_g)}{C_2^g + (T_1 - T_g)} = \log \frac{2 + \sqrt{3}}{2 - \sqrt{3}} \quad \text{.....(A. 1-10)}$$

In the case in which

$$T_2 + T_1 \doteq 2 T_{\max}, \quad \text{.....(A. 1-11)}$$

we have by substituting eq. (A. 1-8) into eq. (A. 1-11),

$$\Delta T_{1/2(s)} = \frac{C_2^g + T_{\max} - T_g}{C_1^g \cdot C_2^g} \log \frac{2 + \sqrt{3}}{2 - \sqrt{3}} \quad \text{... (A. 1-12)}$$

Activation energy ΔHa^w is derived from eq. (7), and

$$\Delta Ha^w = 2.303 R C_1^g \cdot C_2^g T^2 / (C_2^g + T - T_g)^2 \quad \text{(A. 1-13)}$$

Assuming that ΔHa , m^w (ΔHa^w at $T = T_{\max}$) is equal to ΔHa in the Arrhenius type that is, when $\Delta Ha, m^w \doteq \Delta Ha$ (A. 1-14) holds, eq. (A. 1-7) is derived from eqs. (A. 1-13) and (A. 1-14).

Appendix 2 Relationships between ΔHa and $T_{\max}$

When temperature dependence of τ obeys the Arrhenius type equation, we have from eq. (6),

$$\chi_{\max} = \omega\tau_{\infty} \exp(\Delta Ha / RT_{\max}) \quad \text{.....(A. 2-1)}$$

By putting eq. (A. 2-1) into eq. (A. 1-1), eq. (9) can be obtained. When the temperature dependence of τ obeys the WLF type equation, we have from eq. (7),

$$\begin{aligned} \ln \chi_{\max} &= \ln \omega\tau_g - 2.303 C_1^g (T_{\max} - T_g) / \{C_2^g \\ &+ (T_{\max} - T_g)\} \end{aligned} \quad \text{.....(A. 2-2)}$$

Equation (A. 2-3) is derived by substituting eq. (A. 2-2) into the left side term in eq. (A. 1-1).

$$\begin{aligned} 1/2 \ln(1 + a_s) + \ln \omega\tau_g &= 2.303 C_1^g (T_{\max} - T_g) / (C_2^g \\ &+ T_{\max} - T_g) \end{aligned} \quad \text{.....(A. 2-3)}$$

We obtain eq. (12) by eliminating T_g in eq. (A. 2-3) by eq. (A. 1-14).

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