# Application Brief

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## Activation Energy Analysis by Dynamic Viscoelastic Measurements

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### 1.   Introduction

Dynamic viscoelastic measurements provide a method of determining the apparent activation energy of various relaxation phenomena of polymers. The technique of determining the apparent activation energy from the results of dynamic viscoelastic measurements has been investigated by many researchers for many years. Several such techniques have been reported previously[1]. By evaluating the apparent activation energy from dynamic viscoelastic measurements for polymers, it is possible to determine the molecular origin of the observed relaxations, such as the glass transition, local relaxation, or side chain relaxation.

The method of determining the apparent activation energy from a shift factor has been reported Application Brief[2].

### 2.   Principles

Muller and Huff[3] showed that a linear relationship is obtained by plotting log f versus $1/T$, based on the measuring frequency f and the peak temperature $T$ of either loss modulus or loss tangent. The hypothesis that log f versus $1/T$ will plot as a straight line means that the function represented by the slope of the line is an Arrhenius quantity, and that in this temperature range, the activation energy $\Delta E$ can be calculated from this method by the following equation:

$$\Delta E = -R \frac{\ln f}{\partial (1/T)} = -2.303R \frac{\ell og f}{\partial (1/T)}$$

$\Delta E$ : Activation energy
$R$ : The gas constant
f : frequency
$T$ : Absolute temperature

Consequently, an apparent activation energy, $\Delta E$ (kJ/mol), can be calculated by using equation (1) from the measuring frequency f (Hz) and the peak-top temperature $T$ (K) of the tan δ (loss tangent) based on the results of simultaneous measurements of temperature and frequency dispersion.

Table1 shows the activation energy of each kind of relaxation phenomena[4]. By evaluating the activation energy from the result of dynamic viscoelastic measurement of polymer, you can find which relaxation phenomenon (primary dispersion (glass transition), local mode relaxation, side chain relaxation, etc.) cause each dispersion.

Table1 Relaxation phenomena and activation energy[4]

| Relaxation phenomenon | Temperature range | $\Delta E$ (kJ/mol) |
|---|---|---|
| Crystal Relaxation | $(0.8 \sim 0.9)\ Tm$ | $170 \sim 340$ |
| Grain Boundary Relaxation | around $Tc$ | $85 \sim 170$ |
| Primary dispersion | around $Tg$ | $170 \sim 840$ |
| Local mode relaxation | less than $Tg$ | $40 \sim 85$ |
| Side chain relaxation | less than $Tg$ | $40 \sim 125$ |
| Stereo isomer relaxation | less than $Tg$ | $40 \sim 80$ |
| Methyl group relaxation | $T \ll Tg$ | $\sim 20$ |

## 3. Example of Analysis

Figure 1 shows the $E'$, $E''$ and tanδ curves of poly(vinyl chloride) reflecting the results of simultaneous measurements of temperature and frequency dispersion. At around 75 , there is α-dispersion due to the glass transition ; and the β-dispersion due to local mode relaxation, is observed at approximately -70 . Figure 2 is the result of plotting f versus $1/T$ for these two dispersion peaks. Also, the calculation of the apparent activation energy using equation (1) yields a value for the α-dispersion of 590.1 kJ/mol, and for the β-dispersion of 51.1 kJ/mol.



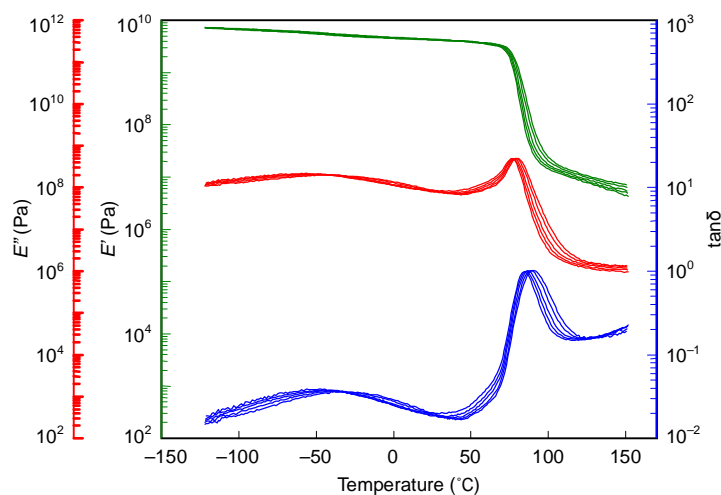Figure 1    $E'$, $E''$ and tanδ curves of poly(vinyl chloride)



