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The time temperature position of the glass-rubber transition of amorphous polymers and the free volume

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With 16 figures and 4 tables

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1. Introduction

Linear viscoelastic shear behaviour of amorphous polymers in the glass-rubber transition region obeys the time-temperature superposition principle, as has been known for more than thirty years (1, 2). This principle states that viscoelastic characteristic functions measured at different temperatures may be brought to coincide by parallel shifts along the logarithmic time or frequency axis. If, for instance, $J(t, T)$ represents the creep compliance as a function of the creep time t at the temperature T, the creep functions at temperatures T and T_0 should be connected by the relation

$$J(t, T) = J(a \cdot t, T_0) \qquad [1]$$

where

$$a = a(T, T_0) \qquad [2]$$

is a function of the temperatures T and T_0 only. $\log a(T, T_0)$ is the shift to be applied along the logarithmic time axis to obtain superposition. It is called the time-temperature shift function.

Obviously the existence of a relation of the type of eq. [1] effects considerable simplification for the engineering task to describe the viscoelastic shear behaviour of those materials. Instead of determining one function J which depends on two independent variables t and T, it is sufficient to determine two functions which each depend on one independent variable: The time-temperature shift as a function of temperature and the creep function at the reference temperature T_0, the "master curve" as a function of time. Consequently considerable interest is connected with the question of the region of validity of the time-temperature superposition and with the shapes of the master curve and the shift function.

In a well known publication *Williams*, *Landel* and *Ferry* (3) have compiled data available at this time on the shear behaviour of amorphous polymers in the glass-rubber transition region. They could superimpose those data by the time-temperature superposition within a temperature region extending from about the glass transition temperature, T_g, of the polymer to about $T_g + 100$. Moreover they found that all polymers obeyed the simple time-temperature shift function

$$\log a(T, T_0) = -\frac{c_1(T - T_0)}{c_2 + T - T_0} \qquad [3]$$

where c_1 and c_2 are constants for one type of polymer but depending on the chosen reference temperature T_0. If instead of T_0, a different reference temperature $\bar{T}_0$ is chosen, the new shift function $\log a(T,\bar{T}_0)$ is easily seen to have the same form as [3] with constants $\bar{c}_1$ and $\bar{c}_2$ given by

$$\bar{c}_2 = c_2 + \bar{T}_0 - T_0, \qquad \bar{c}_1 = c_1 c_2/\bar{c}_2 . \qquad [4]$$

Eq. [3] has been applied very often to the temperature reduction of mechanical and dielectric data for polymers. It is called the W.L.F.-equation.

Finally *Williams*, *Landel* and *Ferry* (3) stated that the constants c_1 and c_2 were of a "universal" nature, not depending on the special chemical type of the polymer. If the reference temperature T_0 were chosen appropriately, viz. about 50 K above T_g, the corresponding values for c_1 and c_2 should be approximately equal for all polymers:

$$T_0 = T_u \sim T_g + 50, \quad c_1^u \sim 8{,}86, \qquad c_2^u \sim 101{,}6\,\mathrm{K}. \qquad [5]$$

If this statement would be valid, the description of the position of the glass-rubber transition in the time-temperature plane would be extremely simple; it would just require knowledge of one temperature for each type of polymer.

The conclusions drawn by *Williams*, *Landel* and *Ferry* were partly based on measurements which extended over a rather narrow experimental window (about 1,5 to 2 decades in logarithmic frequency or time scale). This necessarily rendered difficulties and uncertainties in the verification of the shift procedure and in the determination of the shift function and its constants c_1 and c_2.

Therefore, Ferry has reconsidered the problem in the second edition of his book (4) 15 years later. He then concluded that the statements expressed by eqs. [1] to [3] still hold; the constants c_1 and c_2 of the W.L.F.-equation however seemed not to fit into a universal scheme. When reduced to equivalent temperatures (for instance to T_g), they show large differences for different polymers.

In this situation it seemed worthwhile to obtain more experimental information on the glass-rubber transition. Therefore we tried to perform measurements of the shear behaviour in the glass-rubber transition of various amorphous polymers, extending over a broad experimental window in frequency scale. The following questions should be answered:

1. Is the time-temperature superposition applicable to measurements extending over a broad experimental window? Which are the limits of applicability of this principle?
2. Which is the temperature region, where the shift function can be described by the W.L.F.-equation?
3. Are the constants of the W.L.F.-equation specific for the material in question or are they universal?

Williams, *Landel* and *Ferry* (3) interpreted their results in terms of the free volume. To this end they started with a relation between the segmental mobility of the polymer chains, m, and the fractional free volume, f, which was used by *Doolittle* (5) for the description of the viscosity of liquids

$$\ln m = A - B/f . \qquad [6]$$

In the most simple version A and B are assumed to be constant. Applying this equation to two states at the temperatures T and T_0 with fractional free volumes f and f_0 respectively, yields for the shift function

$$\log a(T,T_0) = \log[m(T_0)/m(T)] = 0.43\,B\left[\frac{1}{f} - \frac{1}{f_0}\right]. \qquad [7]$$

Now it is assumed that the material attains its state of thermodynamic equilibrium at temperatures well above T_g; furthermore it is assumed that the equilibrium value of the fractional free volume is a linear function of temperature within a range of temperatures which extends at least down to T_g:

$$f = \alpha_f(T - T_\infty), \qquad [8]$$

α_f and T_∞ are constants. α_f is related to the thermal expansion coefficient of the free volume; T_∞ is the temperature at which the free volume would vanish, if relation [8] would remain valid down to temperatures in the vicinity of T_∞. In reality the thermodynamic free volume will deviate from [8] in this region, as it cannot vanish at temperatures above the absolute zero point. A schematic drawing of the possible courses of the thermodynamic equilibrium value of f and of the approximation [8] is given in figure 1. The actual value of fractional free volume on cooling will begin to deviate from its thermodynamic value in the vicinity of the glass transition temperature T_g.

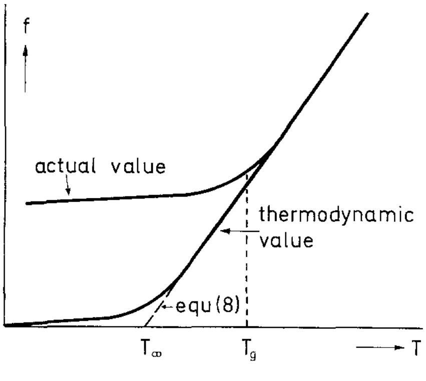

Fig. 1. The temperature dependence of the actual value of fractional free volume, the thermodynamic value of fractional free volume and of approximation [8]

Now assume that both temperatures, T and T_0 are situated above T_g; then we may insert approximation [8] into eq. [7]. The result is the W.L.F.-equation with parameter values, which are related to the free volume parameters:

$$c_1 = 0.43 B/f_0\,, \qquad [9]$$

$$c_2 = f_0/\alpha_f = T_0 - T_\infty\,. \qquad [10]$$

We therefore can determine the constants T_∞ and the ratio B/α_f from the time-temperature shift function. In order to find B and α_f separately, additional information is needed.

This may be obtained from the thermal expansion behaviour of the polymers. Under the assumption that the difference in thermal expansion in the glassy and rubbery region of the polymer is completely due to the contribution of the thermal expansion of the free volume, we may state

$$\alpha_f = \Delta\alpha = \alpha_l - \alpha_g \qquad [11]$$

where α_l and α_g are the thermal expansion coefficients in the rubbery and glassy region respectively. We therefore have complemented this investigation with dilatometric experiments on the same materials.

The questions we want to discuss are:

4. Which additional conclusions may be drawn by simultaneous dilatometric and mechanical measurements on the same polymers?

5. Are the results of those measurements consistent with each other and with the simple hypothesis indicated above?

2. Experimental

2.1. Materials

Three amorphous plastics and two crosslinked rubbers were investigated so far. The plastics were polystyrene, polymethylmethacrylate and polyvinylchloride, all commercial types:

PVC: Solvay & Cie, S.A. Brussels, type Solvic 229,
PS: Hoechst A.G., Frankfurt, type Hostyren N-7000,
PMMA: Röhm G.m.b.H., Darmstadt, type Plexiglas 240/218.

