JOURNAL OF MATERIALS SCIENCE 23 (1988) 1255–1259

Scaling concept and the Williams–Landel–Ferry relationship

F. POVOLO*
Centre d'Etudes Nucléaires de Grenoble, Départment de Recherce Fondamentale, Service de Physique/MP. 85 X - 38041 Grenoble Cédex, France

ELIDA HERMIDA
Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dto. de Física, Pabellón 1, Ciudad Universitaria, (1428) Buenos Aires, Argentina

---

The superposition properties of the Williams–Landel–Ferry relationship, when obtained empirically for different polymer systems and different temperatures, are formulated in terms of more general functions with a scaling property. Finally, an analytical description of these superposition properties is given and the influence of the selected reference temperature on the translations needed to obtain the universal $a_T(T - T_s)$ curve is discussed.

---

1. Introduction

The so-called time–temperature superposition principle is widely used to extend the range of the measurements when transient or dynamic viscoelastic parameters, electrical relaxation processes or the steady state viscosity are studied in polymers, as a function of time and at different temperatures [1–8]. According to this principle, time and temperature are equivalent, that is, a given property measured for short times at a given temperature is identical to one measured for longer times at a lower temperature, except that the curves are shifted on a logarithmic time axis. They can be superimposed once more by proper scale changes on this axis. Similarly, portions of the response curves can be observed at different temperatures and these curve segments can then be shifted along the log(time) axis to construct a composite curve or master curve, applicable for a given temperature, extending many decades of time.

The shift factor for a curve segment is designated by a_T (or b_T for electrical relaxation), $\log a_T$ ($=\log b_T$) being the horizontal displacement to allow it to join smoothly into the master curve. This is the factor by which the time scale is altered due to the difference in temperature, and is a function of temperature. Furthermore, for all linear viscoelastic materials over a limited temperature range, the horizontal shift factors are given by the empirical Williams–Landel–Ferry (WLF) equation [6]

$$\log a_T = -C_1(T_s)\,(T - T_s)/[C_2(T_s) + (T - T_s)] \qquad (1)$$

where T is the temperature, T_s is a reference temperature and C_1, C_2 depend on T_s. Furthermore, according to Williams *et al.* [6], if a reference temperature, T_s, is chosen arbitrarily for one system, the plots of $\log a_T$ against T for other systems can be matched with horizontal and vertical translations, using transparent paper for coincidence in shape. In addition, it was found by these authors that the identical function $a_T(T - T_s)$ applies not only to polymer systems but also to a variety of organic and inorganic glass-forming liquids over a wide temperature range above the vitrification point.

Povolo and Fontelos [9] have shown recently that the time–temperature superposition principle can be considered as a particular case of general functions leading to scaling, with a translation path parallel to the abscissa. In addition, the scaling property has been defined rigorously, to precisely give the meaning of the matching of the different curve segments, when the master or composite curve is constructed. Finally, the WLF equation (Equation 1) has been included within the general formalism presented.

It is the purpose of this paper to study the superposition properties of the WLF equation, for different systems and different reference temperatures, in terms of general functions leading to a scaling behaviour. In addition, how the selection of the reference temperature, T_s, influences the translations needed to obtain the universal $a_T(T - T_s)$ function, is discussed.

2. Theory

A form for the family of curves in the (x, y)-plane, at different z levels, which superimpose under a translation path along a given direction, is given by [9, 10]

$$g[Ax + By + Ch(z)] = ax + by + ch(z) + d \qquad (2)$$

where g is a real function, continuous, single-valued

---

*On leave from: Comisión Nacional de Energia Atómica, Dto. de Materiales. Av. del Libertador 8250, (1429) Buenos Aires, Argentina; Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dto. de Física. Pabellón 1, Ciudad Universitaria, (1428) Buenos Aires, Argentina.

0022-2461/88 $03.00 + .12

and differentiable, A, B, C, a, b, c, d are real constants and $h(z)$ is a real function of z. Furthermore, the translation path in the (x, y)-plane is given by [9, 10]

$$\Delta y/\Delta x = (Ac - Ca)/(Cb - Bc) \qquad (3)$$

with the additional scaling conditions

$$\Delta h(z)/\Delta y = (Ba - Ab)/(Ac - Ca) \qquad (4)$$

and

$$\Delta x/\Delta h(z) = (Cb - Bc)/(Ba - Ab) \qquad (5)$$

Δ indicates finite increments of the corresponding variables. It has also been demonstrated that the WLF equation can be obtained from the scaling condition expressed by Equation 5 [9], if

$$h(z) = p + q/(r + z) \qquad (6)$$

where p, q and r are constants, independent of z. In fact, Equation 5 written as

$$\Delta h(z)/\Delta x = K = \text{constant} \qquad (7)$$

and combined with Equation 6, leads to [9]

$$\Delta x = -C_1(z_0)\,\Delta z/[C_2(z_0) + \Delta z] \qquad (8)$$

with $\Delta z = z - z_0$, where z_0 is a reference value and C_1, C_2 depend on z_0, A more detailed analysis of the relationships between p, q, r and C_1, C_2 is presented in the Appendix.

