polymer papers

Dependence of relaxation times of glassy polymers on their specific volume

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This paper deals with the volume relaxation and simultaneous changes in mechanical properties that occur after complicated thermal histories. The histories were chosen such that, at the final measuring temperature, the specific volume v passes through a maximum with increasing time. It is shown that, for polystyrene, poly(vinyl chloride) and polycarbonate, the mechanical creep properties change as if the position on the log time scale of the creep curve is uniquely determined by the momentary value of v. Thus, a maximum in the volume relaxation curve implies that the creep curve first shifts to the left and later to the right.

INTRODUCTION

Previous work[1] showed that isothermal volume relaxation is accompanied by changes in the position on the log time scale of the mechanical creep curve. During isothermal contraction, the creep curve gradually shifts to longer creep times, i.e. to the right; during isothermal dilatation, it shifts to the left, and when the volume relaxation curve shows a maximum, the creep curve first shifts to the left, but later shifts to the right. This is shown for polystyrene (PS) in figures 82–85 of ref. 1, and also in *Figures 1* and *2* here. The various volume relaxation curves in *Figure 1* were obtained after the thermal pretreatments specified in *Figure 2*, and log a is the shift relative to the creep curve measured 25 min after a quench from 100 to 85°C.

The similarity between the two diagrams of *Figure 1* strongly suggests that the position on the time scale of the creep curve, i.e. log a, is uniquely related to the momentary value of specific volume v. Thus, a plot of log a vs. specific volume v, both measured at the same value of elapsed time t_e at 85°C, should result in a unique curve. As shown in *Figure 2*, this is indeed the case.

Similar results were obtained for polystyrene (PS) at 40–85°C, poly(vinyl chloride) (PVC) at 40–70°C and polycarbonate (PC) at 100–140°C. Only a few of the results have been published so far[1,2]; the full set is reported now.

EXPERIMENTAL

Materials

The materials investigated are listed in *Table 1*. PVC and PC were provided by the suppliers in the form of 3.5–4 mm thick sheets; PS was compression moulded at TNO.

The materials were first annealed and dried by heating for 1–2 days at 0.1 mmHg to a temperature T_a well above T_g (see *Table 1*). This was done to avoid possible complications due to moisture (PC), internal stresses (warping of torsional creep specimens) or crystallization processes (PVC).

Type of experiments

To obtain diagrams such as those of *Figure 1*, we used an experiment outlined in *Figure 3*. The polymer is first heated to a temperature $T_0 \simeq T_g + 15°C$. Thermodynamic equilibrium is reached rapidly. Within half an hour all previous thermal histories are erased, and a reproducible standard initial state is reached[1]. Next, the material is quenched to a temperature $T_1 < T_g$ and kept at T_1 for time t_1 (120 h in *Figure 3*). Finally, the polymer is reheated to temperature $T_e \leqslant T_g$ for a measuring period of 48 h.

We symbolize this *quench–upquench* by $T_0(\infty)\downarrow T_1(t_1)\uparrow T_e$, in which the symbol ∞ after T_0 indicates that we start from thermodynamic equilibrium at T_0. Omitting the intermediate period at T_1, we have the *direct quench*, $T_0(\infty)\downarrow T_e$.

At T_e, the isothermal changes in specific volume v and in mechanical properties are measured simultaneously, respectively, by dilatometry and by torsional creep (see below).

A schematic illustration of v as a function of elapsed time t_e at T_e is given in *Figure 3*. In the general experiment $T_0(\infty)\downarrow T_1(t_1)\uparrow T_e$, v passes through a maximum, but for a direct quench $T_0(\infty)\downarrow T_e$, v decreases monotonically.

The changes in creep properties with elapsed time t_e are measured as shown in *Figures 3* and *4*. We determine the creep curves at the moments indicated in *Figure 3* by 1 to 6. In order to obtain instantaneous views of the properties at these six moments, the duration of each creep test is kept short ($< 20\%$) in comparison with the elapsed time t_e at the beginning of the test. The resulting creep curves are given schematically in *Figure 4*. Going from test 1 to test 3, volume v increases (*Figure 3*) and the creep curve shifts to shorter times; from tests 3–6, v decreases, and the creep curve shifts to the right. The creep curve appears to shift without significant change in shape[1], and therefore its momentary position on the time scale can be specified by its shift, log a, from some arbitrary reference creep curve (in *Figure 4*, curve 6).