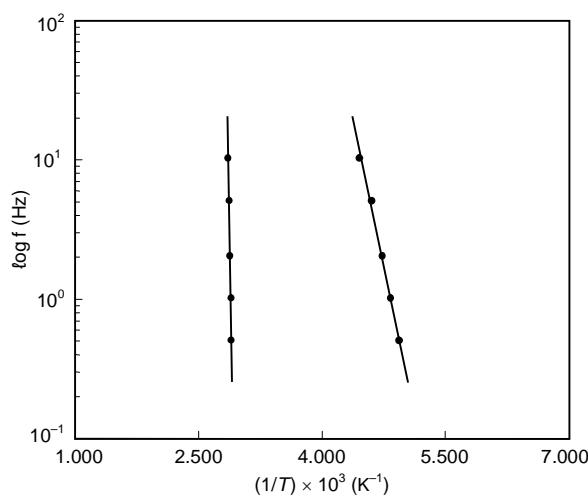Figure 2    ℓog f vs. $1/T$ plots of α- and β-dispersion for poly(vinyl chloride)

Figure 3 shows the tanδ curves of poly(methylmethacrylate) in the primary dispersion (glass transition) region using 13 different frequencies ranging from 0.01 to 100 Hz. Figure 4 shows a log f versus $1/T$ plot of the dispersion peak of poly(methylmethacrylate) shows in Figure 3. From this plot, the apparent activation energy is 399.5 kJ/mol.
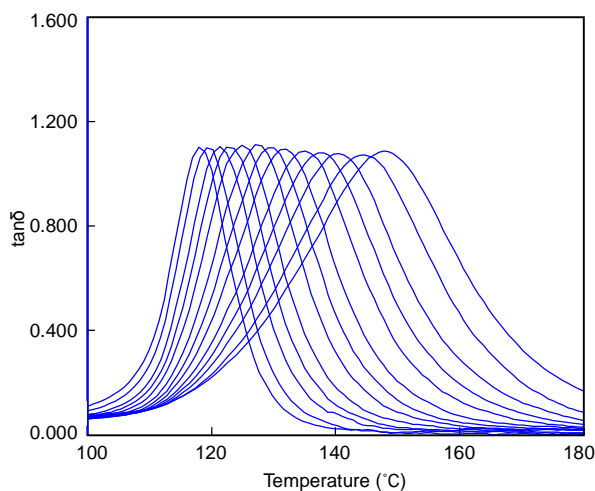


Figure 3    tanδ curves of poly(methylmethacrylate) in α-dispersion region
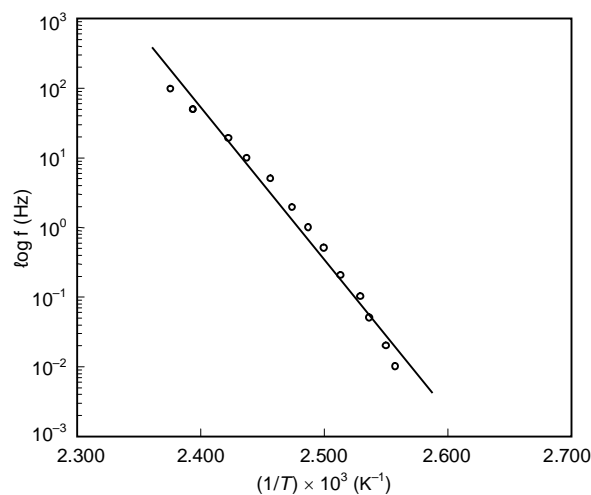


Figure 4    ℓog f vs. $1/T$ plots of α-dispersion for poly(methylmethacrylate)

This Arrhenius plot yields a bow-shaped curve, as shown in Figure 4. This result indicates that the glass transition can not be explained as an Arrhenius type phenomenon. This method of determination is based on the assumption that even if the temperature dependency of relaxation follows WLF behavior, in a narrow frequency range the phenomenon is an Arrhenius type. For this reason, the activation energy obtained by this method is called the "apparent" activation energy.

References
1) J.D Ferry, "Viscoelastic Properties of Polymers", Wiley, New York (1970)
2) Nobuaki Okubo, Application Brief DMS No.6, Hitachi High-Tech Science Corporation (1990)
3) F.H.Muller, K.Huff, Kolleid z., 166, 44 (1959)
4) The Society of Rheology, Japan, "Rheology course", Koubunshikankoukai (1992)

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