Equation 1 can easily be obtained from Equation 8 with the change of variables $x = \log(a_T)$, $z_0 = T_s$ and $z = T - T_s$. Furthermore, it can be shown that [9]

$$C_1(T_s) = C_1(T_g)\,C_2(T_g)\,[C_2(T_g) - T_g + T_s]^{-1} \qquad (9)$$

$$C_2(T_s) = C_2(T_g) - T_g + T_s \qquad (10)$$

where $C_1(T_g)$ and $C_2(T_g)$ are the values of C_1 and C_2, respectively, when the reference temperature is taken at the glass transition, that is, $T_s = T_g$. From Equations 9 and 10 it is easy to show that

$$C_1(T_s)\,C_2(T_s) = C_1(T_g)\,C_2(T_g) \qquad (11)$$

where [9]

$$C_1(T_g) = -\beta^*\,v^*/v_{fg} \qquad (12)$$

$$C_2(T_g) = v_{fg}/\alpha v_g \qquad (13)$$

and

$$C_1(T_g)\,C_2(T_g) = -\beta^*\,v^*/\alpha v_g \qquad (14)$$

v_g and v_{fg} are the total and the free volume, respectively, associated with each polymer segment at the glass transition, v^* is the critical free volume, v_f is the free volume associated with each segment, above the glass transition, α is the expansion coefficient for the gross liquid minus the expansion coefficient for the glass, and

$$\beta^* \simeq [\ln(v^*/v_f) - 1] \qquad (15)$$

$C_1(T_g)$ and $C_2(T_g)$ do not depend on the system considered [2] and, consequently, will be indicated in what follows simply as C_1 and C_2.

2.1. Reference temperature at T_g

The situation will be considered, next, in which several log a_T against T curves have been determined, in different systems, by taking T_g as the reference temperature. Then, each curve can be expressed by

$$\log a_T = -C_1\,(T - T_g)/[C_2 + T - T_g] \qquad (16)$$

where T_g has different values for the different systems. Equation 16 can be written as

$$\log a_T/-C_1 = \{1 + 1/[(T/C_2) - (T_g/C_2)]\}^{-1} \qquad (17)$$

which can be reduced to the form of Equation 2 by making the change of variables $x = T$, $y = \log a_T$ and $z = T_g$, that is,

$$-\frac{1}{C_1}y = g\left(\frac{x}{C_2} - \frac{z}{C_2}\right) \qquad (18)$$

then, $A = 1/C_2$, $B = 0$, $C = -1/C_2$, $a = 0$, $b = -1/C_1$, $c = 0$, $d = 0$ and $h(z) = z$. The scaling relationships, given by Equations 3, 4 and 5, are reduced to

$$\Delta y/\Delta x = \Delta\log a_T/\Delta T = 0 \qquad (19)$$

$$\Delta y/\Delta h(z) = \Delta\log a_T/\Delta T_g = 0 \qquad (20)$$

$$\Delta h(z)/\Delta x = \Delta T_g/\Delta T = 1 \qquad (21)$$

showing that Equation 16 has a scaling relationship in the log a_T against T diagram with a translation path parallel to the abscissa. Furthermore, because $\Delta T_g = \Delta T$ the magnitude of the translation depends only on the difference between the glass transition temperatures of the different systems. Then, if a system is selected as reference, a master log a_T against T curve can be constructed for all the systems by translations parallel to the T-axis. It is evident from Equation 16 that a plot of log a_T against $(T - T_g)$ would lead to an unique curve for all the systems.

