Korea-Australia Rheology Journal
Vol. 21, No. 1, March 2009 pp. 13-16

Geometric interpretation of time-temperature superposition

Kwang Soo Cho*
Department of Polymer Science and Engineering, Kyungpook National University, Daegu 702-701, Korea
(Received May 2, 2008; final revision received October 23, 2008)

Abstract

We investigate time-temperature superposition from the viewpoint of geometry. The arc length of viscoelastic plots provides powerful resolution for check of the validity of time-temperature superposition. We also suggest a new algorithm for determination of shift factor which is base on the minimization of the total arc length and does not assume any functional form of viscoelastic function.

Keywords : time-temperature superposition, geometric interpretation, linear viscoelasticity

1. Introduction

Time-temperature superposition (TTS) principle (Ferry, 1980) reads

$$G'(\omega,T) = b_T G'(a_T\omega, T_{ref})$$
$$G''(\omega,T) = b_T G''(a_T\omega, T_{ref}), \qquad (1)$$

where a_T and b_T are respectively horizontal and vertical shift factors. The vertical shift factor results from the temperature dependence of product of density and absolute temperature while the horizontal shift factor represents the characteristics of relaxation process of polymeric materials.

Determination of the horizontal shift factor looks like a numerical problem of data fitting, although time-temperature superposition is a problem of physics. In this paper, we interpret TTS from the viewpoint of geometry and provide a new algorithm to determine the horizontal shift factor, which is based on inherent physical nature of polymeric materials and a geometric interpretation of viscoelastic data.

2. Theory

2.1. Definition of arc length and TTS

In geometry, curve is a function from real number to vector such that $t \in R \to \mathbf{x}(t) \in E^n$. When the motion of a particle in 3-dimensional space is considered, the parameter t can be considered as time and the vector $\mathbf{x}(t)$ is the position of a particle. Among several representation of curve, parametric representation is one of the most convenient representations of curve. The arc length is the integral of speed over the range of time and may be used as a parameter in parametric representations of curves. Use of arc length as a parameter simplifies various formulas of differential geometry (Kreyszig, 1983).

Viscoelastic data can be considered as a 2-dimensional curve when they are represented by graph. For example, loss modulus as a function of frequency is considered 2-dimensional curve whose parametric representation is $\omega \to (\omega, G''(\omega))$. The modified Cole-Cole plot can be represented by $\omega \to (G'(\omega), G''(\omega))$.

From the viewpoint of geometry, Eq. (1) represents the curves of dynamic moduli for different temperatures in the plane of $\log G'$ and $\log G''$. Let us call the plane the modulus space. Since horizontal shifting superposes the curves in a single continuous curve identified by the reference temperature, so called master curve, one may consider reparameterization of the master curve with corresponding arc length. We want to define the new parameter that should be inherent for viscoelastic nature of materials. One of the most promising parameters is the arc length of the curve such that

$$\sigma(\omega, T_i) - \sigma(\omega_o^{(i)}, T_i) = \int_{\log\omega_o^{(i)}}^{\log\omega} \sqrt{\left[\frac{\partial \log G'(\omega', T_i)}{\partial \log\omega'}\right]^2 + \left[\frac{\partial \log G''(\omega', T_i)}{\partial \log\omega'}\right]^2}\, d\log\omega', \qquad (2)$$

where $\omega_o^{(i)}$ is the lower limit of the frequency range for temperature T_i.

Comparison of Eqs. (1) and (2) yields

$$\sigma(\omega, T_i) - \sigma(\omega_o^{(i)}, T_i) = \sigma(a_T\omega, T_{ref}) - \sigma(a_T\omega^{(i)}, T_{ref}). \qquad (3)$$

It is noteworthy that the arc length is a monotonically increasing function of frequency. Therefore, we can determine uniquely frequency from the corresponding arc length. It is reasonable to assume that for any temperature

$$\lim_{\omega\to 0} \sigma(\omega, T) = 0. \qquad (4)$$

Eq. (4) implies that

*Corresponding author: polphy@knu.ac.kr

$$\sigma(\omega, T_i) = \sigma(a_T\omega, T_{ref}). \tag{5}$$

It is usual that for homopolymers the vertical shift factor is nearly unity. Then the modified Cole-Cole plot from the data for different temperatures forms a single curve without any manipulation of the data because of Eq. (1). Thus, we can calculate the arc length numerically from the point of the modulus plane from the lowest to the highest of G' as follows

$$s_n = \sum_{k=1}^{n-1} \sqrt{\left(\log\frac{G'_{k+1}}{G'_k}\right)^2 + \left(\log\frac{G''_{k+1}}{G''_k}\right)^2}. \tag{6}$$