Shift, log a, is taken as positive (i.e. acceleration factor $a > 1$) when the creep curve lies to the left of the reference curve, i.e. when the creep is accelerated, and it is negative when it lies to the right.
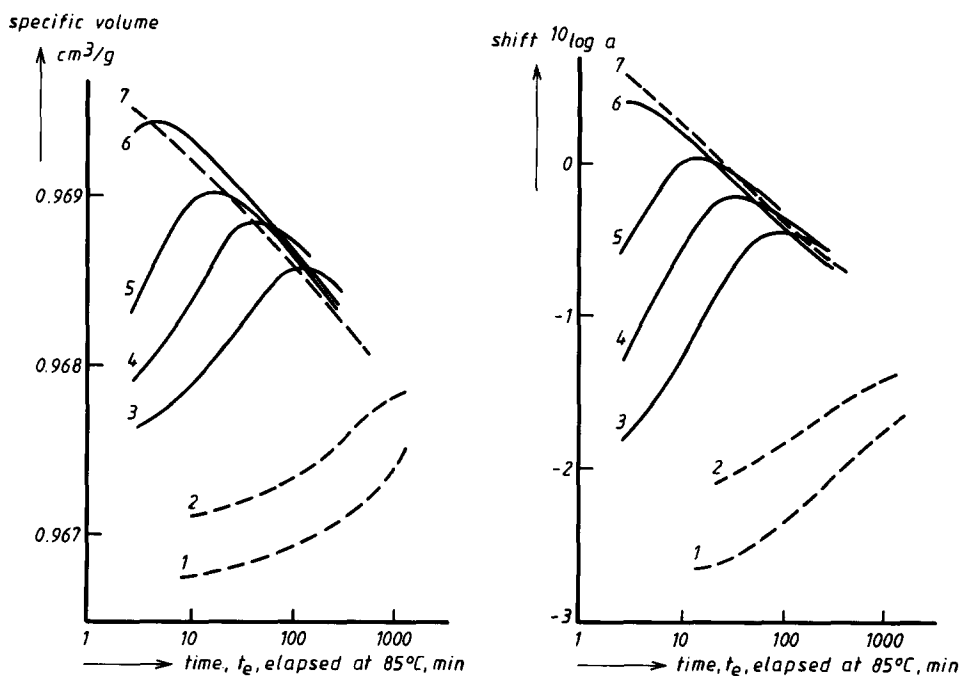
Figure 1 Isothermal volume relaxation and simultaneous changes in mechanical creep properties of polystyrene (Styron 666) at 85°C after the thermal pretreatments specified in *Figure 2*. (Reproduced with permission from ref. 1)
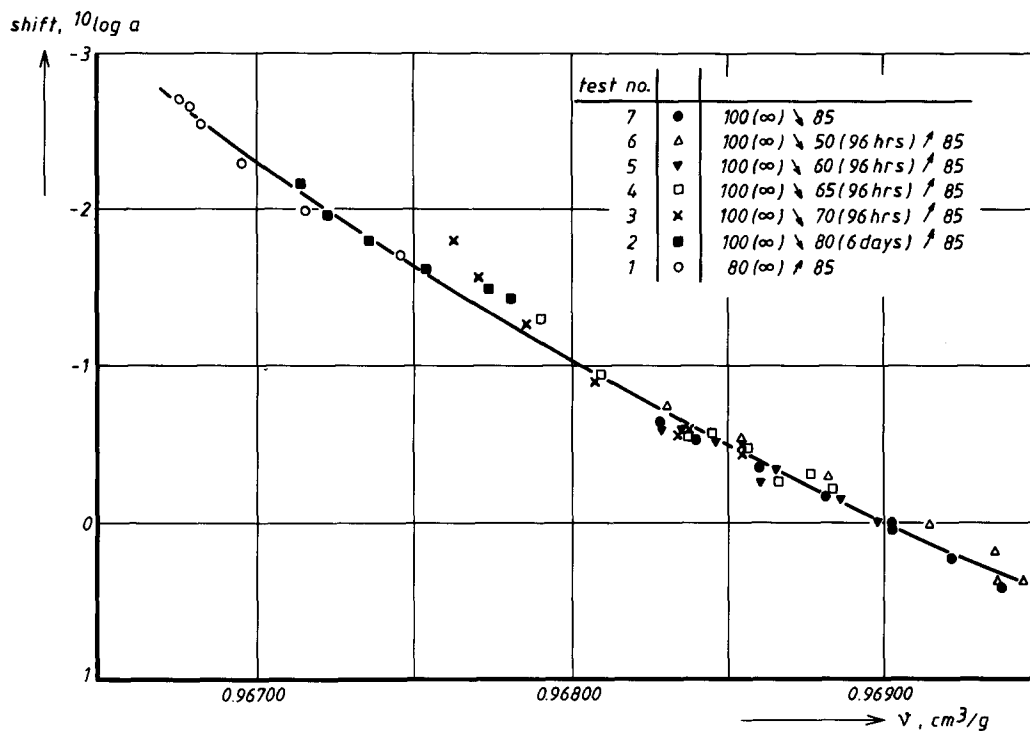

Figure 2 Shift, log a vs. momentary value of specific volume v for the various experiments of *Figure 1*. (Reproduced with permission from ref. 1)

Table 1 Materials investigated

Code no. in appendix B of ref. 1	Polymer	Supplier	Annealing temp., T_a (°C)	Density at 23°C (g cm^{-3})
19	PS, Dow Styron 666	TNO	95	1.047
3	Rigid PVC, practical formulation	Solvay	110	1.383
13	PC, Macrolon 8032	Philips	165	1.196

Having obtained v and shift, log a, in this manner as functions of elapsed time t_e, we construct diagrams similar to *Figures 1* and *2*. The question whether or not v and log a are uniquely related can then be answered straightforwardly.