2.2. Reference temperature at a constant value above T_g

If instead of T_g, a reference temperature T_s is selected in such a way that $T_s = T_g + \delta$, where δ has a constant value for all the systems, then, according to Equations 9 and 10

$$C_1(T_s) = C_1C_2/(C_2 + \delta) \qquad (22)$$

$$C_2(T_s) = C_2 + \delta \qquad (23)$$

and

$$\log a_T = -C_1C_2[T - (T_g + \delta)]/(C_2 + \delta) \times [C_2 + \delta - (T_g + \delta)] \qquad (24)$$

According to Equations 22 and 23, $C_1(T_s)$ and $C_2(T_s)$ have the same values for all the systems because δ is constant. By using the same procedure as in the previous case, except that $z = T_s = T_g + \delta$, Equations 20 and 21 are obtained again and Equation 22 is changed to

$$\Delta T_s/\Delta T = \Delta(T_g + \delta)/\Delta T = \Delta T_g/\Delta T = 1 \qquad (25)$$

Then, a master log a_T against T curve can be obtained for all the systems by a translation along the abscissa. Furthermore, it is evident from Equation 24 that a unique curve is obtained if log a_T is plotted as a function of $(T - T_s) = [T - (T_g + \delta)]$.

2.3. Arbitrary reference temperature

According to Equations 1, 9 and 10, log a_T not only depends on T_s, that is on the reference temperature, but also on T_g, which means that it depends also on the system considered. Then, it can be stated that the log a_T against T curves can be described by the implicit function

$$F(T, \log a_T, T_s, T_g) = 0 \qquad (26)$$

In order to analyse the translations needed to superimpose two log a_T against T curves, corresponding to a given system P_1 at the reference temperature T_{s1} and to another system P_2 at the reference temperature T_{s2}, it is necessary first to consider the translation on the surface characterized by T_{g1} where a displacement is produced from $T_s = T_{s1}$ to $T_s = T_{g1}$. Then, on considering the surface $T_s = T_g$, a new translation is performed to go from the curve for system P_1 to the one corresponding to system P_2. Finally, on the surface for system P_2, characterized by T_{g2}, an additional translation is performed to go from $T_s = T_{g1}$ to $T_s = T_{g2}$.

It will be shown, next, that the first and the third translations are parallel to the log a_T-axis, while the second one is parallel to the T-axis, in the log a_T against T diagram. In fact, the first translation is performed under the condition $T_g = T_{g1} =$ constant. As shown in the Appendix

$$C_1(T_s) = q/K(r + T_s) \qquad (27)$$

$$C_2(T_s) = r + T_s \qquad (28)$$

where r depends on T_g. On substituting Equations 27 and 28 into Equation 1 it is easy to show that

$$-\frac{K}{q}\log a_T = \frac{1}{r + T_s} - \frac{1}{r + T} \qquad (29)$$

On making the change of variables $x = T$, $y = \log a_T$ and

$$h(z) = \frac{1}{r + z} \qquad (30)$$

Equation 29 can be written as

$$x + r = 1\Big/\left[\frac{K}{q}y + h(z)\right] = g\left[\frac{K}{q}y + h(z)\right] \qquad (31)$$

Equation 31 is of the form of Equation 2 with $A = 0$, $B = q/K$, $C = 1$, $a = 1$, $b = 0$, $c = 0$ and $d = r$, so that Equations 3 to 5 are reduced to

$$\Delta y/\Delta x = \Delta\log a_T/\Delta T = 1/0 \qquad (32)$$

$$\Delta y/\Delta h(z) = -q/K \qquad (33)$$

$$\Delta h(z)/\Delta x = (-q/K)/0 \qquad (34)$$

Then, Equation 32 shows that the first translation is parallel to the log a_T-axis.

The second translation, with $T_s = T_g$, has been already considered in Section 2.1, where it has been shown that the displacement is parallel to the T-axis (Equation 19). Finally, the third translation is analogous to the first, on considering $T_s = T_{g2}$, and, consequently, the translation path is parallel to the log a_T-axis.

In summary, on going from the log a_T against T curve, at the reference temperature T_{s2} and for a given system characterized by T_{g2}, to the log a_T against T curve for another system characterized by T_{g1} and at the reference temperature T_{s1}, it is necessary to perform a translation $(\Delta x, \Delta y) = (\Delta T, \Delta\log a_T)$ where

$$\Delta x = \Delta T = (T_{g2} - T_{g1}) \qquad (35)$$

The increment Δy is given by

$$\Delta y = \Delta y_1 + \Delta y_2 \qquad (36)$$

where Δy_1 and Δy_2 correspond to the translations at T_{g1} and T_{g2}, respectively. In fact, according to Equation 33

$$\Delta y = -\frac{q}{K}\Delta h(z) \qquad (37)$$

and, from Equation 30

$$\Delta h(z) = -\Delta z/(r + z)(r + z + \Delta z) \qquad (38)$$

so that

$$\Delta y = \frac{q}{K}\Delta z/(r + z)(r + z + \Delta z) \qquad (39)$$

In particular, for $T_g = T_{g1}$ and $T_s = T_{s1}$, Equation 39 leads to

$$\Delta y_1 = q(T_{g1} - T_{s1})/K[r(T_{g1}) + T_{s1}] \times [r(T_{g1}) + T_{g1}] \qquad (40)$$

and, for $T_g = T_{g2}$ and $T_s = T_{s2}$ to

$$\Delta y_2 = q(T_{s2} - T_{g2})/K[r(T_{g2}) + T_{s2}][r(T_{g2}) + T_{g2}] \qquad (41)$$

