

# polymer communications

## On the van Krevelen/Hofter relationship for the high-temperature limiting viscosities of polymer melts

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The van Krevelen/Hofter limiting viscosities ( $T \rightarrow \infty$ ) of polymer melts are often lower than the high-temperature viscosity of low-molecular weight liquids or the viscosity of air at 20°C and 1 bar. The origin of this surprising result is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

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In refs 1 and 2, van Krevelen and Hofter discussed the temperature dependence of the viscosity of polymer melts. Viscosity  $\eta_{cr}$  at the critical molecular weight (transition from  $M^{+1}$  to  $M^{3,4}$  dependence) was plotted in the normalized Arrhenius diagram shown in *Figure 1*. At low temperatures (just above  $T_g$ ) the line is curved and follows a Vogel/WLF course<sup>3</sup>; at high temperatures, the line is more or less straight suggesting true Arrhenius behaviour. Assuming such Arrhenius behaviour, the limiting flow-activation energy  $E_{\eta}(\infty)$  and the limiting viscosity  $\eta_{cr}(\infty)$  are determined as indicated.

According to the procedure of *Figure 1*, van Krevelen and Hofter determined  $E_{\eta}(\infty)$  and  $\eta_{cr}(\infty)$  for various polymers. The data sources are given in ref. 1 and examples of viscosity vs temperature curves can be found in ref. 1 or in Fig. 15.3 of ref. 2. The resulting activation energies (from Table 15.5 of ref. 2) are reproduced in *Table 1*.

Interestingly, van Krevelen and Hofter found an empirical correlation between the flow activation energy  $E_{\eta}(\infty)$  and the limiting viscosity  $\eta_{cr}(\infty)$ . It is given by equation (15.38) of ref. 2 reading

$$^{10}\log \eta_{cr}(\infty) = -1.4 - 0.085E_{\eta}(\infty) \quad (1)$$

with the viscosity in Pa s and the activation energy in  $\text{kJ mol}^{-1}$ . The last column of *Table 1* gives the limiting viscosity  $\eta_{cr}(\infty)$  as calculated with equation (1) from the activation energies given in *Table 1*. The remarkable point is that the limiting viscosity  $\eta_{cr}(\infty)$  decreases with increasing activation energy and drops to values as low as  $10^{-8}$  Pa s (see also Fig. 15.5 of ref. 2).

For non-associated and low-molecular weight liquids, the limiting viscosity ( $T \rightarrow \infty$ ) generally lies at about  $10^{-4}$  Pa s<sup>4,6</sup>. Moreover, the viscosity of air at 20°C and 1 bar is  $1.7 \times 10^{-5}$  Pa s. Thus, the values of  $10^{-5}$ – $10^{-8}$  Pa s shown by *Table 1* are really surprising.

*Figure 2* shows that van Krevelen's limiting viscosity decreases with increasing  $T_g$ . This is related to the decrease in  $\eta_{cr}(\infty)$  with increasing activation energy [equation (1)] since  $T_g$  roughly increases with the flow activation energy (see *Table 1* and refs 7 and 8). Assuming that the limiting viscosity of polymers exceeds that of low-molecular weight liquids ( $10^{-4}$  Pa s), we

conclude from *Figure 2* that van Krevelen's extrapolations fail for polymers with a  $T_g > 200$  K.

A tentative explanation for this failure is given in *Figure 3*. As an example, we take rigid PVC. This material has a  $T_g$  of 81°C. The thermal stability of the polymer prevents viscosity measurements at temperatures far above 200°C. So, the viscosity is measured for  $T_g/T > 0.70$ , i.e. most probably in the curved part of the plots of *Figures 1* and *3*. This would lead to an activation energy ( $E_a$ ) that is too high [ $> E_{\eta}(\infty)$ ] and a  $\eta_{cr}(\infty)$ -value that is too low (see extrapolated dashed line in *Figure 3*). In contrast, viscosities of low- $T_g$  materials such as PE or PDMS can be measured at temperatures much further removed from  $T_g$ , i.e. at  $T_g/T$  values considerably lower than 0.70. For such materials, the linear (Arrhenius) part of the curve will be reached more easily and the activation energy as well as  $\eta_{cr}(\infty)$  will approach the correct values.