In Eq. (6), we assumed that $G'_m \geq G'_n$ whenever $m \geq n$. It is not necessary that the adjacent points (G'_k, G''_k) and (G'_{k+1}, G''_{k+1}) are the data at the same temperature. Eq. (6) is the discrete version of Eq. (2). Since the modified Cole-Cole plot is independent of temperature, the re-parameterization $s_n \to (G'_n, G''_n)$ allows the plot of dynamic modulus as a function of the arc length to be independent of temperature.

It is straightforward that the plot of $\partial\log G'/\partial\log\omega$ versus $\partial\log G''/\partial\log\omega$ is independent of the vertical factor because the vertical factor is cancelled by the partial differentiation with respect to $\log\omega$. Although the plot of $\log G'$ versus $\log G''$ may not form a single curve when the vertical factor is significantly different from unity, the plot of $\partial\log G'/\partial\log\omega$ versus $\partial\log G''/\partial\log\omega$ always forms a single curve whether the dynamic moduli are measured at different temperatures. If experimental data satisfy TTS perfectly, then the plot of $\partial\log G'/\partial\log\omega$ versus $\partial\log G''/\partial\log\omega$ must be independent of temperature. Errors from numerical differentiation and measurement may result in incomplete superposition of the plot of $\partial\log G'/\partial\log\omega$ versus $\partial\log G''/\partial\log\omega$. However, the plot can be used as the barometer to check whether a material satisfies TTS.

One can define several versions of arc length from the plot of any viscoelastic functions. For example, we can define an arc length from the plot of $\log\tan\delta$ as a function of $\log G'$, or an arc length from the plot of loss tangent as a function of frequency too.

2.2. Determination of shift factors from the arc length

For convenience, we assume that data sets of all temperatures are measured for the same set of frequencies, namely $\omega_1 < \omega_2 < \cdots < \omega_N$. Under the assumption that $b_T = 1$, we can give the increasing order to the data points of all temperatures from the lowest value of storage modulus because storage modulus is monotonically increasing function of frequency. We define the arc length difference between nth data point and the first as Eq. (6). Assume that nth data was measured at (ω_j^k, T_k), $(n+1)$th data at $(\omega_i^{k+1}, T_{k+1})$, and $(n+2)$th data at (ω_{j+1}^k, T_k). This implies that G'_n, G''_n, G'_{n+1}, G''_{n+1} and G'_{n+2}, G''_{n+2} are overlapping points between two adjacent temperatures T_k and T_{k+1}. Then from TTS and the definition of the arc length, we have

$$\left.\begin{array}{c} s_n = \sigma(a_{T_k}\omega_j^k, T_{ref}) \\ s_{n+1} = \sigma(a_{T_{k+1}}\omega_j^{k+1}, T_{ref}) \\ s_{n+2} = \sigma(a_{T_k}\omega_{j+1}^k, T_{ref}) \end{array}\right\} \Rightarrow \left\{\begin{array}{c} \log a_{T_k}\omega_j^k = \sigma^{-1}(s_n) \\ \log a_{T_{k+1}}\omega_i^{k+1} = \sigma^{-1}(s_{n+1}) \\ \log a_{T_k}\omega_{j+1}^k = \sigma^{-1}(s_{n+2}) \end{array}\right. . \tag{7}$$

Numerical interpolation gives $\sigma^{-1}(s_{n+1})$ by

$$\sigma^{-1}(s_{n+1}) = \frac{\log\omega_j^k - \log\omega_{j+1}^k}{s_n - s_{n+2}}(s_{n+1} - s_n) + \log\omega_j^k. \tag{8}$$

And finally we have

$$\log a_{T_{k+1}} = \frac{\log\omega_j^k - \log\omega_{j+1}^k}{s_n - s_{n+2}}(s_{n+1} - s_n) + \log\frac{\omega_j^k}{\omega^{k+1}}. \tag{9}$$

The validity of Eq. (9) is dependent on whether the experimental data shows good superposition in the plot of $\log G'$ versus $\log G''$ and the effectiveness of the linear interpolation used. In most case that $b_T \approx 1$, experimental data shows good superposition in the modified Cole-Cole plot and the curvature of the curve in the plot is not severely large.