Dilatometry

A detailed description of the technique is given in Appendix A.1 of ref. 1. The only difference with ref. 1 is
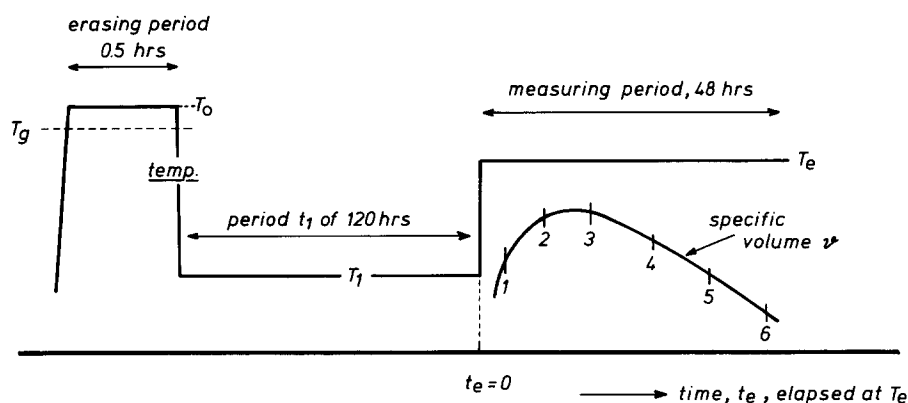
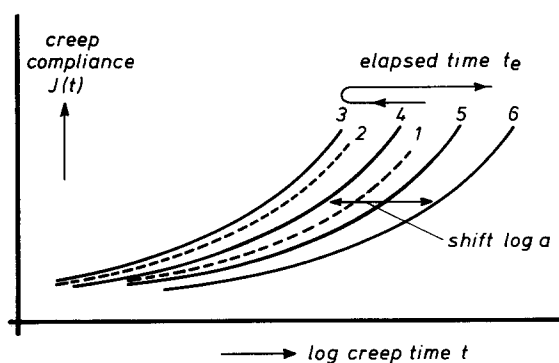**Figure 3** Outline of the experiment $T_0(\infty){\downarrow}T_1(t_1){\uparrow}T_e$

Figure 4 Creep curves at final temperature T_e, measured at various values of elapsed time t_e in the experiment $T_0(\infty){\downarrow}T_1(t_1){\uparrow}T_e$ (compare *Figure 3*)

that we now use the annealing temperatures given in *Table 1*.

Mechanical tests

All measurements were made with the automatic torsional creep systems described in Appendix A.4 of ref. 1. At each final temperature T_e, the creep curves were determined at elapsed times t_e of 1/3, 2/3, 4/3, 8/3, 16/3, 32/3 and 64/3 h. The specimens were prepared in exactly the same way as for the dilatometry, but the thermal programme of *Figure 3* was realized in a slightly different way.

PS and PVC. First, the specimens, sandwiched between 6 mm thick aluminium sheets, are heated to temperature T_0 for 1 h in an air oven. Next, the sandwich is quenched to 20°C by putting it between two heavy aluminium sheets, originally at 20°C. Then the specimen is put in a Pyrex tube, and the closed tube is placed in a 9 litre liquid thermostat for the intermediate period at temperature T_1. At the end of this period, the tube is taken out of the thermostat, the specimen is clamped in the torsional creep system, and immediately heated to the final measuring temperature T_e. Direct quenches from T_0 to T_e, however, were performed entirely in the gas thermostat of the creep tester (Appendix A.11 of ref. 1). The procedure with the (cheap) liquid thermostats was chosen in order to prevent the (expensive) torsional creep testers standing idle during the 120 h waiting period at the intermediate temperatures T_1 (see *Figure 3*).

PC. Because this polymer is sensitive to moisture, the following more complicated procedure had to be

followed. Before each test, the specimen was dried in a vacuum oven (one day at 120°C, followed by one night at 155°C, and finally by cooling to 20°C over several hours). The specimen was then immediately placed in the dry nitrogen oven of the torsional creep tester, heated to $T_0 \geqslant T_g$, and quenched to 20°C. Next, it was placed in a Pyrex tube, and further treated as described before for PS and PVC.

RESULTS

The experimental results are summarized in *Figures 5–7*. The diagrams are similar to those of *Figure 1*. Each figure concerns one polymer, and for 4–6 final temperatures T_e, it gives a diagram of v vs. log t_e, together with a diagram of log a vs. log t_e.

The final temperatures range from about $T_g - 50$°C to T_g. For each T_e, there is always one direct quench $T_0(\infty){\downarrow}T_e$, and a set of 3–4 tests of the type $T_0(\infty){\downarrow}T_1(t_1){\uparrow}T_e$, all with the same value of t_1 of 120 h, but with different values of T_1, which are indicated in the diagrams. As a rule, T_1 is below T_e, but sometimes T_1 was chosen equal to or even higher than T_e.

