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# Some Remarks Concerning the WLF-Relation

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## Summary

The limitations of the WLF-relation are discussed with respect to their inherent demands concerning universality. The problem of the reference temperature is discussed in some detail, and their constants are related to the temperature $T_\infty$ where the apparent activation energy of flow gets infinite, as well to the characteristic activation energy of viscous flow at infinitely high temperature, $E_\infty$ .

It is concluded that the use of experimentally derived temperature dependent apparent activation energy of flow, E(T), from the slopes of crossing isochrone and isotherm viscoelastic curves substitutes the WLF-relation favourably. Thus, the problematic choice of a reference temperature is avoided. The two kinetically specific constants, $E_\infty$ and $T_\infty$ , may be admitted to characterize the energetic and entropic contribution, respectively, to the viscous flow. Experimental data are presented for some polymers.

## Introduction

In rheology the WLF-relation is still the most used equation for representing the temperature dependence of the viscoelastic properties of polymers although it is well known that the ARRHENIUS law is respected at higher temperatures (sufficiently above $T_g$). Initially, however, it was attempted only by the WLF-relation to correlate the experimental deduced shift factors for constructing composite curves, starting with isothermal rheological data.

The controversy concerning the "universality" of the equation is connected in fact with the need of choice of a reference temperature which has been desired to be universal. Both $T_g$ and $T_0$ were proposed as reference temperatures [1]. Whereas choice of $T_g$ is supported by the DOOLITTLE "hole" model of viscoelastic flow, $T_0$ actually is an arbitrary reference temperature at all.

## Theoretical consideration

The well known WLF-relations depending on the choosen reference temperature are

$$\log a_T = - c_1{}^g(T-T_g)/(c_2{}^g + T - T_g)$$

and

$$\log a_T = - c_1{}^o(T-T_o)/(c_2{}^o + T - T_o) \quad , \qquad (1)$$

with the following correlations between the constants:

$$c_1^g c_2^g = c_1^o c_2^o = \text{constant} \quad ,$$

$$T_g - c_2^g = T_o - c_2^o = T_\infty \qquad (2)$$

and

$$T_o - T_g = c_2^o - c_2^g = 101.6 - 51.6 = 50^o \quad .$$

The corresponding "universal" values of the $c_1$ constant are $c_1^g = 17.44$, $c_1^o = 8.86$.

From the equations (2) it is evident that beside the WLF constants there exist two other constants, the product $c_1c_2$ and $T_\infty$ , respectively, which are independent of the chosen reference temperature.

Consequently, the WLF-relation may be rewritten

$$\log a_T = -c_1^o + c_1^o c_2^o/(c_2^o+T-T_o) = C' + B'/(T-T_\infty) \qquad (3)$$

which shows that the WLF-relation finally is related with the older TAMMANN equation [2]. Due to the similarity of this last expression with an equation suggessted first by VOGEL [3], $T_\infty$ is often called "Vogel" temperature.

Equation (3) again demonstrates the dependence of the WLF-relation on the reference temperature $T_o$. The derivative, however, is depending only on the two constants $c_1c_2$ and $T_\infty$.

The initial assumed universality of the WLF constants is contradicted not only by the experiment, but also by the GIBBS-DI MARZIO theory of glass transition. Applying statistical thermodynamics and assuming a real second order transition at a temperature, $T_2$, far below $T_g$, characterized by a critical entropy of configurational change, $S_c^*$, GIBBS and ADAM [4] get a WLF like expression, which definitely contains a temperature variant $c_2$ constant,

$$c_2^o = a_2(T) = T_o \ln(T_o/T_2)/[\ln(T_o/T_2)+(1+T_o/(T-T_o))\ln(T/T_o)] \ . \qquad (4)$$

The $c_1$ constant, on the other hand, is related to the critical configurational entropy connected with the mobility of the polymer chain,

$$c_1^o = a_1 = 2.303(\Delta\mu S_c^*)/[\Delta C_p T_o \ln(T_o/T_2)] \ . \qquad (5)$$

Thus $c_1^o$ is at least a polymer specific constant. Considering that in fact the product $c_1^o c_2^o$ is the actual temperature invariant constant, $c_1^o$ has to be temperature dependent also.

Beside the WLF-relation an Arrhenius like expression is effective at higher temperatures, which is deduced assuming the validity of EYRING's transition state model for the viscous flow [5]. When written for the temperature dependence of the viscoelastic isotherm shift factor, $\log a_T$, the ARRHENIUS equation yields the expression

$$\log a_T = (E/2.3R)(T^{-1}-T_g^{-1}) = -(E/2.3RT_g)[(T-T_g)/T] \ . \qquad (6)$$

Comparison with the WLF-relation (1) demonstrates that within the range of the ARRHENIUS like temperature dependence of the shift factor, the reference temperature $T_g$ equals the $c_2^g$ constant, and the Vogel temperature $T_\infty$ reaches absolute zero.