A semi-quantitative check of the idea is obtained by applying the WLF equation with the 'universal' constants  $c_{1g} = 17$  and  $c_{2g} = 51^\circ\text{C}^3$  (subscript  $g$  denotes that  $T_g$  was taken as reference temperature). For simplicity, we omit the Arrhenius term which is sometimes added for a better description at very high temperatures<sup>3</sup>; such omission hardly affects the results. We write the WLF equation in the Vogel form<sup>3</sup>

$$\ln \eta/\eta_{\infty}^* = B/(T - T_{\infty}) \quad (2)$$

where

$$T_{\infty} = T_g - c_{2g} \quad (3a)$$

$$B = 2.303c_{1g}c_{2g} \quad (3b)$$

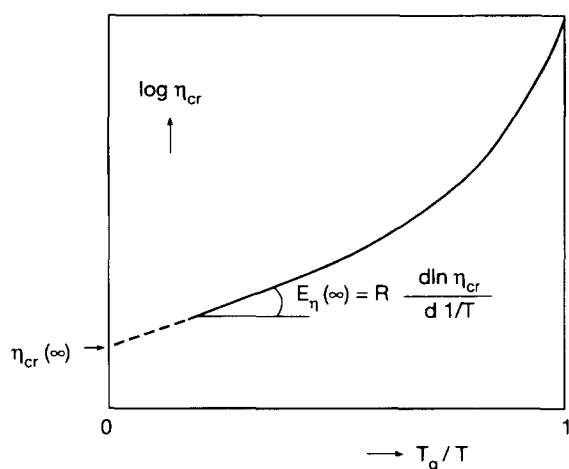
and  $\eta_{\infty}^*$  is the assumed quasi-universal limiting value for  $T \rightarrow \infty$ :

$$\eta_{\infty}^* = 10^{-4} - 10^{-3} \text{ Pa s} \quad (4)$$

The apparent activation energy defined in *Figure 3* equals

$$E_a = R d \ln \eta / d(1/T) = RB T^2 / (T - T_{\infty})^2 \quad (5)$$

If we extrapolate according to this apparent activation energy (as van Krevelen did), we do not find  $\eta_{\infty}^*$  but



**Figure 1** Plot of viscosity  $\eta_{cr}$  vs  $T_g/T$ ; for details see text; the dashed part of the curve is an extrapolation

**Table 1** Parameters of van Krevelen/Hoflyzer  $\eta_{cr}$  correlation<sup>1,2</sup>. First columns taken from Table 15.5 of ref. 2;  $\eta_{cr}(\infty)$  (third column) was calculated with equation (15.38) of ref. 2 (equation (1) of present paper). Subscript cr indicates that the viscosities were taken at the critical molecular weight,  $M_c$ , where the  $M$ -dependence changes from  $M^{1.1}$  to  $M^{3.4}$

Polymer	$T_g$ (K)	$E_{\eta}(\infty)$ (kJ mol <sup>-1</sup> )	<sup>10</sup> log $\eta_{cr}(\infty)$ $\eta$ in Pa s
Polyethylene	195	25	-3.53
Polypropylene	253	44	-5.14
Polyisobutylene	198	48	-5.48
Polystyrene	373	59	-6.42
Poly(vinyl chloride)	354	85	-8.63
Poly(vinyl acetate)	301	67	-7.10
Poly(methyl methacrylate)	378	65	-6.93
Poly(butyl methacrylate)	300	72	-7.52
Polybutadiene(cis)	171	26	-3.61
Polyisoprene	220	23	-3.36
Poly(ethylene oxide)	206	27	-3.70
Poly(decamethylene succinate)	210	28	-3.78
Poly(decamethylene adipate)	217	29	-3.87
Poly(decamethylene sebacate)	197	30	-3.95
Poly(ethylene terephthalate)	343	45	-5.23
Nylon 6	323	36	-4.46
Polycarbonate	414	85	-8.63
Poly(dimethyl siloxane)	150	15	-2.68

viscosity  $\eta_{\infty}$  given by (see Figure 3)