The polyvinylchlorid is a rigid PVC of the suspension type. It was extruded to a rod at 190°C. The polystyrene is a suspension polymer without any additives, extruded into a sheet by the manufacturer. The polymethylmethacrylate is a bulk polymerized product in the form of a sheet without any additives or plasticizers. From the rod or the plates, rectangular specimen were prepared by milling. Specimen for the torsional measurements had the dimensions ($100.0 \times 10.0 \times 7.0\,\mathrm{mm}^3$), specimen for the dilatometry were rods of 100 mm length and 9 mm diameter.

One of the rubbers investigated was an unfilled polyurethane rubber, carefully prepared by allowing 100 p.b.w. of polyether Desmophen 3600 (Farbenfabriken Bayer) to react with 19.6 p.b.w. of toluene diisocyanate and 4 p.b.w. of trimethylol propane at 80°C. The product has a rubbery network structure with trifunctional bulky crosslinks. The linear ether chains between adjacent crosslinks have a molecular weight of 2000 g/mol. The other rubber was a natural unfilled rubber, slightly crosslinked with sulphur. Specimen of the size ($150 \times 7.0 \times 3.5\,\mathrm{mm}^3$) were prepared by milling.

2.2. Apparatus for the determination of the torsional creep compliance

A combined torsional pendulum (6) and torsional creep apparatus (7), developed and manufactured by the Central Laboratory TNO, Delft, was used for the determination of the shear properties of the materials in the glass transition region. It is shown schematically in figure 2.

The rectangular specimen is clamped between a fixed lower clamp and a movable upper clamp. The latter is suspended by means of a torsional wire from a balance, and the weight of the part of the apparatus above the specimen is balanced by a counterweight. This construction prevents the occurence of longitudinal (thermal) stresses in the specimen. The twist of the upper clamp is measured by a transducer. This essentially consists of a transformer driven by a carrier frequency of 1000 Hz and having a transfer ratio proportional to the angle of torsion. Alignement of the system is achieved by using an air bearing.

For measurement of free vibrations a cross bar is inserted into the part between the air bearing and the upper clamp. The torsional moment of inertia of the cross bar can be varied by attaching different weights to it. The system is moved from its equilibrium position by hand, and its motions during return to equilibrium

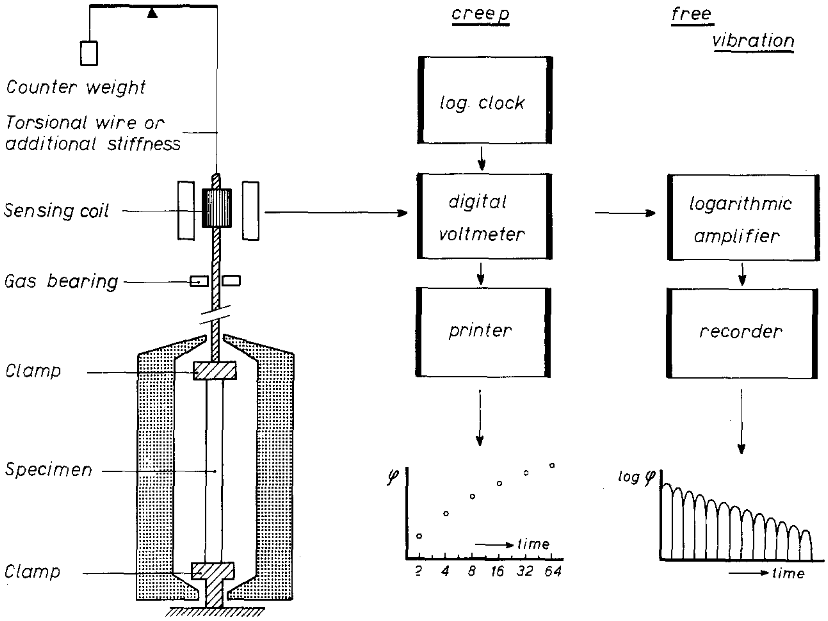

Fig. 2. Combined torsional pendulum and creep apparatus (schematic)

are recorded. From the eigenfrequency and the logarithmic decrement of the damped torsional vibration the storage shear modulus and the damping of the specimen can be calculated. The measurement is usually performed with three different values of the torsional moment of inertia. In regions where the shear modulus is only weakly dependent on frequency the three frequencies of the vibration measurement are spaced at distances of approximately log 3 in logarithmic frequency scale. In the glass transition the spacing is wider, namely about log 4.

When the vibration of the specimen tends to become aperiodic or too heavily damped, the soft torsional wire is replaced by a stiffer, calibrated wire. The torsional stiffness of this wire then restores the periodicity of the system. The value of the applied torsional stiffness has to be adjusted to the stiffness of the specimen.

For measurements of creep the cross bar is removed and replaced by weights and pulleys to apply a constant torque to the upper clamp. The angle of torsion is measured digitally. A logarithmic clock (8) is started at the instant of loading; it activates the measuring system at times uniformly spaced on a logarithmic time scale, namely $2, 2^2, 2^3, \ldots 2^k$ seconds after beginning of the creep. Therefrom the creep compliance in shear at the corresponding creep times is calculated.

2.3. Thermostating device

The temperature of the specimen is controlled by means of a gas thermostat developed at the Central

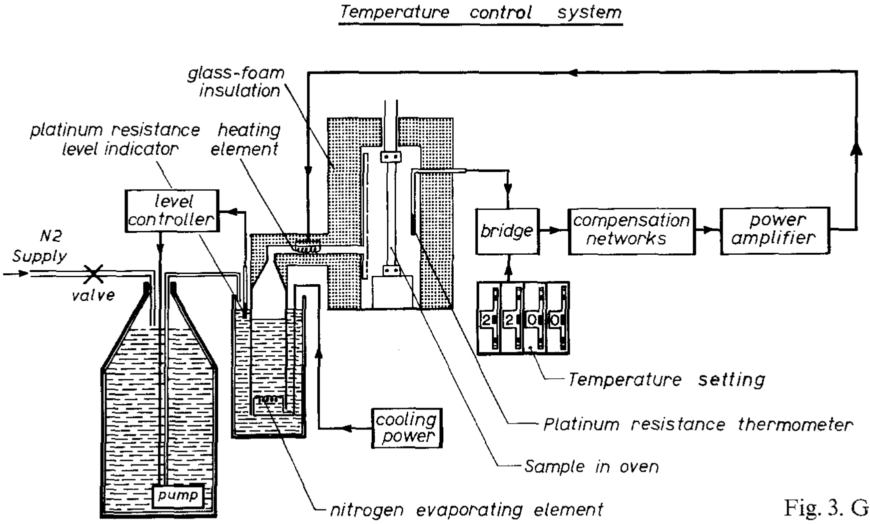

Fig. 3. Gas thermostat (schematic)

Laboratory TNO (9) (see fig. 3). By evaporating liquid nitrogen a constant stream of nitrogen gas is produced which is heated to the desired temperature and fed to the thermostat chamber. The temperature of the gas is measured by a platinum resistance thermometer close to the specimen; its resistance is compared with a preset resistance in a Wheatstone bridge. A special proportional control circuit was designed to transform the signal of the bridge into the heating current. The preset resistance is composed of fixed resistances and can be set manually to within 0.1 °C. The characteristics of the thermostat are:

temperature range: $-180°\mathrm{C} \leq T \leq 300°\mathrm{C}$,
absolute accuracy: 1 °C,
long term stability and reproducibility: 0.1 °C,
maximum cooling rate of gas: 50°C/min,
arbitrarily programmable in steps of 0.1 °C.

2.4. *Data conversion*

Several conversion problems had to be solved before the results of both different measuring techniques could be compared and evaluated. First the result of the measurement of the free damped vibration had to be converted into that of a forced harmonic vibration, i.e. into storage and loss compliances. This problem was discussed for linear viscoelastic materials by *Struik* (10), who has shown that real and imaginary part of the complex modulus at a complex frequency may be derived from eigenfrequency and logarithmic decrement of the vibration. The value of the complex modulus at a complex frequency is converted by an error bound numerical method [1]) to the storage shear compliance $J'(\omega)$ and the loss shear compliance $J''(\omega)$ [2]).

