

1. Introduction

One of the methods of evaluating the frequency dependency of viscoelastic properties of polymers is the technique of preparing a master curve by dynamic viscoelastic measurements.

A certain relationship based on a principle of “time-temperature superposition” exists between frequency and temperature of results of dynamic viscoelastic measurements. Because of this relationship, it is possible, for example, to convert temperature changes into frequency changes, and to study the frequency dependency of viscoelastic properties at a given temperature. By this method, it is possible to predict the viscoelastic properties over a wide frequency range, beyond the range in which actual measurements can be carried out, to determine the viscoelastic properties of a substance at an arbitrary temperature. Also, by determining the shift factor a_T from a master curve, it is possible to obtain the information necessary for conducting more detailed investigations on the relaxation phenomenon.

In this paper, the preparation of master curves by the WLF method will be explained.

2. Principles

The general reviews of the principle of “time-temperature superposition” is given by Leaderman¹⁾. In his reviews, Leaderman reported that by shifting the creep curves obtained at various temperatures horizontally along the time axis, it is possible to obtain a single creep curve extending over an extremely wide time range. A curve obtained in this manner is called “a master curve”.

Subsequently, Tobolsky^{2,3)}, Williams, Landel, and Ferry^{4,5)} carried out further studies on the principle of “time-temperature superposition”. In particular, the WLF method developed by three researchers, Williams, Landel, and Ferry, relating to the amount of horizontal shift and temperature, is most widely used today.

The WLF equation has the following general formula:

$$\log a_T = -C_1 \frac{T - T_0}{C_2 + T - T_0} \quad (1)$$

For a given reference temperature T_0 , this equation determines the amount of horizontal shift a_T , for data measured at T_0 and T . This horizontal shift quantity, a_T , is called the “shift factor”. In this case, C_1 and C_2 are empirical constants that are determined by the reference temperature T_0 . Substituting the glass transition temperature T_g for the reference temperature T_0 , causes Equation (1) to become:

$$\log a_T = -C_1 \frac{T - T_g}{C_2 + T - T_g} \quad (2)$$

It is known that for most amorphous polymers that C_1 and C_2 assume the following values:

$$C_1 = 17.44 \quad C_2 = 51.6$$

By substituting these numerical values into Equation (2), one obtains:

$$\log a_T = -17.44 \frac{T - T_g}{51.6 + T - T_g} \quad (3)$$

The shift factor a_T for most amorphous polymers can be approximated by this equation.

However, the principle of “time-temperature superposition”, as proposed, was intended to be applied to amorphous polymers only. It should also be noted that the WLF equation holds only in the temperature range between the glass transition T_g and a temperature 100 higher than T_g .

3. Example of Analysis

Figure 1 shows data obtained on poly(methylmethacrylate), PMMA. The curves shown in the figure are the E' (storage modulus) data and the $\tan \delta$ (loss tangent) data for the main dispersion (glass transition) of poly(methylmethacrylate), obtained by simultaneous measurements of temperature and frequency dispersion using 13 different frequencies ranging from 0.01Hz to 100Hz.

Figure 2 shows the frequency dispersion data at constant temperatures ranging 115 to 143 for the E' curves of figure 1. Figure 3 is an example of a master curve prepared from these data shown in figure 2. This is a master curve based on the WLF equation, from which the reference temperature T_0 is set at 130. From 10^{-3} Hz through 10^5 Hz, the individual curves merge into a single master curve.

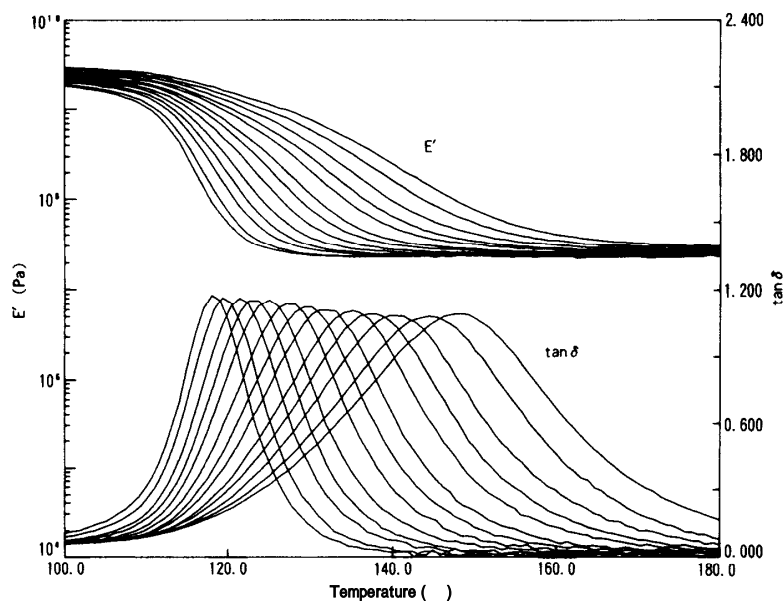


Figure 1 E' and $\tan \delta$ curves of poly(methylmethacrylate)