In case of $b_T \neq 1$, we have to do vertical shifting. Fig. 1 shows that the total arc length of the data of all temperatures becomes the minimum when the superposition is complete. Since the total arc length is given by

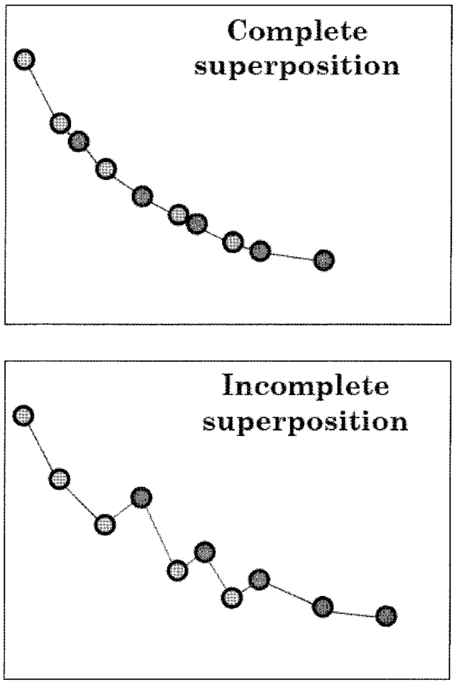

Fig. 1. Superposition minimizes the total arc length. The schematic expression of superposition indicates that when two sets of data do not form the complete superposition, the arc length of the whole data is larger than that of complete superposition

$$S(b_{T_1}, b_{T_2}, \cdots, b_{T_p}) \equiv \sum_{k=1}^{n-1} \sqrt{\left(\log\frac{G'_{k+1}}{G'_k}\right)^2 + \left(\log\frac{G''_{k+1}}{G''_k}\right)^2}\,. \tag{10}$$

A minimization algorithm for S gives the vertical shift factors $\{b_{T_1}, b_{T_2}, \cdots, b_{T_p}\}$ which allow good superposition in the modified Cole-Cole plot.

The algorithm for the vertical shift factor can be applied to the determination of horizontal shift factor. Since the loss tangent is free from the vertical factor because of cancellation, the minimization of the total arc length defined as follows will give the master curve for the plot of loss tangent as a function of frequency

$$L(a_{T_1}, a_{T_2}, \cdots, a_{T_p}) \equiv \sum_{k=1}^{n-1} \sqrt{\left(\log\frac{\tan\delta_{k+1}}{\tan\delta_k}\right)^2 + \left(\log\frac{\tilde{\omega}_{k+1}}{\tilde{\omega}_k}\right)^2}\,, \tag{11}$$

where $\tilde{\omega}_k$ is the reduced frequency which is the frequency multiplied by the horizontal shift factor of corresponding temperature. The ordering k is given from the lowest to the highest value of reduced frequency. Hence it is noteworthy that the minimization requires sorting process previously.

3. Results and discussion

3.1. The master curves from the arc length

Fig. 2 is the modified Cole-Cole plot of polystyrene (PS6 in Schausberger *et al.*, 1985). As shown in the figure, the data do not need vertical shifting. From the plot of Fig. 2, we calculate the arc length (Eq. (6)) and plot the dynamic moduli as functions of s in Fig. 3. Data of storage modulus form a single curve perfectly while those of loss modulus show big separation in the range of $5 \le s \le 15$. The region of the separation in loss modulus corresponds to the local minimum of Fig. 2. Magnification of the region is shown in Fig. 4 where incomplete superposition is shown. Hence it can be said that the plot of loss modulus as a function of