$$\ln \eta/\eta_{\infty} = E_a/[RT] = BT/(T - T_{\infty})^2 \quad (6)$$

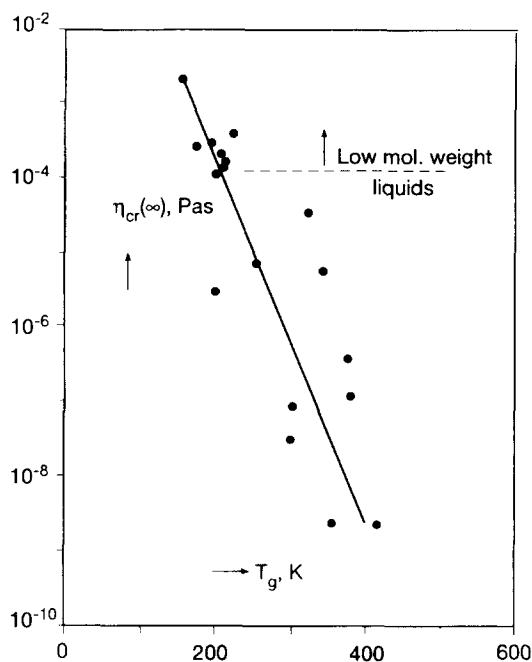
Subtracting equations (2) and (6), we find with equation (5)

$$\ln \eta_{\infty}^*/\eta_{\infty} = BT_{\infty}/[T - T_{\infty}]^2 = E_a T_{\infty}/[RT^2] \quad (7)$$

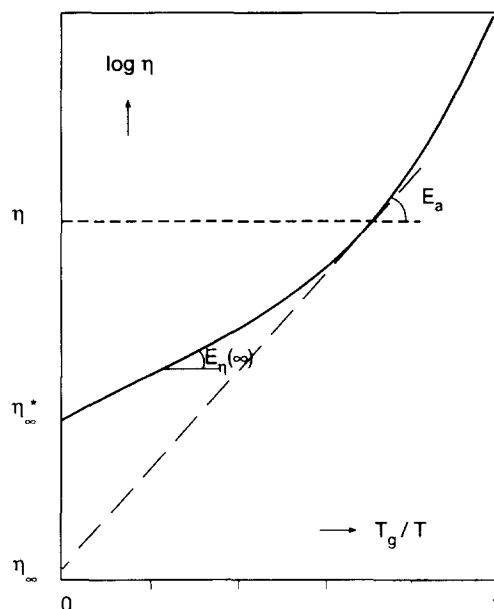
With equations (3)–(5) and using the quasi-universal WLF parameters (17 and 51), we find:

$$\begin{aligned} \log \eta_{\infty} - \log \eta_{\infty}^* &= -[E_a/(2.303RT_{\infty})] \\ &\quad \times [1 - \sqrt{(RB/E_a)}]^2 \\ &= -52.2E_a[1 - \sqrt{(16.6/E_a)}]^2 / \\ &\quad \times (T_g - 51) \end{aligned} \quad (8)$$

in which  $E_a$  is expressed in kJ mol<sup>-1</sup>. Figure 4 below shows that the  $\eta_{\infty}$  predicted with this equation correlates with the limiting viscosity as predicted by van Krevelen's equation. This agreement is not perfect which may be