In order to compare them with the results of the creep experiment, values of $J'(\omega)$ and $J''(\omega)$ were converted into the creep compliance $J(t)$ by means of the numerical formula (11)

$$J(t) \sim J'(\omega) + 0.566 J''(\omega/2) - 0.203 J''(\omega) \qquad [12]$$

with $t = 1/\omega$. This formula has a bound for the relative error smaller than 8%. The values of J' and J'' needed for this calculation were obtained by interpolation of measured values. With those precautions the data derived from the vibration technique and those from the creep technique were found to be in good agreement.

2.5. *Dilatometry*

Specific volume vs. temperature was determined by a standard dilatometric technique. Dilatometers were prepared by fusing a precision capillary of 0.8 mm diameter, 1% accuracy (Schott) to a glass tube (Duran 50). After inserting the rod shaped specimen the dilatometer was sealed at the bottom, the specimen was degassed by heating 24 hrs to temperatures 10 K below T_g at 10^{-5} torr. Finally, the dilatometer was filled with pure mercury under vacuum. The ratio of the volume of the specimen to the volume of the mercury was approximately 2.5.

The course of the specific volume with temperature during cooling under various speeds was measured in a programmed oilthermostat by automatic photography. To calculate the volume changes of the specimen, corrections for the expansion of the mercury and the glass had to be made. To this end a dilatometer filled with mercury only is observed simultaneously during the experiment. In order to calculate absolute values of the specific volume, the specific volume of the specimen was determined at a temperature 20 K above T_g with a self constructed pycnometer filled with mercury.

3. Results

At the low temperature flank of the glass rubber transition, shear properties of polymers do not only depend on temperature and creep time, but also on the details of the previous temperature history of the specimen. We therefore carefully standardized the temperature history of the specimen as follows:

The specimen was heated between glass plates to temperatures 10 K above the glass transition temperature, and was then cooled at a rate of 1.5 K/h to the lowest measuring temperature. Then it was clamped in the torsional pendulum and conditioned for further 30 minutes at this temperature. Vibration measurements were performed at three frequencies, followed by a creep measurements during 2048 seconds. Next, the specimen was unloaded, heated to the next higher temperature and allowed to recover at this temperature for another half hour. The measuring cycle was then repeated at this temperature. With this procedure, it took about five days to measure the complete shear behaviour of one specimen. During this period, the specimen remained clamped in the apparatus, and the thermostat was kept over night at the temperature of the previous recovery period. For the measurement of the rubberlike materials, the complete thermal treatment was performed in the thermostat of the torsional pendulum.

Figure 4 shows the creep compliance in shear vs. the creep time in double logarithmic plot for polystyrene at various temperatures. Open circles indicate measuring points as obtained directly by the digital creep technique; crosses indicate the values of the creep compliance as calculated from the free vibration technique at the frequencies of the vibration experiment. The agreement between the results of both methods is satisfactory.

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[1]) unpublished.

[2]) ω is the angular frequency of the vibration.

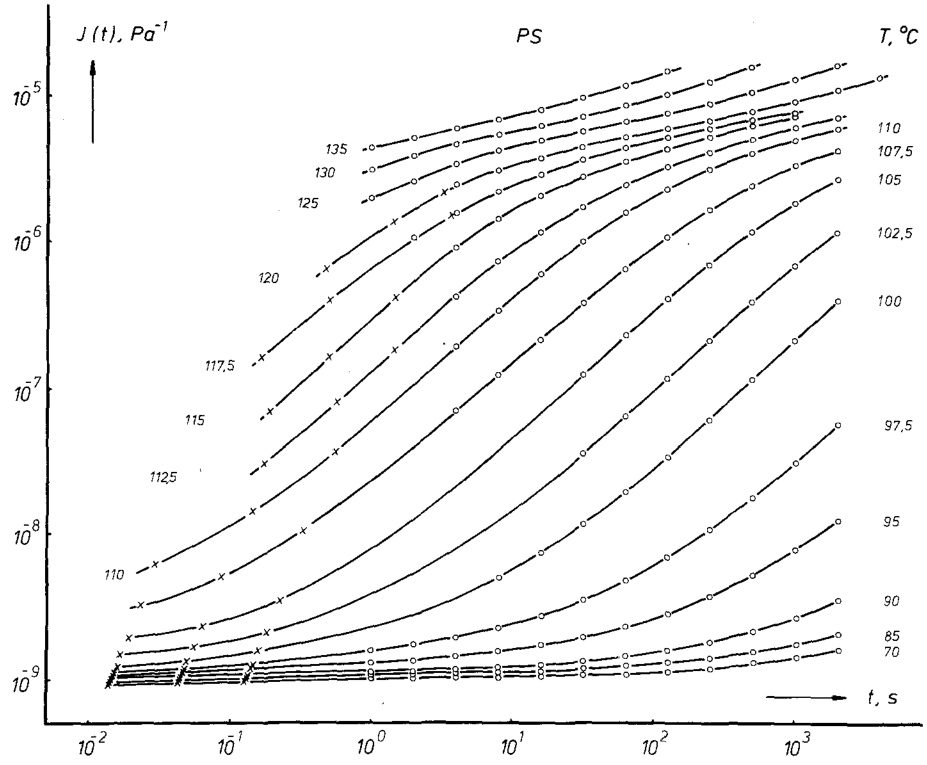

Fig. 4. Creep compliance in shear vs. time for polystyrene at various temperatures

The plot covers four orders of magnitude on the compliance scale, and five orders of magnitude on the time scale. In spite of this it is impossible to cover the complete glass-rubber transition at a single temperature. The strong influence of time and temperature on the compliance in the transition region is evident. An increase in temperature of 3 K either increases the com-

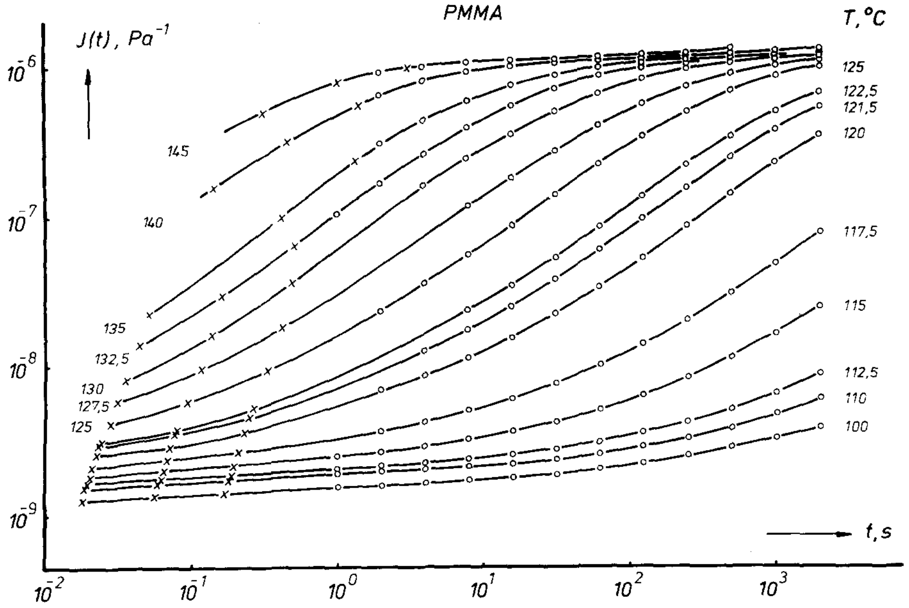

Fig. 5. Creep compliance in shear vs. time for polymethyl methacrylate at various temperatures

pliance by a factor of 3, or shifts it to shorter times by a factor 10. The maximum value of the double logarithmic slope of the compliance vs. time is very high, appr. 0.85.