Inspection of *Figures 5–7* reveals that the v vs. log t_e plots are very similar to the log a vs. log t_e plots. Thus, for the three polymers investigated, *Figure 1* could indeed be reproduced at various temperatures below T_g.

DISCUSSION

From *Figures 5–7*, we can obtain diagrams similar to *Figure 2*. These are given in *Figures 8–10*. Shift factor a is plotted vs. the momentary value of specific volume with the final temperature T_e as a parameter. The different symbols distinguish between the different tests (direct quenches, or tests of the type $T_0(\infty){\downarrow}T_1(t_1){\uparrow}T_e$ with various values of T_1). A key is given in each figure.

The log a vs. v correlations of *Figures 8–10* are not always as satisfactory as in *Figure 2*. The correlation is good for PC (*Figure 8*), but considerable deviations are observed for PVC (*Figure 9*), and, in particular, for PS (*Figure 10*). These deviations are systematic, as is shown in *Figure 10* by the thin curves drawn through groups of data points corresponding to the same value of T_1. We observe a set of loops, the origin of which is revealed by inspection of *Figure 7*. In this figure, the maxima in v at T_e values of 80 and 85°C occur at an elapsed time t_e about twice as long as the time at which the corresponding log a curve passes through its maximum. Such a delay
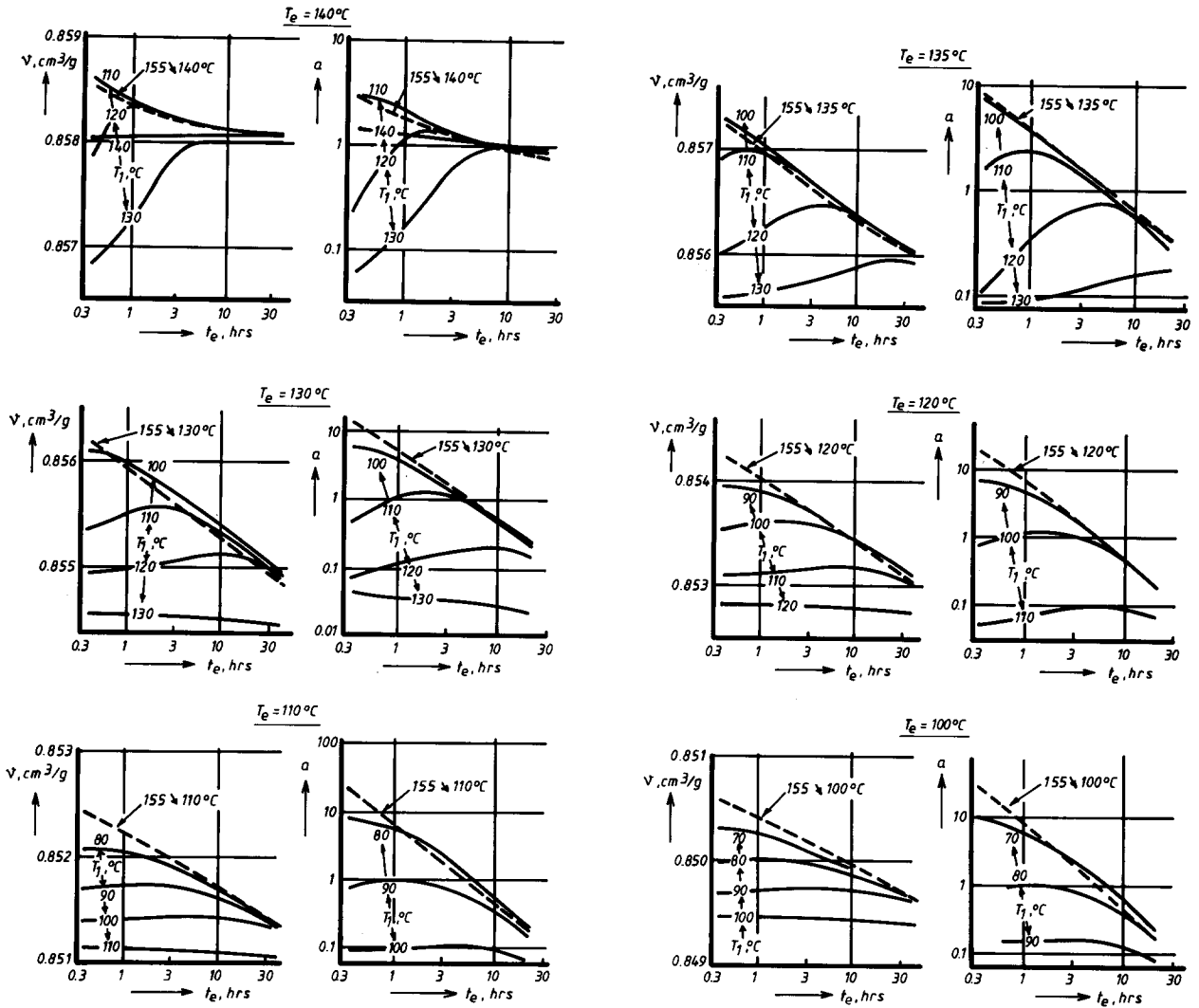
Figure 5 Polycarbonate. Isothermal volume relaxation and simultaneous shift of the creep properties at various temperatures T_e. Broken curves, direct quench 155°C↓T_e; full curves, 155°C↓T_1(120 h)↑T_e. Shift, log a, is the shift of the creep curve from that measured at T_e at 16/3 h after the direct quench

