The mobility of polymer melts

Servaas Vleeshouwers* **and Erik Nies**
Centre for Polymers and Composites, Department of Polymer Technology, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

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An empirical equation is presented to describe the mobility of polymer melts as a function of temperature and pressure. This is accomplished in terms of the order parameter in a hole theory and temperature, combined in a Fulcher–Tammann–Hesse type equation. Experimental data for various amorphous polymers are described successfully.

(Keywords: polymer melt; mobility; free volume)

INTRODUCTION

The description of the relaxation times of polymer melts as a function of structure, temperature and other variables such as pressure, is not only of great interest from a fundamental point of view, but also for applications such as melt processing and injection moulding. The dependence of mobility on structure and/or temperature has still many unsolved aspects. At atmospheric pressure, the relaxation time (i.e. mobility) can be described as a function of structure. Often free volume is used to define the structure. A well known expression in this respect is the Doolittle relationship[1]. The influence of temperature is only taken into account implicitly, via its influence on the free volume. The assumption of a linear relationship between free volume and temperature and the existence of a temperature at which the free volume vanishes, yields an explicit temperature dependence, the Williams–Landel–Ferry (WLF) equation[2]. This latter equation is particularly successful in describing mobility data at atmospheric pressure.

However, it is well known that the influence of pressure is not well described by these equations[3]. In order to obtain a good description of the relaxation times at elevated pressure these functions have been extended or modified[4,5]. A relationship that combines the description of pressure and temperature dependence is also of value because it offers a way to separate the influences of structure and temperature. In this work a new empirical equation is presented, which uses a minimum of parameters and also reduces to other well known equations, such as the Doolittle and WLF, in limiting cases under well defined conditions.

A MODIFIED FULCHER–TAMMANN–HESSE EQUATION

First, we will introduce a relationship to describe the mobility at atmospheric pressure, which we will subsequently extend to elevated pressures. As a measure for the mobility, the shift factor a_T, defined as the ratio of a relaxation time at a temperature T to a reference relaxation time, is used. In practice, the shift factor can be based on a variety of properties, such as viscosity, dielectric relaxation, stress relaxation and creep. To describe the shift factor as a function of temperature *at atmospheric pressure*, a WLF-like relationship, based on free volume instead of temperature[6], is adopted in this work. The free volume serves as a structure parameter. The expression of a shift factor as a function of the order parameter h in a hole theory[7] was first utilized by Curro *et al.*[8]. This order parameter h is equal to $1-y$, with y being the fraction of occupied sites on the lattice used in the hole theory. Generally, for a given substance in equilibrium, h is a unique function of temperature and pressure. Proceeding along similar lines, in this work the free volume will be identified with the order parameter $h \equiv 1-y$ from the Holey–Huggins (HH) theory[9]. The temperature dependence of the shift factor a_T can be expressed as follows:

$$\log a_T = -\frac{c_1[h(T)-h(T_0)]}{c_2+h(T)-h(T_0)} \tag{1}$$

where $h(T)$ and $h(T_0)$ are the free volumes at T and T_0, respectively, and c_1 and c_2 are constants. Equation (1) can be rewritten as follows:

$$\log a_T = \frac{B}{h-A} + D \tag{2}$$

where $D=-c_1$, $B=c_1c_2$, and $A=h(T_0)-c_2$, while omitting the explicit dependence of h on temperature. Equation (2) resembles the Fulcher–Tammann–Hesse (FTH) equation[10,11], where h is used instead of T. Several sets of experimental data have been used to fit the parameters A, B and D in equation (2). In the fitting procedure, only experimental data obtained in the equilibrium melt have been used. Several sets of shift factors, derived from different experimental techniques, are used simultaneously and each set has been allowed to have a different value for D. Thus, D shifts the different data sets relative to each other. For the fitting, a multiparameter fitting program is used, which is described elsewhere[12]. Whereas the value for D depends on, for

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[*] To whom correspondence should be addressed

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Table 1 Parameters obtained from the fit to equation (2) of the shift factors a_T as a function of temperature, measured at atmospheric pressure for several polymers. A simultaneous description of different sets of experimental data is obtained by allowing a different value of D for each set of experimental data. Since D is not a characteristic parameter of the polymer, the values for D are not shown

	A	B	Experimental data used for fit[a]	Ref.
Poly(vinyl acetate)	0.0581	0.392	Dielectric	13
			Stress relaxation	14
			Creep	15
Polystyrene	0.0518	0.156	Viscosity	16
			Creep	17
			Creep	18
Bisphenol-A polycarbonate	0.0797	0.358	Viscosity	16
			Viscosity	19
			Stress relaxation	20
Poly(methyl methacrylate)	0.0646	0.309	Viscosity	16
			Creep	18