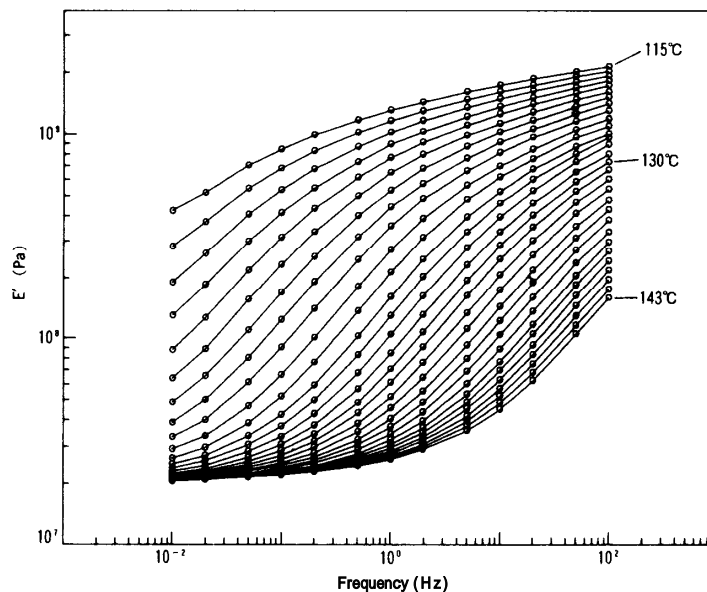


Figure 2 Frequency dispersion data for E' on the main dispersion of poly(methylmethacrylate)

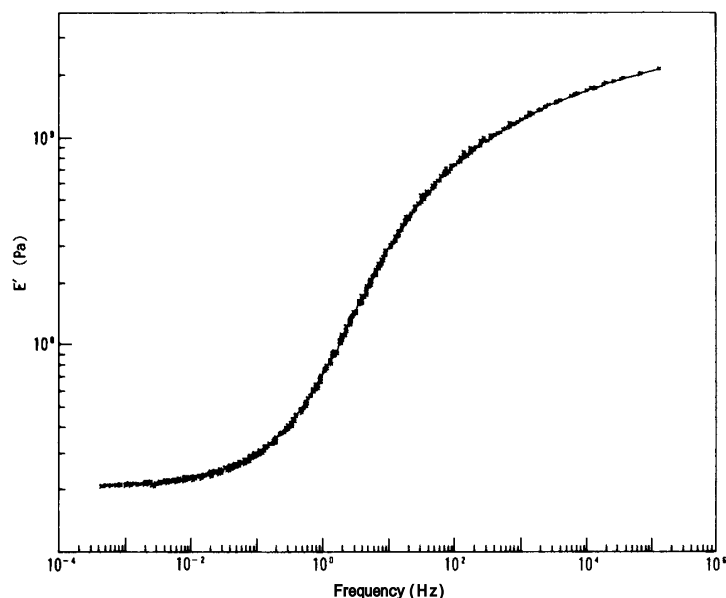


Figure 3 The master curve on the main dispersion of poly(methylmethacrylate)
Reference temperature : 130
Glass transition : 100

Figure 4 shows the relationship between the calculated $\log a_T$, shift factors, at various temperatures according to Equation (3) and the reciprocal temperature, $1/T$. Such a plot, called the Arrhenius plot, allows one to obtain the apparent activation energy E of the relaxation event from the slope of the straight line. In the example of figure 4, an apparent activation energy of 382.9 kJ/mol was obtained on the main dispersion of poly(methylmethacrylate).

Further, by plotting $\log a_T$ versus $1/T$, as shown in figure 4, one can determine whether the relaxation phenomenon is due to a single mechanism or to an interplay of several mechanisms. The $\log a_T$ versus $1/T$ plot of figure 4 is obtained as a single straight line with a certain slope. This indicates that the main dispersion of poly(methylmethacrylate) is due to a single mechanism, consisting of the glass transition.

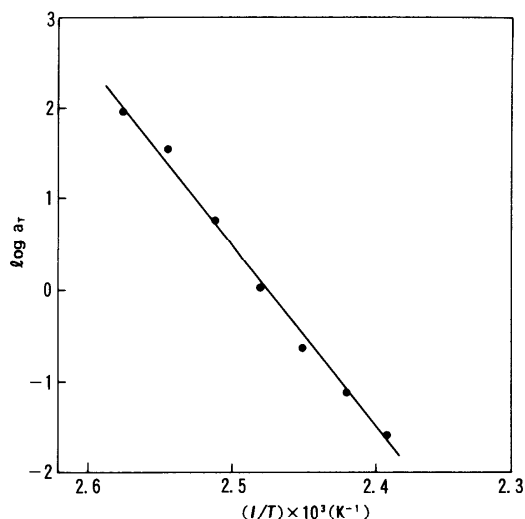


Figure 4 $\log a_T$ vs. $1/T$ plot of the main dispersion of poly(methylmethacrylate)

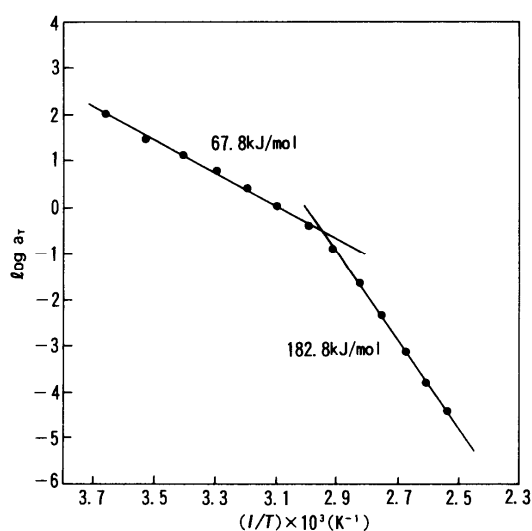


Figure 5 $\log a_T$ vs. $1/T$ plot of the α -dispersion of high-density polyethylene

Figure 5 shows a $\log a_T$ versus $1/T$ plot for the α -dispersion region ($10 \sim 120$) of high-density polyethylene. The figure gives two straight lines with different slopes. This indicates that the α -dispersion region of high-density polyethylene consists of two different mechanisms having significantly different values of the apparent activation energy.

References

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