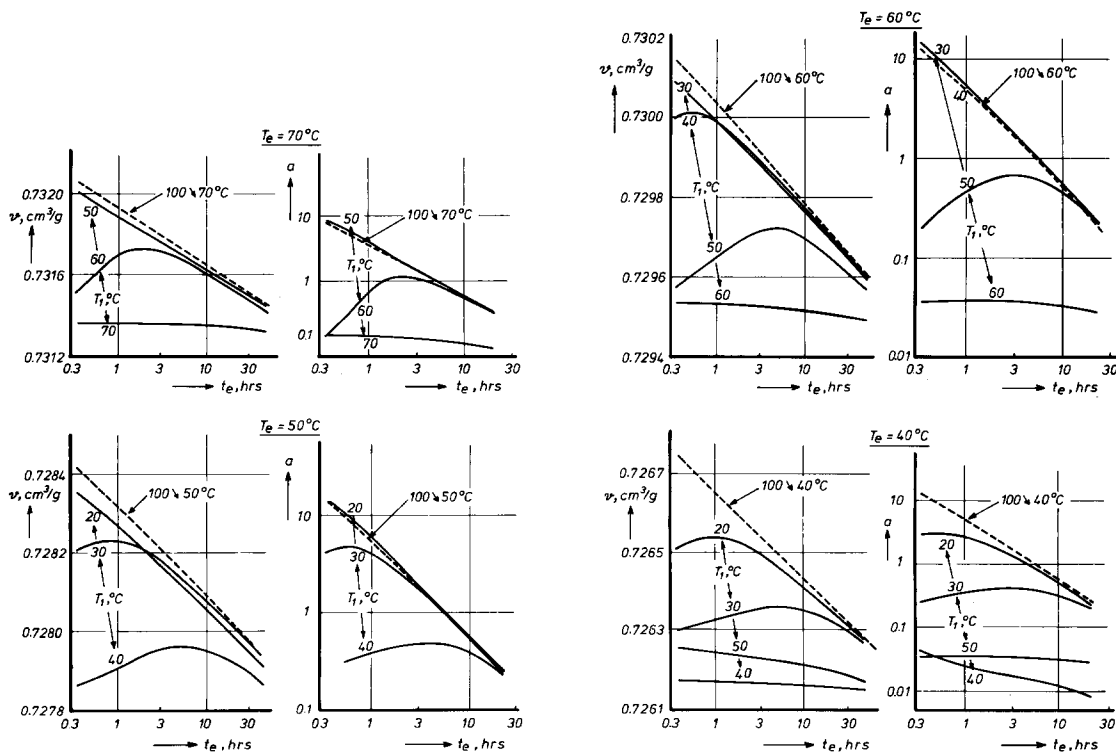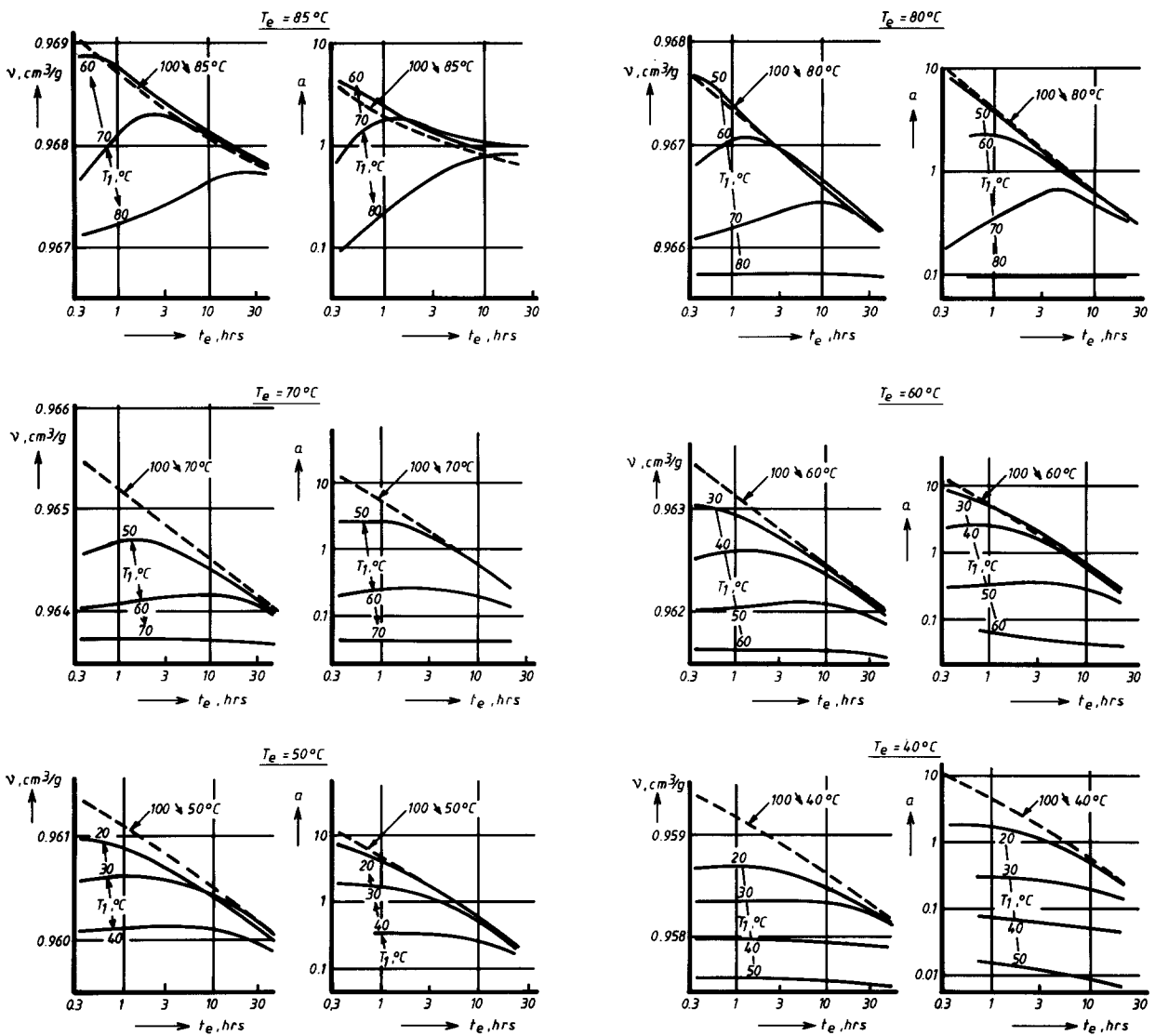**Figure 6** Rigid PVC. Same as *Figure 5*, but $T_0 = 100$°C