On taking into account that $r = C_2 - T_g$, Equations 40 and 41 can be written as

$$\Delta y_1 = q(T_{g1} - T_{s1})/K\,C_2[C_2 - T_{g1} + T_{s1}] \qquad (42)$$

and

$$\Delta y_2 = q(T_{s2} - T_{g2})/K\,C_2[C_2 - T_{g2} + T_{s2}] \qquad (43)$$

By adding Equations 42 and 43 it can be easily shown that

$$\Delta y = \Delta\log a_T = \frac{q}{K\,C_2}\{[(T_{g1} - T_{s1})/(C_2 - T_{g1} + T_{s1})] + [(T_{s2} - T_{g2})/(C_2 - T_{g2} + T_{s2})]\} \qquad (44)$$

The slope of the translation path, in the log a_T against T diagram, is obtained by combining Equations 35 and 44, on taking into account that $C_1C_2 = q/K$, leading to

$$\mu = \Delta\log a_T/\Delta T = C_1C_2[(T_{g1} - T_{g2}) - (T_{s1} - T_{s2})]/[(T_{g2} - T_{g1}) \times (C_2 - T_{g1} + T_{s1}) \times (C_2 - T_{g2} + T_{s2})] \qquad (45)$$

Finally, in the particular case in which $T_{s1} - T_{g1} = T_{s2} - T_{g2} = \delta$, Equation 45 reduces to

$$\mu = \Delta\log a_T/\Delta T = 0 \qquad (46)$$

and the translation path is parallel to the abscissa. This is the particular case already considered in Section 2.2.

3. Discussion

As pointed out earlier in the paper, according to Williams *et al.* [6], if a reference temperature is chosen arbitrarily for one system, the plots of log a_T against T for other systems can be matched with horizontal and vertical translations, using transparent paper for coincidence in shape. This rather unclear and empirical procedure can be understood in terms of the scaling concept and the equations developed in the paper. In fact, if several log a_T against T curves are plotted, for different systems and at different reference temperatures, they can be superimposed to form a master curve, along the translation path given by Equation 45. It should be pointed out that the translation path is different for different pairs of curves, because μ depends on T_s and T_g. In addition, the translation path μ will not, in general, be parallel to the coordinate axes, that is, horizontal and vertical translations are needed, to compose the master log a_T against T curve. This explains the statement of Williams *et al.*

As pointed out in Section 2, the same log a_T against T master curve, once a given system is selected as reference, would be obtained by means of only horizontal translations, if the reference temperature for all the systems is chosen as $T_g + \delta$, where δ is a fixed value. Furthermore, Williams *et al.* computed only the total horizontal displacement for each pair of curves, which is independent from the vertical translation and, consequently, the value $\Delta T = \Delta T_g$ will always be obtained for each pair of systems. In addition, as these authors selected $T_s = T_g + \delta$, with $\delta = 44\,K$, for the reference temperature of the first system (a high molecular weight polyisobutylene), on which the master log a_T against T curve will be constructed, the horizontal displacements will be given by taking the reference temperature $T_g + 44\,K$ for the other systems, where T_g changes accordingly with the system used. In other words, the matching of the different curves, with respect to the reference curve, will be obtained for reference temperatures, T_s, such that $T_s - T_g = 44\,K$. Williams *et al.* obtained empirically $T_s - T_g = 50 \pm 5\,K$, due to the uncertainties in T_g and the errors involved during the translations performed with tracing paper.

Finally, as shown by Equation 24, an universal log a_T against $[T - (T_g + \delta)]$ curve will be obtained, for all the systems, if δ is constant. As Williams *et al.* selected $T_s = T_g + 44\,K$ or, roughly, $T_s = T_g + 50\,K$, they obtained an universal log a_T against $(T - T_s)$ curve. It should also be pointed out that a universal curve should have been obtained for $\delta = 40, 60\,K$ etc., that is, for any fixed value of the reference temperature above the glass transition temperature, in the temperature region where the model is valid.

4. Conclusions

The superposition properties of the WLF relationship, obtained in different polymer systems, have been analysed in terms of a more general formalism of functions with a scaling property.

An analytical description of the scaling properties of the function log a_T against T has been presented and the influence of the selected reference temperature on the translations needed to obtain the universal $a_T(T - T_s)$ curve, has been discussed.