Supposing that the equilibrium energy distribution is not perturbed by the viscous flow, the only physical sensefull temperature derivative of $\log a_T$ is that with respect to the reciprocal temperature. This assumption is suggested also by the ARRHENIUS type equation (6), taking into account the resulting relation

$$d(\log a_T)/d(1/T) = E/2.3R \ . \tag{7}$$

The corresponding derivative of the WLF-relation yields

$$d(\log a_T)/d(1/T) = c_1^g c_2^g T^2/(c_2^g+T-T_g)^2 = E(T)/2.3R \ . \tag{8}$$

The second right hand term is written in analogy to the respective ARRHENIUS equation (7). It suggests in the WLF range a temperature dependent activation energy of the local flow which increases when approaching $T_g$.

The equation claims an extrem value of E(T) for $T=T_g$. This is meaningless because energy driven relaxation processes ar still possible below $T_g$ except viscous flow. This may be an explanation too for the fact that the WLF-relation fails in vicinity of $T_g$ 6).

## Kinetic origin of the constants of viscous flow

It has been shown already that E(T) is accessible directly from experimental data, and that it may be computed from the ratio of the slopes at a given point of the intersecting isochrone and isotherm viscoelastic curves 7). Than the shift factor can be determined by integration of equ. (8)

$$\log a_T = \int_{1/T_g}^{1/T} [E(T)/2.303R] d(1/T) \quad . \tag{9}$$

As a consequence $\log a_T$ always is depending on the integration constant, which is related to the reference temperature, whereas E(T) is not. Consequently E(T) only will characterize the temperature dependence of the viscoelastic behaviour of a polymer system unequivocally.

Some representative data of the temperature dependence of the activation energy of flow are illustrated in Figure 1. The respective values for poly(n-octylmethacrylate) were calculated applying the original data of FERRY et al. 9). It is quite evident that for most of the polymers the WLF range of increasing activation energy of flow is restricted, starting around $T_g + 50^{o}$. Polystyrene seems to be an exception, with a broader WLF range 10). A decrease of the temperature dependent activation energy very near $T_g$ is evident too. It may be an explanation of the failure of the WLF approach in this range 6). It may be stated, however, that in the region of polymer processing constant activation energy either is given or valid approximately.

The right hand terms in equ. (8) may be rearranged as follows

$$[2.3R/E(T)]^{0.5} = [1/c_1^g c_2^g]^{0.5}(1-T_g-c_2^g)/T = [c_1^g c_2^g]^{-0.5}(1-T_\infty/T) \ . \tag{10}$$

The intersection with the coordinates of this straight line, which corresponds to WLF behaviour of the viscoelastic system, are

$$\begin{aligned} &(2.3R\ /\ E_\infty)^{0.5} = (1\ /\ c_1^g c_2^g)^{0.5} && \text{for the ordinate} \\ &T = T_\infty && \text{for the abscissa} \end{aligned} \tag{11}$$