[a] Only data obtained in equilibrium and at atmospheric pressure are used

example, the particular property under consideration or the choice of the reference state, the constants A and B are characteristic of the polymer being examined. For this reason we prefer the form of equation (2) over that of equation (1), where all parameters depend on, for example, the choice of a reference state. When describing data over an extended temperature range, the value for A must be allowed to have a finite value. Thus, a Doolittle expression (i.e. $A=0$) cannot satisfactorily describe the complete temperature interval. *Table 1* lists the results obtained from fitting equation (2) to the experimental data, which is shown for polystyrene (PS) in *Figure 1*. In general, the description given by equation (2) is excellent over the complete temperature range where experimental data are available, not only for PS but also for several other polymers.

However, equation (2) does not describe the pressure dependence of the shift factors (see *Figure 2a*). From this it can be concluded that the free volume (described by the order parameter h from the HH theory) does not solely describe the mobility in the polymer. In choosing a function to describe both the temperature and pressure dependence of the mobility, several considerations can be made, thus resulting in several empirical functions. The most obvious way is to add a pressure term to equation (2), as follows:

$$\log a_{T,p} = \frac{B}{h + C_p p - A} + D \qquad (3)$$

For $p=0$, equation (3) reduces to equation (2). The parameters in this relationship have been successfully determined, resulting in an excellent description of the temperature and pressure dependence of the mobility. The value for C_p is found to be positive. Choosing p and h as parameters to describe the mobility apparently leads to a contradiction: at a constant h and increasing pressure the shift factor *decreases*, i.e. the mobility *increases*. Of course, in equilibrium a constant h and increasing pressure are accompanied by an increase in temperature, which makes an increase in mobility obvious. This situation is illustrated by some data obtained by Cogswell and McGowan[16] on polystyrene. Three of these sets of data have the same order parameter, i.e. $h = 0.0772 \pm 0.0001$. The shift factors decrease (from 2.69 via 2.16 to 1.74) with increasing pressure and temperature (70 MPa and 443 K, 105 MPa and 463 K, and 140 MPa and 483 K, respectively). Therefore, it seems more natural to take h and T as the parameters to describe the mobility. The following equation, which describes all of the experimental data quantitatively, was chosen for further analysis:

$$\log a_{T,p} = \frac{B'}{h + C'T - A'} + D \qquad (4)$$

where A', B', C' and D are constants. As explained above, the parameter D is not a physically important parameter, but only serves to shift the experimental data derived from different sources. For $C'=0$, equation (4) reduces to equation (2). At constant pressure, the free volume parameter h is approximately a linear function of T, thus reducing equation (4) to equation (2). If $C'T \gg h - A'$ (at relatively high temperatures), equation (4) reduces to an Arrhenius equation. If h is constant, which is the case in a frozen structure, equation (4) reduces to a FTH