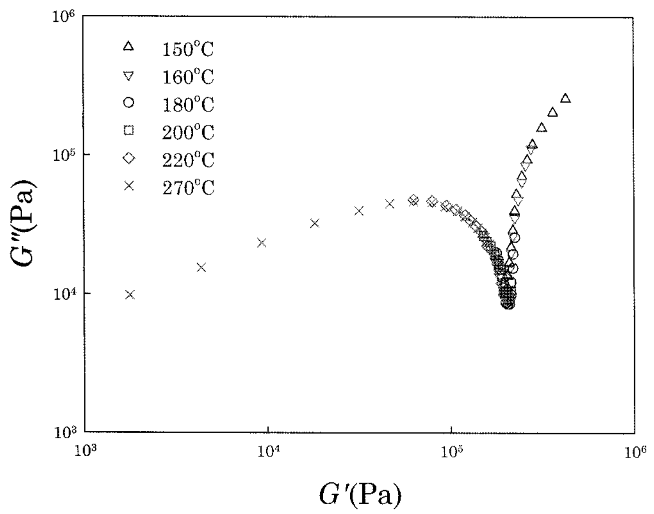

Fig. 2. Modified Cole-Cole plot of polystyrene. (Data from Schausberger *et al.*, 1985, PS6).

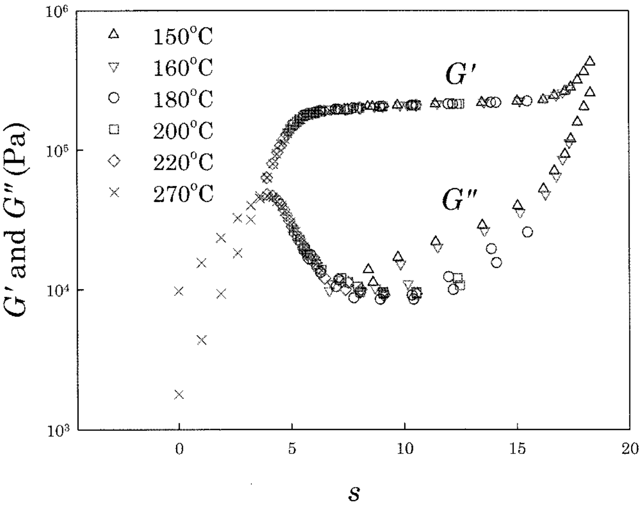

Fig. 3. The master curve obtained from the arc length.

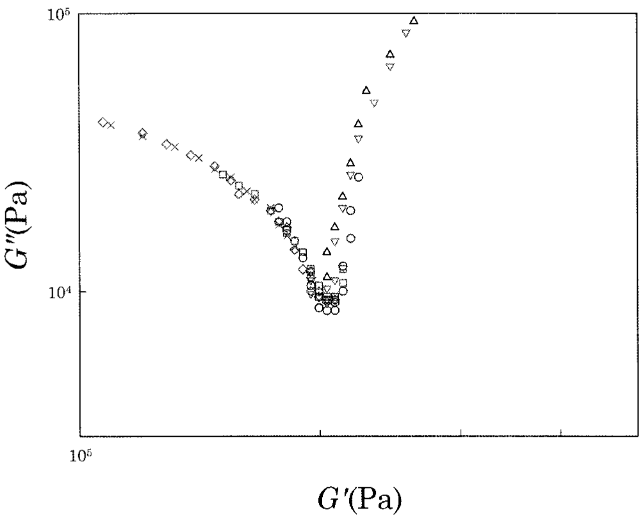

Fig. 4. The magnification of the region of local minimum in Fig. 2.

the arc length has a high resolution power for TTS because the error in calculation of the arc length for the region of the separation is magnified in Fig. 3. Furthermore, the separation of loss modulus in Fig. 3 cannot be cured by vertical shifting.

If we eliminate the data of 150 and 160°C in the region of the separation, the quality of the superposition of loss modulus significantly increases. The quality of the superposition in Fig. 4 can also be increased if the data is eliminated. For polystyrene, temperatures 150 and 160°C are very close to the glass transition. Thus the data of 150 and 160°C in the region of the separation may be considered as less available for the time-temperature superposition.

3.2. The minimization of the total arc length

We have suggested two methods for determination of horizontal shift factor. Both methods, interpolation of Eq.