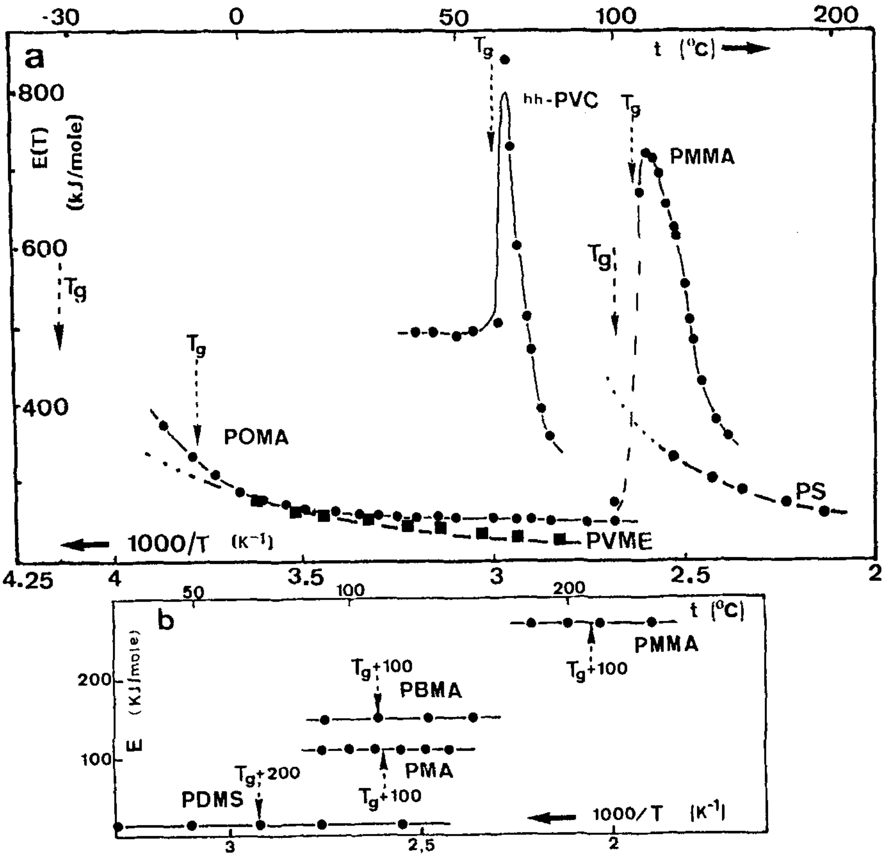

Figure 1 : Apparent activation energy of flow versus reciprocal temperature for head-to-head polyvinylchloride (hh-PVC), poly(methylmethacrylate) (PMMA), poly(n-butylmethacrylate) (PBMA), poly(n-octylmethacrylate) (POMA), poly(methacrylate) (PMA), polystyrene (PS) and poly(dimethylsiloxane) (PDMS)

Thus, $T_\infty$ represents a critical temperature at which the activation energy of flow gets inifinite and the viscous flow becomes impossible. When assuming that $T_\infty$ equals $T_2$ of the GIBBS - DI MARZIO theory, $T_\infty$ will be the characteristic temperature at which the flow becomes entropically impossible. Similarly the $E_\infty$ - value represents the characteristic activation energy of viscous flow at infinite temperature. It gives a measure of the energetic contribution to the flow process.

A discussion of the role of these two characteristic quantities in the compatible polystyrene - poly(vinylmethylether) blends is presented elsewhere [8].

Equ. (11) evidences also that the product of the two WLF constants is related to the characteristic activation energy $E_\infty$

$$c_1^g c_2^g = E_\infty / 2.303\, R \quad . \qquad (12)$$

This last expression suggests a different physical sense for the constants in the WLF-equation than the "free volume theory" and the DOOLITTLE model of viscous flow [1], $c_1^g c_2^g = B/2.3\ \Delta\alpha_f$, where B is the constant of the Doolittle equation relating the viscosity to the fractional free volume and $\Delta\alpha_f$ its expansion coefficient.

According to equ. (2), the $c_2^g$ constant is given by the difference $T_g - T_\infty$. Thus, the $c_1^g$ WLF constant will be related supplementary to the high temperature limit of the activation energy of flow

$$c_1^g = E_\infty / 2.303\ R\ (T_g - T_\infty)\ . \qquad (13)$$

Applying the above defined constants, which are supported by kinetic considerations, the WLF-relation may be reformulated as follows

$$\log a_T = -(E_\infty/2.303R\ (T_g - T_\infty)][(T - T_g)/(T - T_\infty)]\ . \qquad (14)$$

The assumed "universality" of the WLF constants, $c_1^g c_2^g = 899.9$ K, claims for an "universal" $E_\infty$ value of about 17.23 kJ $mol^{-1}$ too. This means that the straight lines plotted accordingly to equ. (10) all will intersect the ordinat in the same point. This is demonstrated in Figure 2 by the small dotted lines which connect the common intersection point on the ordinate with the respective $T_g$ values of the polymers. It is evident, however, that this requirement of "universality" of the WLF constants is contradicted by the experiment.

The slopes of some straight lines - computed using experimental E(T) data as obtained from the ratio of the slopes of isochrone and isotherm curves - are incidently in acord only with the requirements of universal WLF constants. For most of the polymers shown in Fig.2 the slopes are quite different, and the respective (full) lines are delimited by the respective $T_g$ at the one end, and by the constant activation energy characteristic for the ARRHENIUS range of flow (full horizontal line).

Therefore, a delimitation of the constant and of the temperature-variable ranges of apparent activation energy of flow is unequivocal with this type of representation of viscoelastic data.

Extrapolation of the WLF domain straight lines yield not only the expected polymer specific $T_\infty$ values, but also the $E_\infty$ data from the intercept, which are also specific for a polymer. Table I presents the obtained values, together with the corresponding $T_g$, the $T_g - T_\infty$ differences and the $c_1^g$ values computed according to equ. (13). It is evident that not only the product, but also the individual constants of the WLF-relation are specific for a polymer. The number of the presented data appears to small, however, for a detection of trends and of regularities.

An interesting observation induced by the data in Fig. 2 is the fact that the $T_g$'s may be connected by a (full dotted) straight line approximately, which intersects the abscissa at about 725 K. Apparently, $T_g$ and $T_\infty$ coincide at this limiting temperature. It may be worthwile to reflect on the consequences.