Figures 5 to 8 show the corresponding results for the other materials investigated. In all cases, a strong influence of time and temperature is found. However, significant differences are observed in the behaviour of these different materials. Some of these differencies are illustrated in table 1, where the following characteristics are listed: The height (*H*) of the step of the dispersion, in decades; the maximum value (*n*) of the double logarithmic slope of the compliance-time curves; the width (*w*) of the dispersion of *J*(*t*) in temperature scale at a

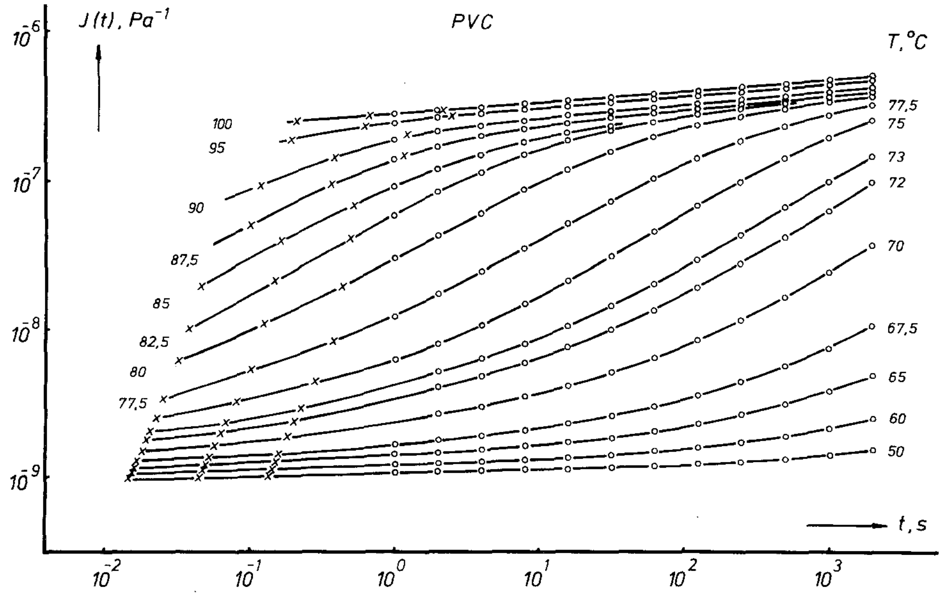

Fig. 6. Creep compliance in shear vs. time for rigid polyvinyl chloride at various temperatures

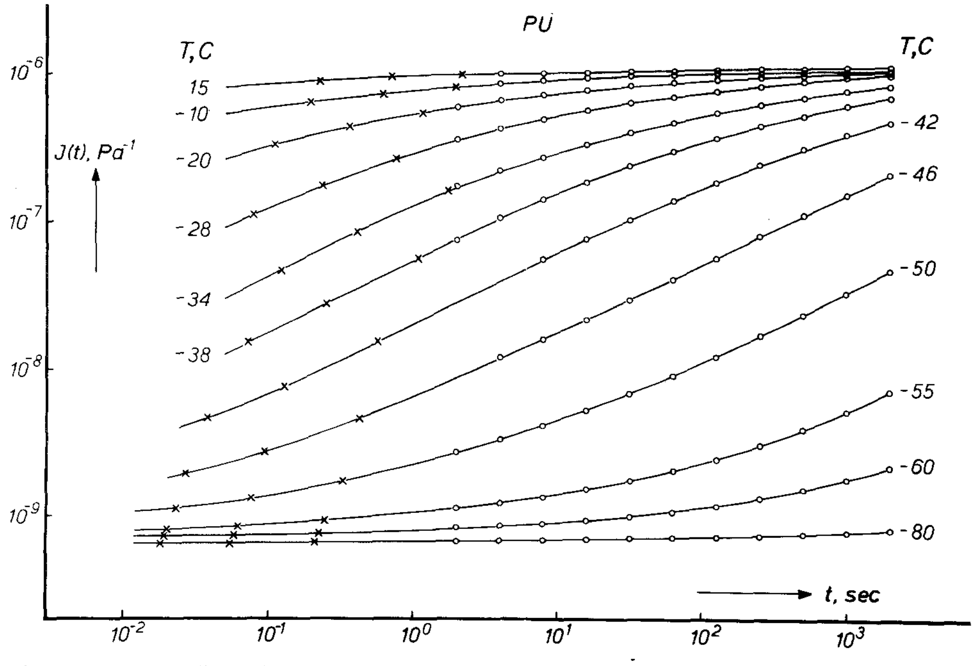

Fig. 7. Creep compliance in shear vs. time for polyurethane rubber at various temperatures

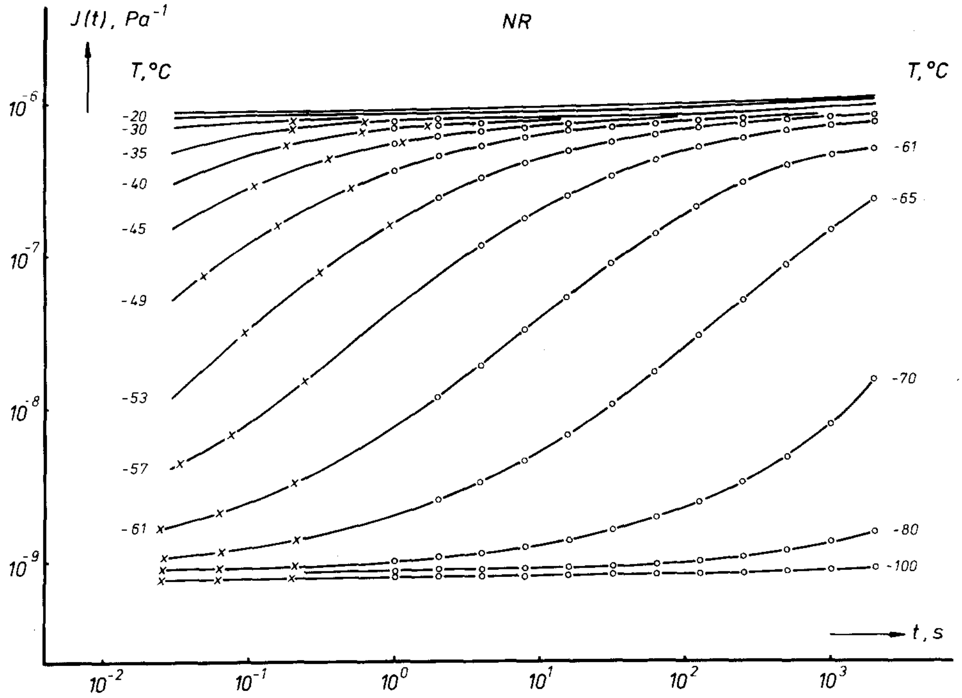

Fig. 8. Creep compliance in shear vs. time for natural rubber at various temperatures

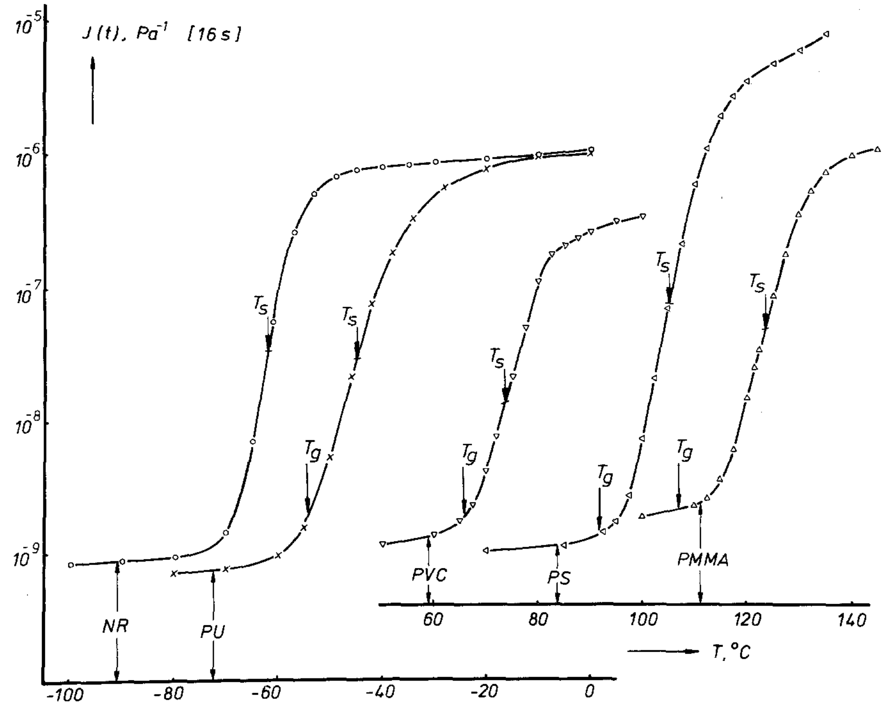

Fig. 9. Creep compliance in shear after 16 seconds vs. temperature for five polymers in the glass transition region. The temperatures, T_s, at the midpoints of the transition, and the glass transition temperatures, T_g, are indicated by arrows

characteristic time of 16 seconds; the characteristic softening temperature (T_s) where the compliance at 16 seconds reaches its logarithmic half-value of the dispersion step; the glass transition temperature (T_g) determined at a cooling speed of $\beta = 3$ K/h.