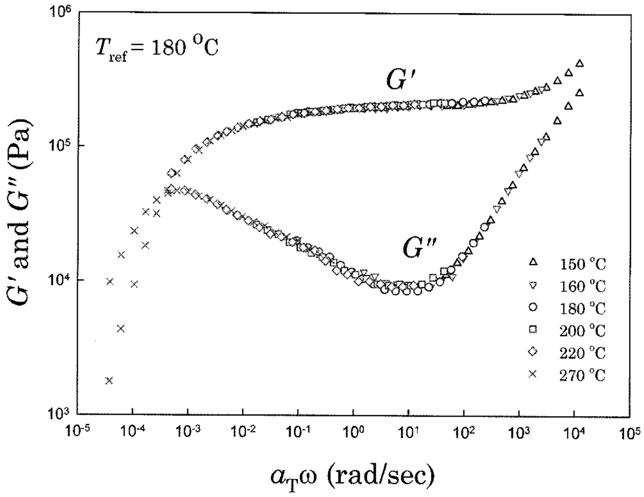

Fig. 5. The master curve from the minimization of the total arc length *L*.

(9) and minimization of Eq. (11) are based on the concept of arc length. In this section we analyze the two methods.

In principle, one can calculate horizontal shift factor by use of Eq. (9). However, this method is not convenient because it is difficult to find overlapping points from experimental data. In some cases, the three adjacent points may belong to three different temperatures. Hence we have to check every pair of three adjacent points to know whether the pair is valid for the application of Eq. (9). Furthermore, we have to calculate the average of the shift factor over the same class of overlapping points. On the other hand, the minimization of the total arc length defined in Eq. (11) is more systematic than the interpolation.

WLF equation is for the temperature dependence of the horizontal shift factor:

$$\log a_T = \frac{-c_1(T-T_{ref})}{c_2+T-T_{ref}}. \tag{12}$$

With varying the values of c_1 and c_2 and ordering the corresponding reduced frequency, we find the values of the parameters for the minimum total arc length defined in Eq. (11). It is the method for determination of horizontal shift factor without assuming the functional form of loss tangent as a function of frequency.

Honerkamp and Weese (1993) used a nonlinear regression for the determination of shift factors by assuming logarithm of dynamic moduli as a polynomial of logarithm of frequency. Their method requires finding the stable range of the order of polynomial and coefficients in addition to the parameters of WLF equations. Although our method does not have to consider the functional form of viscoelastic functions, it requires process of sorting for every step of the minimization of the total arc length L with respect to variation of WLF parameters. The author wants to emphasize that the method of minimization of the total arc length has simple algorithm although it is difficult to compare of the two methods in computation efficiency.

Fig. 5 shows the master curve of the sample of PS6 measured by Schausberger *et al.* (1985). The reference temperature is 180°C. We do not use vertical shifting for the master curve. Fig. 5 shows that our method is efficient for TTS. In order to implement the algorithm, we used the function of SigmaPlot™ called user-defined transform which allows one to code a short program for data processing because SigmaPlot™ is very convenient for scientific graphs as well as for processing of experimental data. For Fig. 5, we adopted full-search to obtain the minimum condition of the total arc length L since user-defined transform of SigmaPlot™ does not provide subroutine or function which is usual in general programming language such as FORTRAN, C, BASIC and so on.

4. Conclusions

The concept of arc length is very useful in analysis of TTS and construction of master curve. The master curve obtained from the plot of dynamic moduli as functions of the arc length magnifies the errors in TTS. The minimization of the total arc length L gives parameters of WLF equation without assumption of functional form of viscoelastic functions.

References

Ferry, J. D. 1980, *Viscoelastic properties of polymers*, John Wiley & Sons, New York.

Honerkamp, J. and J. Weese, 1993, A note on estimating mastercurves, *Rheol. Acta* **32**, 57-64.

Kreyszig, E. 1983, *Advanced engineering mathematics*, John Wiley & Sons, New York.

Schausberger, A., G. Schindlauer and H. Janeschitz-Kriegl, 1985, Linear elasto-viscous properties of molten standard polystyrenes. I. Presentation of complex modulil; Role of short range structural parameters, Rheol. Acta **24**, 220-227.