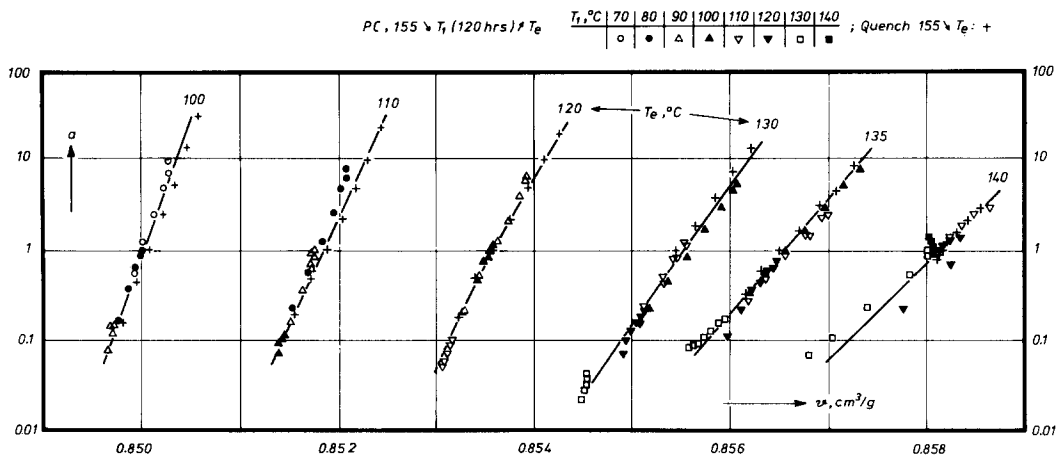**Figure 7** Polystyrene. Same as *Figure 5*, but $T_0 = 100°C$

Figure 8 Log a vs. v correlations for PC, derived from *Figure 5* by plotting log $a(t_e)$ vs. $v(t_e)$

necessarily leads to loops when $v(t_e)$ is plotted against log $a(t_e)$, in the same way as Lissajous loops arise from phase differences.

This delay by a factor of 2 explains nearly all deviations in *Figure 10*, as is shown in *Figure 11*, in which log $a(t_e)$ is plotted vs. $v(2t_e)$, and in which the loops have disappeared.

We thus have to find the origin of this delay, and to answer such questions as: Is the delay characteristic for PS? Why does it not occur for PC, and only to a much lesser extent for PVC?