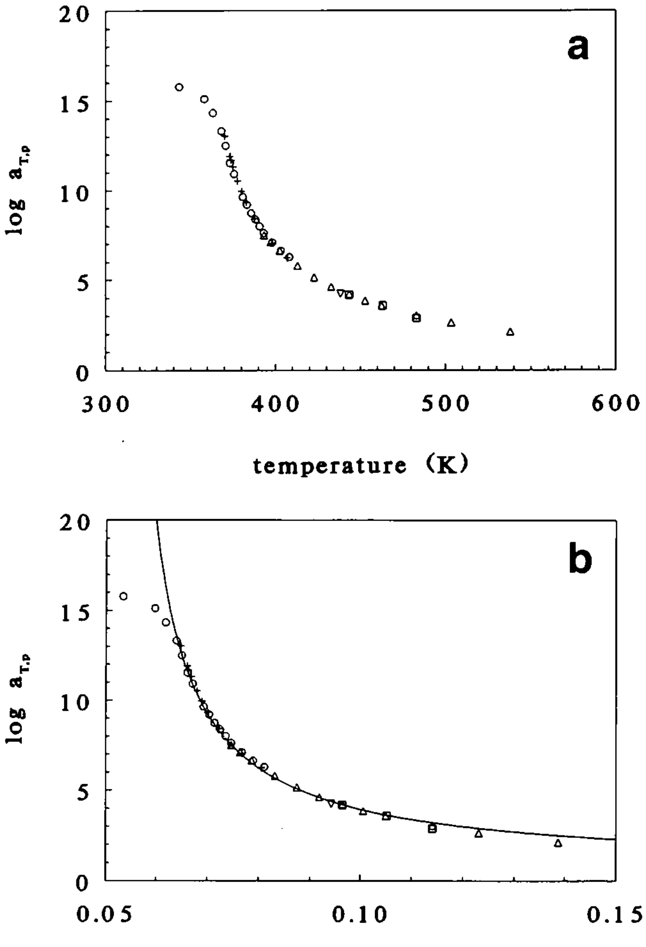

Figure 1 Shift factors for polystyrene measured at atmospheric pressure: (a) *versus* temperature; (b) *versus* the order parameter h. Symbols for experimental data (□) ref. 16; (+) ref. 17; (▽) ref. 21; (△) ref. 22; (○) ref. 18. The continuous line shows the fit of equation (2); the systematic deviations at low h values are due to the non-equilibrium state in some measurements, and these data are not included in the fit

equation, or to an Arrhenius equation if $h_g \sim A'$ (where h_g is the order parameter for a glass). Finally, if T is constant, i.e. under isothermal conditions, equation (4) again reduces to equation (2). All these examples show that equation (4) has, in principle, the ability to describe several types of observed behaviour. Because of the resemblance of equation (4) to equation (2), which in its turn has the same structure as the FTH equation, we have chosen the name 'modified FTH' for equation (4).

If data measured both at atmospheric and elevated pressures are fitted to equation (4) a good description of the behaviour is obtained, as is shown in Figure 2b for PS. The parameters obtained from the fit are listed in *Table 2* for several different polymers.

It is interesting to note that in contrast to the polymers examined here, both the temperature and pressure dependence of viscosity-based shift factors in low-molar-mass liquids, e.g. benzene[26] and cyclohexane[27], are well described by just using the free volume h, e.g. equation (2). This is illustrated in *Figure 3*. Utracki[3] showed that for n-alkanes with 5 to 18 carbon atoms the free volume h (according to the Simha–Somcynsky theory[7]) uniquely determines the temperature and pressure dependence of the viscosity, but however, not via a Doolittle relationship, i.e. $\log(\eta) \propto 1/h$. The difference between the descriptions of the polymers and benzene may be due to the fact that in the regime where data are available the free volume content is generally larger for the low-molar-mass liquids than for the polymers. Therefore,

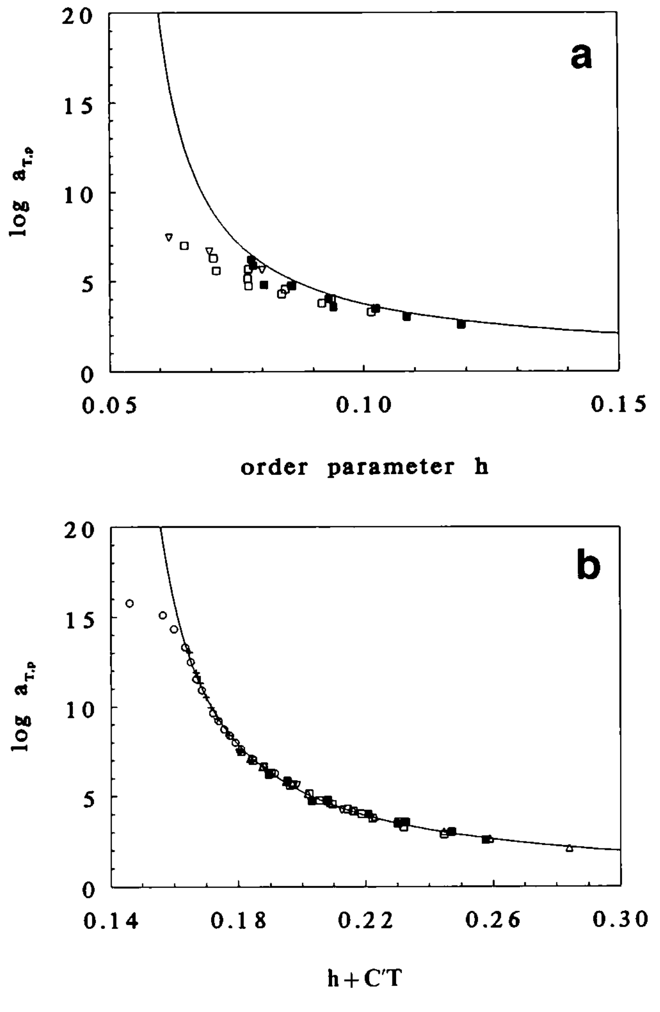

Figure 2 (a) Shift factors for polystyrene measured under pressure *versus* the order parameter h. Symbols for experimental data: (■) ref. 23; (□) ref. 16; (▽) ref. 21. The continuous line representation of atmospheric pressure data obtained by using equation (2). (b) Shift factors for polystyrene measured at different temperatures and pressures *versus* $h+C'T$. Symbols for experimental data: (■) ref. 23; (□) ref. 16; (+) ref. 17; (▽) ref. 21; (△) ref. 22; (○) ref. 18. The continuous line shows the fit of equation (4)