The courses of the creep compliance (at 16 seconds) with temperature are compared in figure 9. Note that the unit of the temperature scale is the same in the case of all materials. A constant shift of the temperature scale has been applied in the case of the rubbers to facilitate comparison. It is remarkable that the slope of the logarithm of the compliance vs. temperature is about the same in the transition zone for all materials, viz. 1.5 decades/10 K. The curve for PVC consists of two parts of different slopes. Only the part with the higher slope is considered to be the proper glass-rubber transition. The other part in the temperature region above 90°C is considered to be connected with a gradual melting or recrystallization process occurring in this material.

Results of dilatometric measurements are presented in figures 10 and 11. Figure 10 shows the specific volume of polystyrene during various rates of cooling, β, as a function of temperature. The specific volume in the rubbery state is independent of temperature history and increases linearly with temperature. The spe-

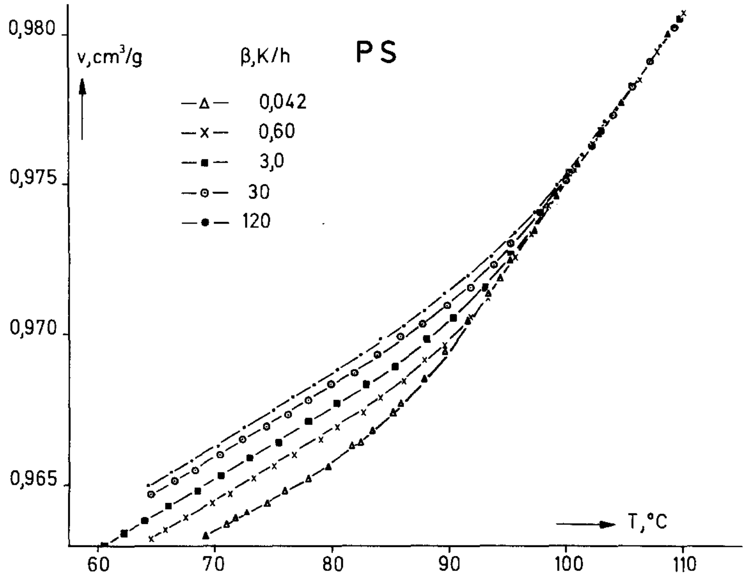

Fig. 10. Specific volume of polystyrene vs. temperature for five different rates of cooling, β, as indicated

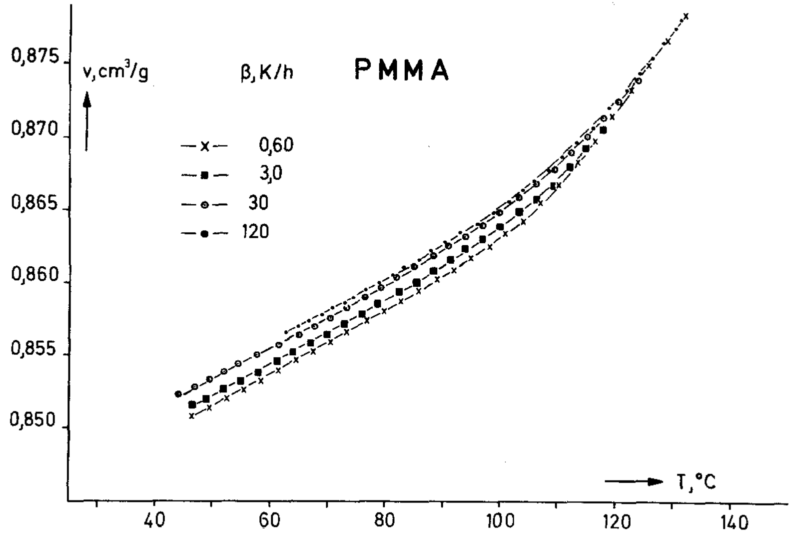

Fig. 11. Specific volume of polymethyl methacrylate vs. temperature for four different rates of cooling, β, as indicated

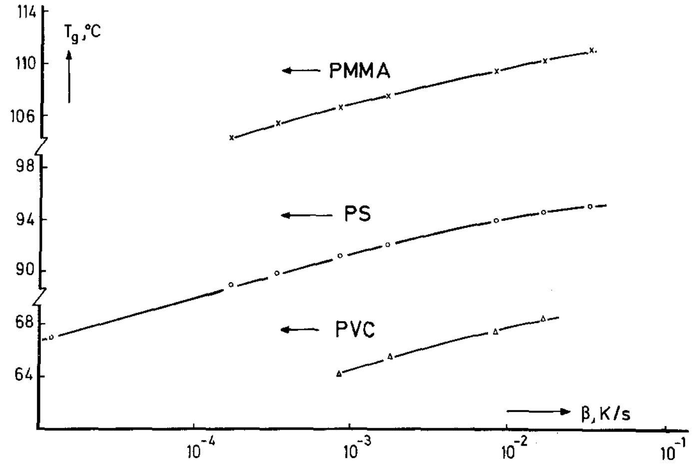

Fig. 12. Glass transition temperature, T_g, vs. rate of cooling, β, for three amorphous polymers

cific volume in the glassy state depends significantly on the rate of cooling. The thermal expansion coefficient in the glassy state is approximately independent of the rate of cooling. Extrapolating and intersecting the both linear parts of the contraction curves in the usual way defines the glass transition temperature T_g, which depends significantly on the rate of cooling. This dependence is shown for the three plastics investigated, in figure 12. Glass transition temperature increases with the logarithm of the rate of cooling. At the region of lower rates of cooling this increase seems to be linear, viz.

$$T_g = T_0 + b \log(\beta/\beta_0)\,. \qquad [13]$$

The constant of proportionality, b, equals about 3 K. In the region of higher rates of cooling, T_g seems to increase less than proportional with the logarithm of β. From dilatometric data we determined the glass transition temperature T_g at a rate of cooling of 3 K/h, the volume expansion coefficients in the glassy and rubbery region, α_g and α_l. These data are compiled in table 2.

Dilatometric data listed for polyurethane rubber were determined by a different and less accurate method (12). They should be considered with some precautions.

4. Discussion

4.1. The time temperature shift and the W.L.F. equation

To check the applicability of the time-temperature shift principle, a reference temperature T_0 was chosen for each polymer, corresponding with that measuring temperature at which the transition was located as nearly as possible to the midpoint of the experimental window. The other curves were shifted along the logarithmic time scale until a single master curve for $J(t)$ was obtained. The shift $\log a(T, T_0)$ was plotted vs. $T - T_0$ and the location of the transition at the temperature T_s was determined by interpolation. Then the shift function $\log a(T, T_s)$ could be calculated and listed in table 4.