As the final consequence, it can be concluded that the use of E(T) data as computed from the slopes of crossing experimental isochrone and isotherm curves substitute the WLF-relation in a favourable way. The crucial choise of a suitable reference temperature is thus avoided. Supplementary, presentation of the data according to equ. (10) delimits the temperature range of both WLF and ARRHENIUS type viscoelastic behaviour. The transition between the two regions is analyzable too. Extrapolation of the range of temperature dependent activation energy of flow yields the two specific kinetic constants, $E_\infty$ and $T_\infty$, which characterize the energetic and the entropic contribution to local flow.

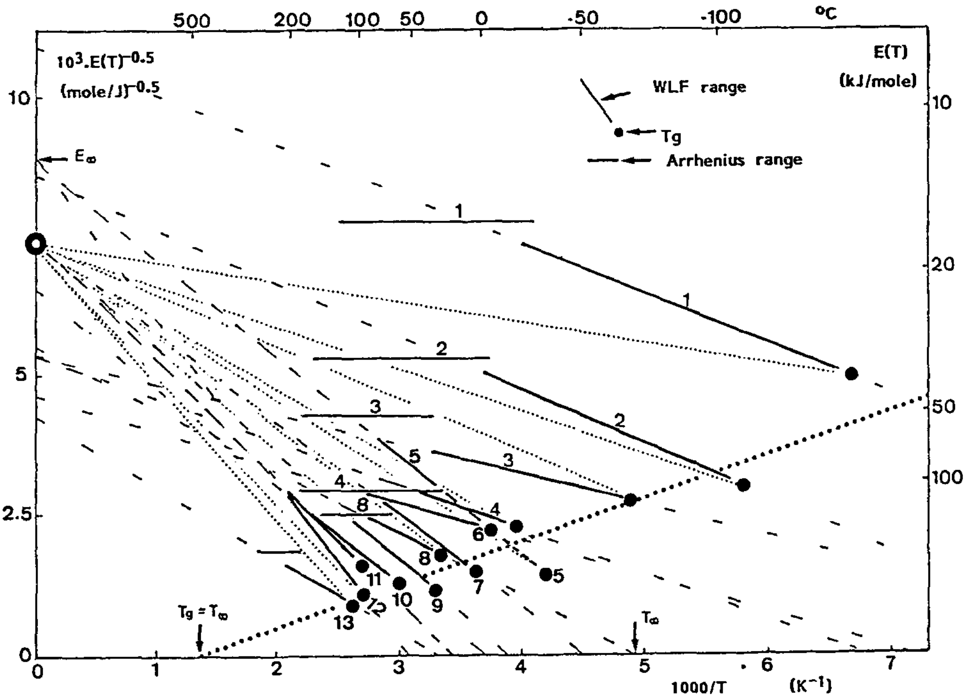

Figure 2. Presentation of viscoelastic data accordingly to equ. (10)
o – Ordinate expected for "universal" WLF-constants. Polymers, see Table I

TABLE I : WLF constants of some polymers

| | Polymer | Ref. | $T_g$ | $E_\infty$ | $T_\infty$ | $T_g - T_\infty$ | $c_1{}^g$ | |
|---|---|---|---|---|---|---|---|---|
| 1. | Poly(dimethylsiloxane) | 7) | 148.0 | 8.08 | 79.8 | 69.2 | 6.11 | |
| 2. | Polybutadiene | 12) | 171 | 13.03 | 108.9 | 62.1 | 10.97 | x (cis) |
| 3. | Poly(isobutylene) | 13-15) | 201.5 | 33.43 | 99.6 | 101.9 | 17.16 | |
| 4. | Poly(n-octylmethacrylate) | 9) | 203 | 31.51 | 145.9 | 57.1 | 28.86 | x |
| 5. | Poly(vinylmethylether) | 11) | 237.9 | 12.12 | 201.5 | 36.4 | 17.81 | |
| 6. | Poly(n-hexamethylacrylate) | 16) | 268 | 44.38 | 137.7 | 130.3 | 17.81 | x |
| 7. | Poly(methylacrylate) | 17) | 283 | 17.23 | 220.0 | 63.0 | 14.30 | x |
| 8. | Poly(n-butylmethacrylate) | 15,17) | 285.8 | 31.18 | 200.7 | 85.1 | 19.16 | |
| 9. | Poly(vinylacetate) | 18,19) | 305 | 17.23 | 255.4 | 49.6 | 18.17 | x |
| 10. | Poly(ethylmethacrylate) | 20) | 338 | 22.64 | 267.6 | 70.4 | 16.82 | x |
| 11. | Polystyrene | 10) | 373.0 | 31.18 | 294.4 | 36.4 | 17.14 | |
| 12. | Polystyrene | 20,21) | 373 | 12.12 | 322.6 | 50.4 | 12.58 | |
| 13. | Poly(methylmethacrylate) | 15,20) | 386.8 | 52.59 | 299.3 | 87.5 | 31.42 | |

x : $T_g$ data from Polymer Handbook [24]

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