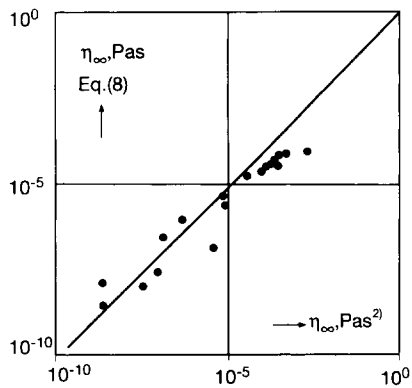


**Figure 2** Limiting viscosity  $\eta_{cr}(\infty)$  vs  $T_g$ ; data from Table 1



**Figure 3** On the problems with van Krevelen's extrapolation to  $T \rightarrow \infty$ . We use the abbreviations:  $\eta = \eta_{cr}$  and  $\eta_{\infty} = \eta_{cr}(\infty)$ . For high- $T_g$  polymers, the measurements are done in the region where the line is still curved. This leads to an (apparent) activation energy  $E_a$  [defined by equation (5)] higher than the limiting activation energy,  $E_{\eta}(\infty)$ , defined (Figure 1) for the high-temperature range where the process is really Arrhenius; moreover, the resulting  $\eta_{\infty}$  value will be lower than the correct value  $\eta_{\infty}^*$ . For low- $T_g$  polymers, the viscosity measurements can be done at temperatures sufficiently above  $T_g$  (lower  $T_g/T$  values); the linear (Arrhenius) part of the line is reached more easily and the limiting values [ $E_{\eta}(\infty)$  and  $\eta_{\infty}^*$ ] are approached better

due to the approximations used (universal WLF constants, a universal value for  $\eta_{\infty}^*$ , omission of an additional high-temperature Arrhenius term). Nevertheless, van Krevelen's results are reasonably reproduced and we conclude that the very low limiting viscosities given by van Krevelen and Hoflyzer are not realistic and due to application of an Arrhenius equation in a temperature range where the viscosity is still changing in a



**Figure 4** Limiting viscosity  $\eta_{\infty}$  calculated with equation (8) from the  $T_g$  values and activation energies of Table 1 vs the  $\eta_{\infty}$ 's given in the last column of Table 1 (calculated with equation (1) = equation (15.38) of ref. 2). In equation (8), we used a  $\eta_{\infty}^*$  value of  $10^{-4}$  Pa s (same value as for low-molecular weight liquids)

*non-Arrhenius way (WLF/Vogel)*. The limiting values have no direct physical significance; they are merely parameters in some useful correlations<sup>11</sup>.

#### Theoretical implications

Linear viscoelastic theory<sup>3</sup> gives the general formula

$$\eta = \int_0^{\infty} G(t) dt \quad (9)$$

where  $G(t)$  is the stress-relaxation modulus of the material and  $\eta$  the viscosity at zero strain rate. For low-molecular weight liquids and narrow relaxations (as usual in such liquids at high temperatures), this equation reduces to<sup>5,6</sup>

$$\eta \approx G_0 \tau \quad (10)$$

where  $G_0$  is the shear modulus of the rigid (glassy) material and  $\tau$  the relaxation time.

For organic materials, bounded by secondary forces, the shear modulus is of the order of 1 GPa<sup>9,10</sup>. The minimum value of  $\tau$  will correspond to the molecular vibration times, i.e. to about  $10^{-14}$ – $10^{-13}$  s. This leads to a limiting viscosity of  $10^{-5}$ – $10^{-4}$  Pa s, just as found experimentally<sup>4-6</sup>. van Krevelen and Hoftzyer's much lower limiting viscosities (down to  $10^{-8}$  Pa s) would completely contradict this generally accepted theoretical picture.

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#### References

1. van Krevelen, D. W. and Hoftzyer, P. J., *Angew. Macromol Chem.*, 1976, **52**, 101.
2. van Krevelen, D. W., *Properties of Polymers*, 3rd Edn. Elsevier, Amsterdam, 1990.
3. Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd Edn. Wiley, New York, 1980.
4. Cogswell, F. N. and McGowan, J. C., *Br. Polym. J.*, 1972, **4**, 183.
5. Angell, C. A. and Sichina, W., *Ann. New York Acad. Sci.*, 1976, **279**, 53.
6. Angell, C. A., in *Relaxation of Complex Systems*, ed. K. N. Ngai and J. B. Wright. Office of Naval Research, 1984, p. 3.
7. Struik, L. C. E., *Polymer* (submitted).
8. Bershtein, V. A., Egorov, V. M., Egorova, L. M. and Ryzhov, V. A., *Thermochimica Acta*, 1994, **238**, 41.
9. Bondi, A., *Physical Properties of Molecular Crystals, Liquids and Glasses*. Wiley, New York, 1968.
10. Tobolsky, A. V., *Properties and Structure of Polymers*. Wiley, New York, 1960.
11. van Krevelen, D. W., Personal communication, 8-07-1996.