If we exclude PVC for the moment, only minor deviations were observed from the shift principle in almost the entire temperature range investigated. However, for the lower right parts of figures 4 to 8 significant deviations from the shift principle were found. At the lowest temperatures and the longest creep times, [e.g. $T < 95\,^\circ\mathrm{C}, t > 10^2$ sec for PS], the creep curves increase less steep than would be expected from the shift. In this region volume relaxation phenomena still occur during the creep measurement, as the conditioning time prior to the creep measurement was not sufficient to establish thermal equilibrium for the specific volume. This is in complete agreement with the findings of *Struik* (13) who has studied volume relaxation and proved the existence of a shift of the glass transition to longer times due to proceeding aging. From his results a lower double logarithmic slope of the creep curves at the low temperature flank of the glass transition is to be expected. In spite of this we determined shift values also for those temperatures to indicate at least the approximate position of the transition.

In the case of PVC (fig. 6) the shift principle also fails at higher temperatures. In this region a horizontal and vertical shift of the creep curves is observed with increasing temperature. This is associated with recrystallization as mentioned earlier.

The shift function for polystyrene is plotted vs. the temperature in figure 13. Shift values derived experimentally are indicated by triangles and connected by a solid line. Through the experimental points the W.L.F. equation with best fitted parameter values c_1^s and c_2^s was drawn as a dashed line. c_1^s and c_2^s were determined from a linear plot of $(T - T_s)/\log a(T, T_s)$ vs. $T - T_s$.

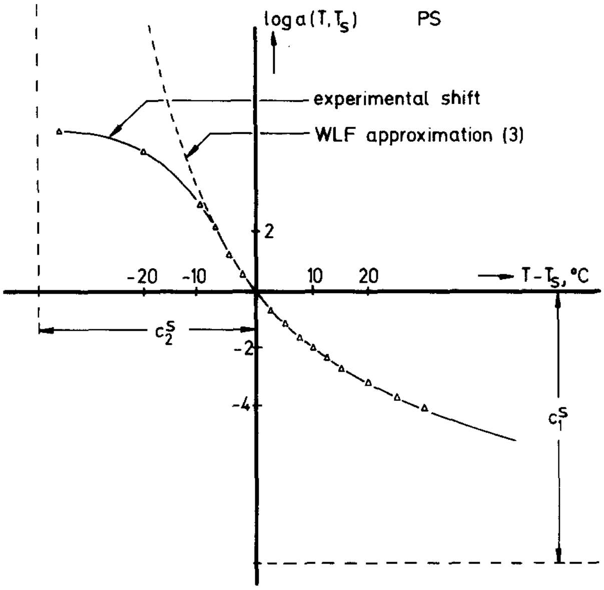

Fig. 13. Time-temperature shift for PS vs. temperature and the parameters of the best fitted W.L.F. equation

The W.L.F. equation is seen to present an excellent fit to all but three experimental points. The latter correspond with the shift of the creep curves near the glass transition temperature, where equilibrium of free volume has not been established within the conditioning time. Therefore, the W.L.F. equation which was derived under the assumption of thermodynamic equilibrium for f (eq. [8]), cannot be expected to hold for those points. We conclude that the lower limit of the region of validity of the W.L.F. equation depends strongly on the details of the temperature history of the specimen.

The parameter values c_1^s and c_2^s represent the distances of the both asymptotes of the W.L.F. equation from the origin. We are especially interested in the distance of the vertical asymptote which yields c_2^s and therefore – by eq. [10] – the value of the "thermodynamic transition temperature" T_∞. The accuracy by which T_∞ is obtained, is poor, as the gap between the first shift point on the W.L.F. line and the position of the asymptote is as wide as 39 K. To improve this accuracy one should try to establish shift points on the W.L.F. line at temperatures as low as possible by extremely slow cooling of the specimen through the glass transition and by using extremely long conditioning times of the specimen prior to the creep measurement. This is now under progress.

Similar results have been obtained for the other polymers. Values of the parameters of the W.L.F. equation are listed in table 1.

A comparison between the shift values of the different polymers is given in figure 14; plotted are the shift values of each polymer, relative to its own softening temperature T_s. If a universal form for the W.L.F. equation were to exist at all, we had expected it to be valid with respect to the reference temperature T_s.

A glance on this figure clearly shows that the shift values of the different polymers differ significantly. No universal representation of

Table 1. Characteristics of the glass transition as obtained from the results of creep measurements

polymer	H	n	w[K]	T_s[°C]	c_1^s	c_2^s	T_∞[°C]	$c_1^s \cdot c_2^s$
PS	3.6	0.85	40	105.0	9.4	39.0	66.0	367
PMMA	2.8	0.69	35	123.5	8.0	36.0	87.5	288
PVC	2.3	0.53	25	73.5	11.2	34.6	38.9	388
PU	3.1	0.48	60	−45.0	12.5	42.5	−87.5	531
NR	3.0	0.72	40	−62.0	11.4	37.8	−99.8	431
universal W.L.F.	–	–	–	–	–	–	–	900

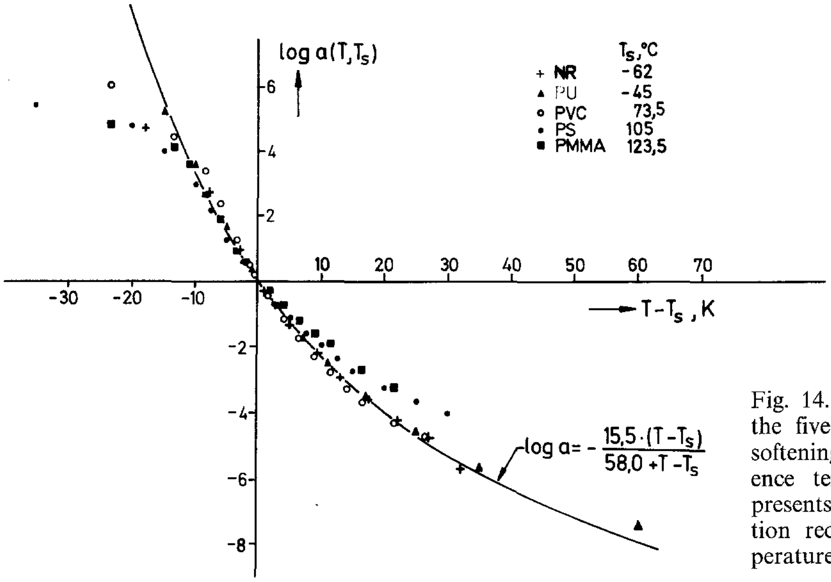

Fig. 14. Time-temperature shifts for the five polymers investigated with softening temperature T_s as the reference temperature. Drawn line represents the universal W.L.F. equation reduced to the reference temperature $T_s = T_u - 43.6$

the shift function is possible with T_s as reference temperature. The drawn line in figure 14 represents the course of the universal W.L.F. eq. [5] under the assumption that

$$T_u - T_s = 43.6\,\mathrm{K}\,.$$

The question remains whether a different choice of a reference temperature could have resulted into a universal representation. This has explicitely tried with the dilatometric glass transition temperature T_g (with $\beta = 3$ K/h) as reference temperature; however with a similar negative result. More generally we can conclude from the numbers in the last column of table 1 that no such reference temperature may be found. Whilst c_1 and c_2 depend on the chosen reference temperature, the product $c_1 \cdot c_2 = \bar{c}_1 \cdot \bar{c}_2$ does not. The mentioned column shows that the products of the W.L.F. constants differ significantly from each other, and also differ from the value $c_1^u \cdot c_2^u = 900$ which would follow from the cited universal W.L.F. representation.

4.2. *The course of free volume derived from dilatometric data*

The way in which the specific volume from dilatometric measurements is decomposed into a free volume and an occupied volume, is explained with reference to figure 15. The contraction curve in the rubbery region is extrapolated as a straight line to the thermodynamic transition temperature T_∞. This leads to a hypothetical state, which' by definition does not contain free volume. Therefore, the occupied volume at T_∞ is known. Assuming that the occupied volume has the same temperature dependence as the total volume in the glassy state, a line parallel to the contraction curve in the glassy state is drawn through this point. This line effects the desired decomposition.