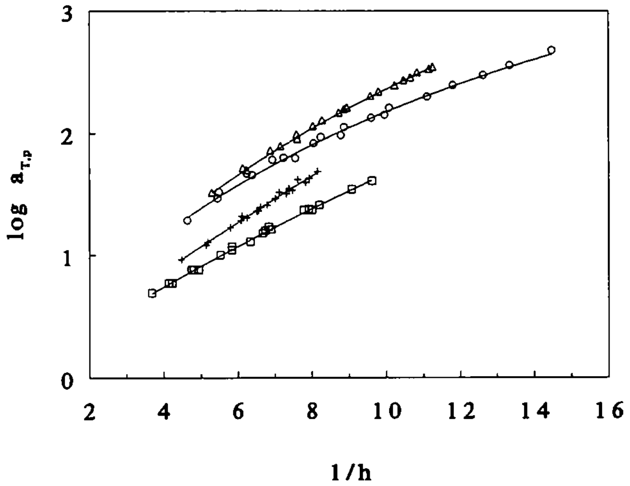

Figure 3 Shift factors for low-molar-mass liquids, measured at different temperatures and pressures, *versus* the reciprocal free volume $1/h$. Symbols for experimental data: (□) benzene[26]; (+) cyclohexane[27]; (○) n-dodecane[28,29]; (△) n-octadecane[29,30]. The continuous lines show the fits obtained by equation (2)

Table 2 Parameters obtained from the fit to equation (4) of the temperature and pressure dependence of the shift factors $a_{T,p}$ for several polymers. A simultaneous description of different sets of experimental data is obtained by allowing a different value of D for each set of experimental data. Since D is not a characteristic parameter of the polymer, values for D are not shown

	A'	B'	C' ($\times 10^4$)	Experimental pressure data used for fit[a]	Ref.
Poly(vinyl acetate)	0.201	0.785	5.52	Viscosity Dielectric	23 24
Polystyrene	0.140	0.315	2.70	Viscosity Viscosity	16 21
Bisphenol-A polycarbonate	0.183	0.558	2.93	Viscosity	16
Poly(methyl methacrylate)	0.211	0.561	4.25	Viscosity Viscosity	16 25

[a] In addition to these data, the atmospheric pressure data listed in *Table 1* are also used in the fit of equation (4)

the constant C' in equation (4) can be undetermined:

$$\frac{\mathrm{d}\log a_{T,p}}{\mathrm{d}h} = \left.\frac{\mathrm{d}\log a_{T,p}}{\mathrm{d}h}\right]_T + \left.\frac{\mathrm{d}\log a_{T,p}}{\mathrm{d}T}\right]_h \frac{\mathrm{d}h}{\mathrm{d}T} \approx \left.\frac{\mathrm{d}\log a_{T,p}}{\mathrm{d}h}\right]_T \qquad (5)$$

because

$$\left.\frac{\mathrm{d}\log a_{T,p}}{\mathrm{d}T}\right]_h = -\frac{C'}{B'}(\log a_{T,p} - D)^2 \qquad (6)$$

The value of the latter term decreases rapidly with increasing free volume h, and is therefore negligible compared to $(\mathrm{d}\log(a_{T,p})/\mathrm{d}h)_T$ in the case of low-molar-mass liquids such as benzene. For these conditions, the influence of pressure coincides with that of temperature. Some intermediate behaviour has also been observed[23], supporting the above mentioned reduction of equation (4) to equation (2) for large values of h.

CONCLUSIONS

In this paper, an expression has been presented to describe the *temperature* dependence of the mobility of polymer melts at atmospheric pressure. The shift factor is used as a measure for the mobility. This expression, which is related to the WLF equation, yields a quantitative description of the shift factors as a function of the order parameter h obtained from the HH theory, which is identified with the free volume. A minimum of parameters is needed.

For the simultaneous description of the *pressure and temperature* dependence of mobility, a successful empirical equation has been presented in which the shift factor is a function of both temperature and the order parameter h.

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