The following considerations may lead to an answer:
(1) The delay cannot be characteristic for PS, as it is absent in *Figures 1* and *2*. Thus, it may very well be due to
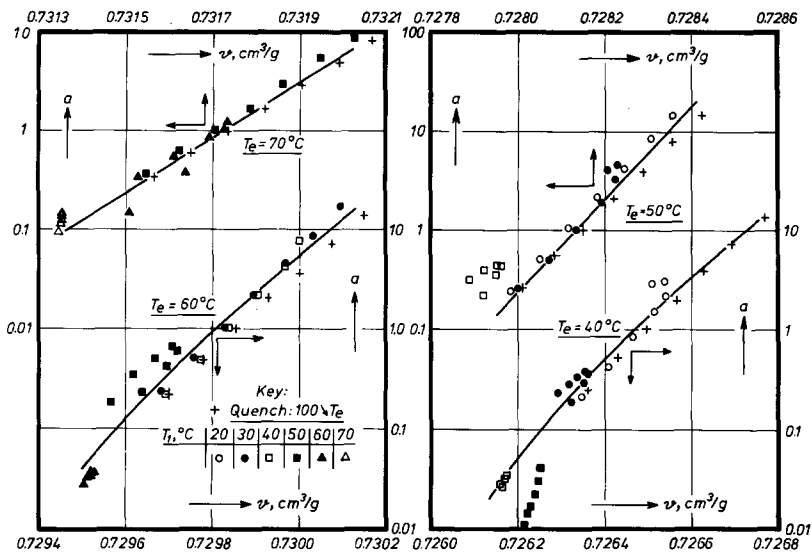
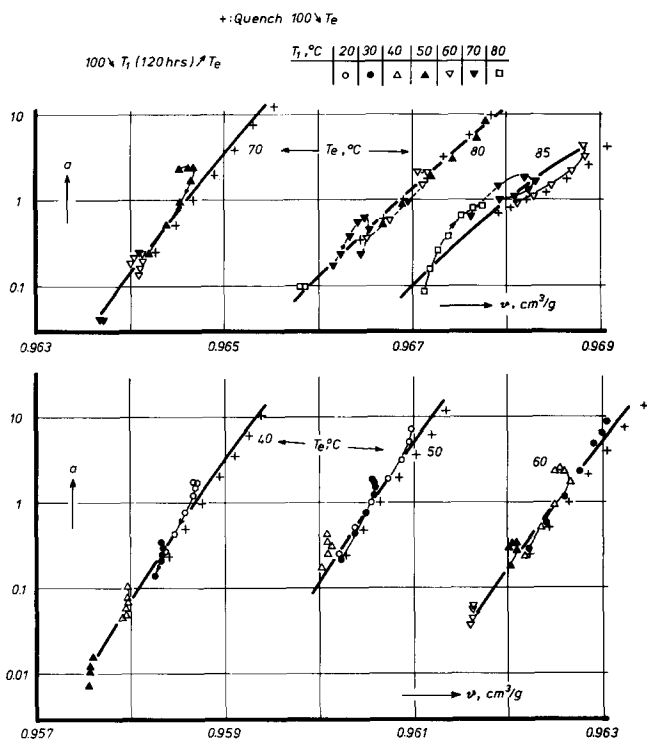**Figure 9** Log a vs. v correlations for PVC, derived from *Figure 6* by plotting log $a(t_e)$ vs. $v(t_e)$

Figure 10 Log a vs. v correlations for PS, derived from *Figure 7* by plotting log $a(t_e)$ vs. $v(t_e)$
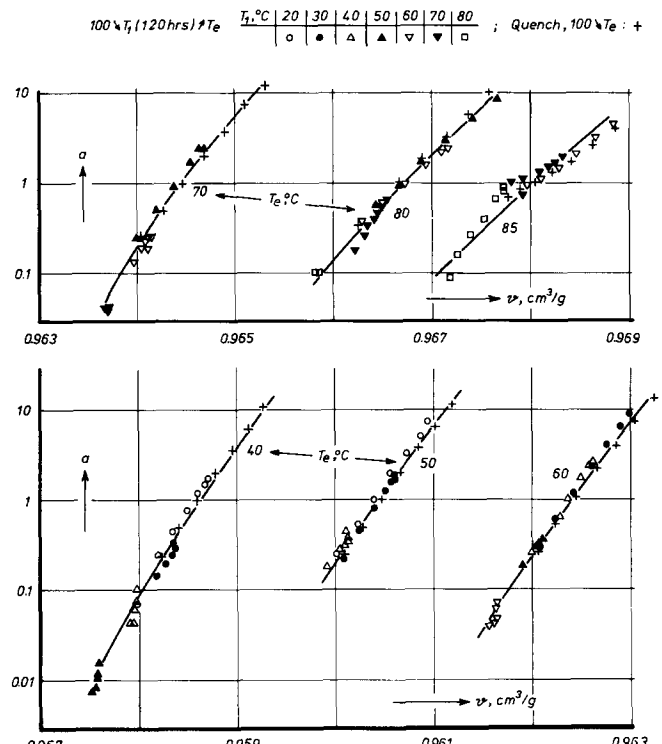

Figure 11 Log a vs. v correlations for PS, derived from *Figure 7* by plotting log $a(t_e)$ vs. $v(2t_e)$

differences between the experimental techniques used in the present work, and used previously to get *Figures 1* and *2*.