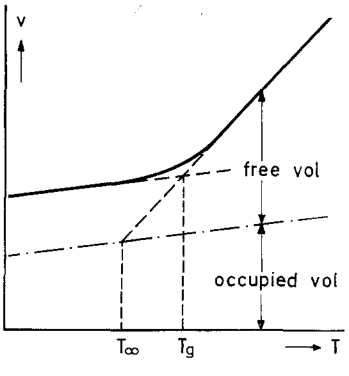

Fig. 15. Specific volume vs. temperature during cooling through the glass transition, and the decomposition into free and occupied specific volume

A survey over the dilatometric data which were obtained on four polymers, is given in table 2. This table lists the glass transition temperature T_g, at a cooling rate of $\beta = 3$ K/h, the volume expansion coefficients in the glassy and rubbery region, α_g and α_l and their difference $\Delta\alpha$.

Table 2. Characteristics of the glass transition from dilatometry

polymer	T_g [°C]	α_g	α_l	$\Delta\alpha$
			$[10^{-4}\,\mathrm{K}^{-1}]$	
PS	90.5	2.14	6.06	3.92
PMMA	107.2	2.66	6.20	3.54
PVC	65.7	2.07	5.83	3.76
PU	−54.3	1.80	5.20	3.40

Polymethylmethacrylate shows the largest value of the expansion coefficient in the glassy state; this is probably connected with the β-transition of this polymer. The differences of the both expansion coefficients are all found between 3.4 and $3.9 \cdot 10^{-4}\,\mathrm{K}^{-1}$. These will be identified with the expansion coefficient of the free volume (of eq. [11]).

Now we are combining the results obtained from torsional creep data with those from dilatometry. Multiplying eqs. [9] and [10] leads to the following expression for the constant B of the Doolittle equation

$$B = 2.3\, c_1 \cdot c_2 \cdot \alpha_f\,. \qquad [14]$$

Inserting $c_1 c_2$ from table 1 and $\alpha_f = \Delta\alpha$ from table 2 yields values for B which are listed in the second column of table 3. They are all considerably smaller than unity.

In the original formulation of the universal W.L.F. equation, the constant B was arbitrarily put equal to unity, as it could not be determined separately. This together with the universal values of c_1 and c_2 yielded for $\Delta\alpha = 4.8 \cdot 10^{-4}$ which is clearly too high when compared with experiment.

Using the values of T_∞, we performed the decomposition into free volume and occupied volume for the dilatometer curves measured under a rate of cooling of 3 K/h. This procedure yielded the fractional free volume at all temperatures under the cooling rate $\beta = 3$ K/h. These are plotted for four polymers as open symbols in figure 16. The values obtained especially for the temperatures T_∞, T_g (3 K/h) and T_s are listed in table 3 as f_∞, f_g and f_s respectively.

The fractional free volume at the glass transition temperature, f_g, has values between 0.8 and 1.1%; the fractional free volume at the softening temperature, f_s, shows values between 1.3 and 1.5%. These are all smaller than the value of 2.5% which is found for f_g under the assumption of the universal W.L.F. shift equation with $B = 1$. One should however take into account that after our assumption, it is not the value of f_g, but that of f_g/B which is characteristic for the process of vitrification of the polymers. Values of f_g/B as listed in the last column of table 3 are even larger than 2.5%.

4.3. The course of free volume derived from the time temperature shift of the glass transition

In the last section we derived the course of the free volume from dilatometric data with one additional information from creep, viz. the thermodynamic glass transition temperature T_∞. Similarly, it is possible to derive the course of the free volume from the time temperature shift with one additional information from dilatometry, viz. the thermal expansion coefficient of free volume in equilibrium, α_f.

For this purpose we apply eqs. [7] and [9] to the reference temperature T_s and obtain

$$\log a(T, T_s) = 0.43\, B \left[\frac{1}{f} - \frac{1}{f_s}\right], \qquad [15]$$

$$c_1^s = 0.43\, B/f_s\,. \qquad [16]$$

Table 3. Characteristics of the glass transition as obtained by combining results of creep and dilatometry

polymer	α_f $[10^{-4}\,\mathrm{K}^{-1}]$	B	f_∞ [%]	f_g [%]	f_s [%]	f_g/B [%]
PS	3.92	0.331	1.0	1.1	1.5	3.3
PMMA	3.54	0.235	0.7	0.8	1.3	3.4
PVC	3.76	0.336	0.9	1.0	1.3	3.2
PU	3.40	0.416	–	1.1	1.5	2.6
universal W.L.F.	4.8	1		2.5		2.5

Combining those equations yields

$$0.43\,B/f = \log a(T, T_s) + c_1^s\,. \qquad [17]$$

Inserting $\Delta\alpha$ from dilatometric data in eq. [14] we find B and can therefore calculate f as function of temperature from the shift function. As the validity of eq. [7] was not restricted to thermal equilibrium, this method may also be used to calculate f in the glassy state, under the condition that the appropriate values of $\log a(T, T_s)$ are available there.

Values for the time temperature shift of the five polymers investigated are summarized in table 4. From these values, fractional free volumes were calculated for the four polymers for which dilatometric data were known. The results are plotted with closed symbols in figure 16.

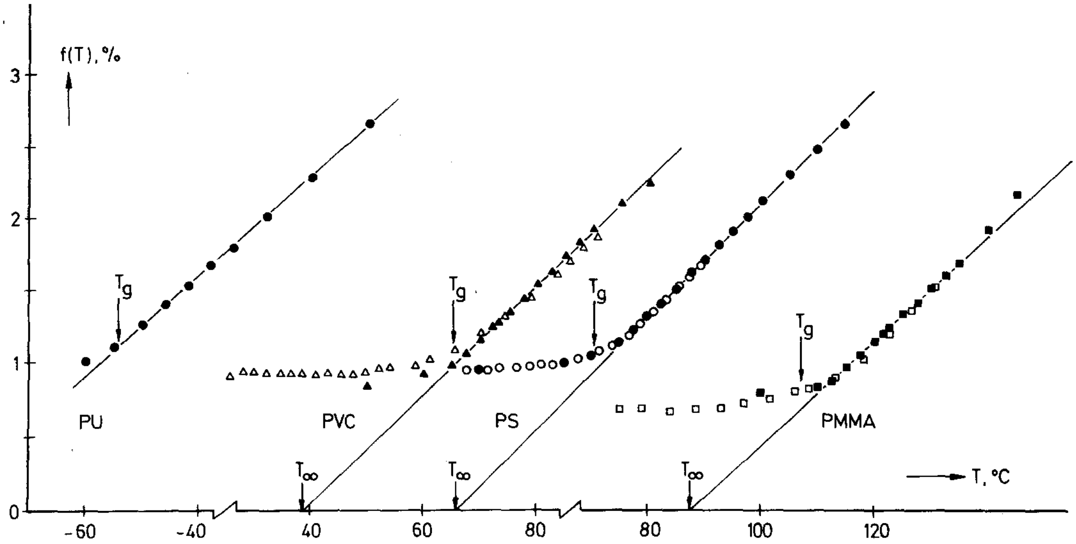

Fig. 16. Fractional free volume vs. temperature for four polymers. Open symbols derived for specimen subjected to dilatometric measurements under rate of cooling $\beta = 3$ K/h. Closed symbols derived for specimen subjected to torsional pendulum measurements

Table 4. Time-temperature shift function with softening temperature T_s as reference temperature, for the five polymers investigated