Acknowledgements

One of the authors (F.P.) would like to thank the CNEG, where part of this work was performed during a sabbatical leave, for hospitality and financial support. This work was supported in part by the Consejo Nacional de Investigaciones Cientificas y Tecnicas (CONICET) and the "Proyecto Multinacional de Tecnologia de Materiales" (OAS-CNEA).

Appendix

Combining Equations 7 and 8 of the text leads to

$$\Delta h(z) = -K\,C_1(z_0)\,\Delta z/[C_2(z_0) + \Delta z] \qquad (A1)$$

In addition, $\Delta h(z)$ can be expressed as

$$\Delta h(z) = \sum_{n=1}^{\infty} [h^{(n)}(z_0)/n!]\,(\Delta z)^n \qquad (A2)$$

where $h^{(n)}(z_0)$ indicates the value of the derivative of $h(z)$ of order n, at $z = z_0$. Then

$$-K\,C_1(z_0)\,\Delta z/[C_2(z_0) + \Delta z] = \sum_{n=1}^{\infty} [h^{(n)}(z_0)/n!]\,(\Delta z)^n \qquad (A3)$$

Equation A3 can be written as

$$-K\,C_1(z_0)\,\Delta z = C_2(z_0)\,h^{(1)}(z_0)\,\Delta z + \sum_{n=1}^{\infty} \{[C_2(z_0)\,h^{(n+1)}(z_0)/(n+1)] + h^{(n)}(z_0)\}\,\frac{(\Delta z)^{n+1}}{n!} \qquad (A4)$$

On comparing both polynomials, term by term, it is easy to show that

$$h^{(n)}(z_0) = (-1)^n\,n!\,K\,C_1(z_0)/C_2^n(z_0) \qquad (A5)$$

and Equation A2 can be written as

$$\Delta h(z) = K\,C_1(z_0) \sum_{n=1}^{\infty} [(-1)^n(\Delta z)^n/C_2^n(z_0)] \qquad (A6)$$

If $|\Delta z| < C_2(z_0)$ the series in Equation A6 converges to $\{1 + \Delta z/[C_2(z_0)]\}^{-1} - 1$ leading to

$$\Delta h(z) = \{K\,C_1(z_0)\,C_2(z_0)/[C_2(z_0) + \Delta z]\} - K\,C_1(z_0) \qquad (A7)$$

and

$$h(z) = h(z_0) + \{K\,C_1(z_0)\,C_2(z_0)/[C_2(z_0) + (z - z_0)]\} - K\,C_1(z_0) \qquad (A8)$$

On comparing Equation A8 with Equation 6 of the text, gives

$$p = h(z_0) - K\,C_1(z_0) \qquad \text{(A9)}$$

$$q = K\,C_1(z_0)\,C_2(z_0) \qquad \text{(A10)}$$

$$r = C_2(z_0) - z_0 \qquad \text{(A11)}$$

Moreover, making the change of variable $z_0 = T_s$, leads to

$$C_1(T_s) = q/K\,(r + T_s) \qquad \text{(A12)}$$

and

$$C_2(T_s) = r + T_s \qquad \text{(A13)}$$

Finally, on taking increments of Equation 6 it is easy to show that [9]

$$h(z) = -q\Delta z/(r + z)\,(r + z + \Delta z) \qquad \text{(A14)}$$

References

1. F. S. CONANT, G. L. HALL and W. JAMES LYONS, *J. Appl. Phys.* **21** (1950) 499.
2. F. BEUCHE, "Physical Properties of Polymers" (Interscience, New York, 1962).
3. DONALD J. PLAZEK, *J. Phys. Chem.* **69** (1965) 3480.
4. DONALD J. PLAZEK and JOSEPH H. MAGILL, *J. Chem. Phys.* **45** (1966) 3038.
5. K. A. GROSCH, *Proc. R. Soc.* **A274** (1963) 21.
6. MALCOLM L. WILLIAMS, ROBERT L. LANDEL and JOHN D. FERRY, *J. Amer. Chem. Soc.* **77** (1955) 3701.
7. F. R. SCHARZ, C. W. VAN DER WAL and H. W. BREE, *Chim. Ind.* **54** (1984) 51.
8. U. MEIER, J. KUSTAR and F. MANDELL, *Rubber Chem. Technol.* **57** (1972) 254.
9. F. POVOLO and M. FONTELOS, *J. Mater. Sci.* **22** (1987) 1530.
10. F. POVOLO, *J. Mater. Sci. Lett.* **4** (1985) 619.

Received 19 March
and accepted 22 September 1987