(2) There is indeed such a difference. Previously, the temperatures in the creep tester and the dilatometer thermostats were continuously compared, and the temperature difference was kept zero by the electronic control system of the creep tester. Thus, in the previous experiments, the temperatures were indeed equal. In the present work, the thermostats of dilatometer and creep tester worked independently. Therefore, the temperature in the creep tester may have been somewhat higher than in the dilatometer thermostat. This would explain the shift of the log a vs. log t_e curves relative to the v vs. log t_e curves.

(3) A check afterwards showed that the temperature in torsion tester I, in which PS was measured, was 0.6–1°C too high, and that the thermometer used for dilatometry over the range between 50 and 100°C was defective, which caused the dilatometer temperature to be 0.6°C too low. For PS, the total difference in temperature thus amounted to 1.2–1.6°C, which leads precisely to the correction that we need to explain the delay by a factor of 2. This can be seen as follows: around 85°C the temperature coefficient d log a/dT is about 0.25°C^{-1} for PS (see figure 9 of ref. 3). So, a ΔT of 1.2°C explains the delay by a factor of 2. At temperatures considerably below T_g, d log a/dT becomes smaller (sections 4.10 and 9.4 of ref. 1); this explains why the deviations seen in *Figure 10* become less at lower

temperatures (compare the data at 85 and 40°C in *Figure 10*).

(4) PVC and PC were measured in another, new creep instrument (torsion tester II). Further, the thermometer used for the volume relaxation tests on PC, was a different one than used for PS and PVC. It is highly improbable that this one was defective too. Thus, the satisfactory correlation found for PC in *Figure 8* indicates that the temperature in creep tester II was nearly correct. For PVC, we used torsion tester II, with its (assumed) correct temperature, but the dilatometer tests were done with the defective thermometer (0.6°C too low). This explains the deviations in *Figure 9*, at least partially. We can understand why at the highest T_e (70°C in *Figure 9*) the deviations are less than in *Figure 10* ($T_e = 85$°C); for PS the temperature error is twice as large as for PVC. The deviations seen in the PVC data at T_e values of 40 and 50°C remain unexplained, however.

In view of these considerations, we believe that the deviations in *Figures 8–10* are mainly due to inaccuracies in the temperatures, and that they could have been avoided by coupling the thermostats as done previously. Consequently, we do not believe that these troubles will weaken the general conclusion that log a and v are indeed uniquely related.

Before concluding this paper, some remarks seem appropriate:

Magnitude of the volume changes. Figure 6, in particular, shows that the volume changes that 'cause' the considerable shifts in the creep properties are in fact very small (10^{-4}–10^{-3}). This implies that specific volume (or density) cannot be used as a practical index of the state of ageing in a material. Other factors, such as additives, structure or crystallinity, degree of polymerization, method of processing, etc., may easily influence the density to the same or even much greater amount than the ageing process. Thus, in practice, the density changes responsible for ageing are overshadowed by the effects on density of many other factors, and density cannot be used as a practical ageing index.

Crystallization of PVC. Figures 6 and *9* show that reproducible volume relaxation tests are possible with rigid PVC, at least when it has previously been annealed at 110°C, and when the measuring temperature does not exceed T_g. Thus, complications due to crystallization processes can be avoided. For the unannealed polymer, however, one can easily observe considerable density changes due to crystallization, especially above 70°C.

Polycarbonate. It has been reported[4-6] that, in the narrow temperature range between 110 and 135°C, PC shows a singularity, related to the ageing effects. This is not revealed by the present data. Dry PC behaves in the same way as PS and PVC, and does not show any pronounced secondary process in the above-mentioned temperature interval.

Relation between free volume v_f and specific volume v. The present results suggest that free volume v_f and macroscopic specific volume v are intimately related, a change in v_f being reflected by an equal change in v. Such a conclusion indeed seems correct, but one should be aware of its limitations. As discussed on pp. 176–7 of ref. 1, large volume changes as produced by densification (cooling through T_g under a high pressure) or by high tensile strains are not correlated one-to-one with changes in free volume. A clear explanation for this has been offered by Matsuoka[7]. So, we can only conclude that the unique relation between specific volume and mechanical creep properties (shift, log a) holds when the isothermal volume changes result from previous thermal treatments, and not from mechanical pressures and strains. But even in this restricted form, the conclusion is challenging: the theories for the relation between free volume and mobility are equilibrium theories designed for the region above T_g. The present results show that the relation also holds for the non-equilibrium states (just) below T_g, even when complicated thermal histories produce memory effects (volume relaxation peaks).

CONCLUSIONS

In the non-equilibrium state below T_g, the location of the mechanical creep curve on the log time scale is uniquely determined by the momentary value of the specific volume, even when, owing to complicated thermal histories, the isothermal volume relaxation shows a maximum.

The above conclusion, however, only holds when the isothermal volume changes result from previous thermal treatments, and not from high hydrostatic pressures or tensile strains.

ACKNOWLEDGEMENTS

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