Polymer	PS		PMMA		PVC		PU		NR	
T_s [°C]	105		123,5		73.5		−45		−62	
	$T - T_s$	$\log a$	$T - T_s$	$\log a$	$T - T_s$	$\log a$	$T - T_s$	$\log a$	$T - T_s$	$\log a$
	−35	5.49	−23.5	4.81	−23.5	6.01	−15	5.19	−18	4.71
	−20	4.82	−13.5	4.10	−13.5	4.45	−10	3.62	−8	2.72
	−15	4.04	−11	3.61	−8.5	3.39	−5	1.69	−3	0.94
	−10	3.03	−8.5	2.55	−6	2.41	−1	0.34	1	−0.30
	−7.5	2.20	−6	1.65	−3.5	1.29	3	−0.75	5	−1.34
	−5	1,25	−3.5	0.91	−1.5	0.49	7	−1.75	9	−2.22
	−2.5	0.63	−2	0.51	−0.5	0.19	11	−2.49	13	−2.92
	2.5	−0.65	−1	0.26	1.5	−0.45	17	−3.53	17	−3.59
	5	−1.09	1.5	−0.31	4	−1.16	25	−4.62	22	−4.21
	7.5	−1.56	4	−0.77	6.5	−1.76	35	−5.70	27	−4.73
	10	−1.92	6.5	−1.22	9	−2.30	60	−7.46	32	−5.72
	12.5	−2.30	9	−1.61	11.5	−2.77				
	15	−2.68	11.5	−1.92	14	−3.26				
	20	−3.20	16.5	−2.67	16.5	−3.65				
	25	−3.66	21.5	−3.25	21.5	−4.28				
	30	−4.02			26.5	−4.70				

The agreement between the values of the fractional free volumes found by both methods constitutes a check on the consistency of the hypothesis that free volume may be defined by specific volume on the one hand and by its relation to mobility [6] on the other. Agreement in the rubbery state is trivial, as parameter values α_f and B were determined to establish it. Agreement in the beginning of the glassy state however is crucial for consistency. This agreement is best for polystyrene and poorest for polyvinyl chlorid.

5. Conclusions

The following conclusions may be drawn from the results of this work:

1. The time-temperature superposition is applicable with reasonable accuracy to measurements of shear compliance over a broad experimental window for purely amorphous polymers, crosslinked and uncrosslinked. Its validity extends down into the glassy region on the condition that the aging time [time of preconditioning at the measuring temperature] can be chosen long enough when compared with the creep time involved.

2. The shift function may be described with excellent accuracy by the W.L.F. equation for temperatures down to the glass transition temperature. The exact lower temperature limit of validity of the W.L.F. equation depends on aging time.

3. The constants of the W.L.F. equation are material specific; no universal values can be found for the polymers investigated.

4. By simultaneous measurements of specific volume and shear creep compliance of the same polymer, all three parameters of the simple free volume hypothesis discussed, may be determined, viz. the thermodynamic glass transition temperature T_∞, the thermal expansion coefficient of the free volume, α_f, and the constant B of the Doolittle equation. However, the accuracies with which T_∞ and B may be determined depend on the accuracies of determination of respectively c_2 and c_1, and those are still poor.

5. Within experimental error, the results of volume measurements are consistent with those of the time-temperature position of the glass transition measured in shear. The values for B obtained are considerably smaller than unity, the values of the fractional free volume frozen at the glass transition are found between 0.8 and 1.1%.

6. More effort should be made to determine the shear compliance with higher accuracies and within a larger experimental window to improve the accuracy of determination of the W.L.F. constants c_1 and c_2.

Summary

Accurate measurements of the shear creep compliance in the glass rubber transition region have been performed by means of a combined torsional pendulum and torsional creep apparatus over a broad experimental window for commercial PS, PMMA and PVC and for two slightly crosslinked rubbers, NR and PU. For the three plastic materials, specific volume vs. temperature curves were obtained by volume dilatometry under different rates of cooling.

Shear creep compliance was found to obey the time-temperature superposition principle. In the temperature region above the glass transition temperature, the time-temperature shift function could be accurately described by a W.L.F. equation. However, the W.L.F. constants c_1 and c_2 differed for the different polymers and were different from the universal W.L.F. values. No choice for a reference temperature could be found to make the W.L.F. constants of the different polymers to coincide within experimental scatter.

Specific volumes in the rubbery state and the thermal expansion coefficients in the glassy state were found to be independent of rate of cooling. Specific volumes in the glassy state and glass transition temperature both increased with rate of cooling.

A simple hypothesis could be used to discuss the results, in which free volume is defined by the excess specific volume above glass transition on the one hand, and by its relation to mobility (the Doolittle equation), on the other. This hypothesis contains three independent parameter values, viz. the "thermodynamic glass transition temperature" T_∞, the thermal expansion coefficient of the free volume fraction, α_f, and B of the Doolittle equation. By combining the results of both measurements, all three parameters can be separately determined. Values for B are found between 0.2 and 0.4, values of the fractional free volume frozen at the glass transition are found between 0.8 and 1.1%.

Zusammenfassung

Es wurden genaue Messungen der Scher-Kriechfunktion im Glas-Kautschuk-Übergangsgebiet in einem ausgedehnten logarithmischen Zeitintervall mit Hilfe eines Torsionspendel- und Kriechautomaten durchgeführt. Untersucht wurden kommerzielles PS, PMMA und PVC sowie zwei leicht vernetzte Kautschuke, NR und PU. Für die drei Kunststoffe wurde das spezifische Volumen als Funktion der Temperatur bei verschiedenen Kühlgeschwindigkeiten bestimmt.

Die Scher-Nachgiebigkeit erfüllte das Zeit-Temperatur-Verschiebungsprinzip. Im Temperaturbereich über der Glastemperatur kann die Zeit-Temperatur-Verschiebungsfunktion mit großer Genauigkeit durch

die W.L.F.-Gleichung beschrieben werden. Die W.L.F.-Konstanten c_1 und c_2 sind jedoch für die verschiedenen Polymere verschieden und stimmen nicht mit den Universalwerten dieser Konstanten überein.

Spezifisches Volumen im gummielastischen Zustand und thermischer Ausdehnungskoeffizient im Glaszustand hängen nicht von der Kühlgeschwindigkeit ab. Spezifisches Volumen im Glaszustand und die Glastemperatur nehmen mit steigender Kühlgeschwindigkeit zu.

Die Ergebnisse konnten mit Hilfe einer einfachen Hypothese beschrieben werden, in der das freie Volumen einerseits aus dem spezifischen Volumen definiert wird, das oberhalb der Glastemperatur zusätzlich auftaut, andererseits durch seinen Zusammenhang mit der molekularen Beweglichkeit eingeführt wird (Doolittle-Gleichung). Diese Hypothese enthält drei unabhängige Parameter, nämlich die thermodynamische Glastemperatur T_∞, den Ausdehnungskoeffizienten des relativen freien Volumens α_f und den Parameter B der Doolittle-Gleichung. Durch Kombination der Meßresultate können alle drei Parameter bestimmt werden. Wir finden für B Werte zwischen 0,24 und 0,42 und für das beim Glasübergang eingefrorene relative freie Volumen f_g Werte zwischen 0,8 und 1,1%.

References

1) *Leaderman, H.*, Elastic and Creep Properties of Filamentous Materials and Other High Polymers, The Textile Foundation (Washington 1943).

2) *Tobolski, A. V., R. D. Andrews*, J. Chem. Phys. **11**, 125 (1943).

3) *Williams, M. L., R. F. Landel, J. D. Ferry*, J. Am. Chem. Soc. **77**, 3701 (1955).

4) *Ferry, J. D.*, Viscoelastic Properties of Polymers, 2. Ed., p. 316, John Wiley (New York 1970).

5) *Doolittle, A. K.*, J. Appl. Phys. **22**, 1471 (1951); **23**, 236 (1952).

6) *Nederveen, C. J., C. W. van der Wal*, Rheol. Acta **6**, 316 (1967).

7) *van der Wal, C. W., R. H. J. W. A. Drent*, Rheol. Acta **7**, 265 (1968).

8) *Struik, L. C. E., G. A. Schwippert*, TNO-Nieuws **21**, 285 (1966).

9) *Schwippert, G. A., C. W. van der Wal*, A Gasthermostat, Internal Communication P 71/21, Central Laboratory TNO (Delft, the Netherlands).

10) *Struik, L. C. E.*, Rheol. Acta **6**, 119 (1967).

11) *Schwarzl, F. R.*, Pure Appl. Chem. **23**, 219 (1970).

12) *van der Wal, C. W., H. W. Bree, F. R. Schwarzl*, J. Appl. Pol. Sci. **9**, 2143 (1965).

13) *Struik, L. C. E.*, Physical aging in amorphous polymers and other materials, thesis techn. Univ Delft (1977).

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