Volume relaxation and secondary transitions in amorphous polymers

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For a number of polymers, the volume relaxation occurring after quenching from above to below glass transition temperature, T_g, has been studied by length dilatometry. By varying the test temperature between -180°C and T_g, the temperature regions of several secondary transitions were covered. Volume relaxation rate $r = -\mathrm{d}\ln v/\mathrm{d}\log t$ was found to show similar (secondary) peaks as the mechanical damping tan δ. The theoretical implications of these findings are discussed.

(Keywords: amorphous polymers; secondary transitions; volume relaxation rate; thermal expansivity; mechanical damping; two-potential well model)

INTRODUCTION

It is well known[1,2] that amorphous polymers show volume relaxation effects when these materials are quenched from above to below the glass transition temperature, T_g, and that these effects are generally explained by changes in the free volume. Most experimental work has been done in a region rather close to T_g; much less attention has been paid to the behaviour at such low temperatures that the secondary relaxation modes[3] become active. A study of such low-temperature volume relaxation is reported in this paper.

EXPERIMENTAL

The experiments were done on two groups of materials. The first group (*Table 1*) were polymerized at TNO by Dr Heijboer; details of the preparation of these materials are given in ref. 4.

The other materials (*Table 2*) were obtained from commercial firms (between 1968 and 1971). Except for impact PS I, details have been given in Appendix B of ref. 2; the code numbers used in ref. 2 are given in the last column of *Table 2*. Most materials were obtained as sheets, compression moulded by the supplier; polystyrene (PS), polycarbonate (PC), poly(vinyl chloride) (PVC) III and poly(phenylene oxide) (PPO) were compression moulded at TNO, PVC I was obtained as an extruded sheet. The commercial materials, except for three, were annealed to release frozen-in stresses. The annealing temperature T_a and the density at 21°C after annealing are given in *Table 2*; see also ref. 2.

Volume relaxation was measured with a quartz (length) dilatometer. Full details have been given in Appendix A.2 of ref. 2 and will not be repeated here. Typically, the sample (rectangular rod of $3.5 \times 7 \times 190$ mm) was first heated to a temperature T_0 just above T_g. Heating and all further thermal treatments were executed in the dry nitrogen gas thermostat of the dilatometer. After the brief period above T_g (0.5 h), the sample is 'quenched' to the measuring temperature $T < T_g$. Quenching is achieved by switching the set temperature of the controller from T_0 to T. At final temperature T, we measured the isothermal changes in length for times t_e, elapsed at T, between 2048 s and several hours (maximum 1 day; actually, t_e is the time elapsed after switching the set temperature).

An example of the results is given in *Figure 1*. The changes in length, which are actually very small (<0.02%), are plotted vs. log t_e. From this and similar results for other polymers, it appears that after showing some curvature at short times ($t_e \lesssim 3000$ s), the curve of l vs. log t_e becomes almost straight, and the relaxation can be characterized by the slope, r, of the straight lines, where r is defined by:

$$-r = \frac{3}{l}\frac{\mathrm{d}l}{\mathrm{d}\log t_e} = \frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}\log t_e} \tag{1}$$

The initial curvature in *Figure 1* is caused by a delay in the approach of the sample towards thermal equilibrium, as could be verified by experiments on steel rods. In general, the time needed to approach thermal equilibrium closely enough was 2000–3000 s. In these experiments close attainment of a constant temperature is a very important factor, because the thermal expansivity of the sample is such that the length changes by 10–20 μm/°C, which is large compared to the isothermal length changes (cf. *Figure 1*).

The volume relaxation process can be characterized by plotting the 'rate' r, defined above, as a function of temperature. For styrene acrylonitrile (SAN) such a plot is given in the inset of *Figure 1*. It is seen that r falls steeply with decreasing temperature.

Tests with the length dilatometer are much simpler and much less laborious than those with a volume (mercury) dilatometer. Moreover, since mercury solidifies at -38.9°C, the temperature range in which the length dilatometer can be applied is much wider. The method appeared to be very reproducible and its results agree satisfactorily with those of volume dilatometry (*Figures 2* and *3*).

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Table 1 Materials prepared at TNO

Material	Abbreviation	Density, 20°C (g cm^{-3})
Poly(methyl methacrylate)	MMA	1.186
Poly(ethyl methacrylate)	EtMA	1.121
Poly(n-propyl methacrylate)	n-PrMA	–
Poly(n-butyl methacrylate)	n-BuMA	1.056
Poly(tert-butyl methacrylate)	t-BuMA	1.021
Poly(cyclohexyl methacrylate)	CHMA	1.098
60/40 random copolymer of cyclohexyl methacrylate and methyl methacrylate	60/40 CHMA-MMA	1.130
Poly(cyclo-octyl methacrylate)	COcMA	1.097

Table 2 Commercial polymers studied

Material	Trade name or supplier	T_a (°C)	ρ, 21°C (g cm^{-3})	Code no. in ref. 2
PS	Styron 666	100	1.048	19
Impact PS I	Afcolène 492	100	1.041	–
Impact PS II	Vestyron 617	100	1.040	2
SAN	Kostil AF 1542/5	110	1.073	9
Rigid PVC I	Vink B.V. Holland	–	–	20
Rigid PVC II	Solvay	85	1.389	3
Rigid PVC III	Solvic 229	–	–	–
PVC-VAc	CV-AV MA 6035	70	1.357	8
Post-chl. PVC	Montedison	120	1.561	7
PC	Macrolon 3000 W	155	–	–
Polysulphone	P1700	195	1.239	14
Amorphous PET	Arnite A-200	–	1.143	15
PPO	Akzo	210	1.068	27

RESULTS

The experimental results are presented in *Figures 4–8*. *Figures 4–5* pertain to the TNO polymers of *Table 1*, *Figures 6–8* to the commercial polymers listed in *Table 2*. Each figure deals with a group of four to five polymers and consists of two subfigures: the upper subfigure shows volume relaxation rate *r* vs. temperature, the lower subfigure mechanical damping tan δ for relaxation in shear at a frequency ν of 10^{-3} Hz (*Figures 4* and *5*) or 10^{-4} Hz (*Figures 6–8*). Damping tan δ was obtained from creep data using the approximation formula[6]:

$$\tan\delta(\omega) \simeq \frac{\pi}{2} \mathrm{d} \ln J(t)/\mathrm{d} \ln t \qquad t = 1/\omega \qquad (2)$$

where

$\omega = 2\pi\nu =$ angular frequency

$J(t) =$ creep compliance at time t

For the materials listed in *Table 1*, the creep data were mainly taken from the work described in refs. 4 and 9, for the materials in *Table 2* from the work reported in ref. 2.

The volume relaxation and mechanical data are shown together in order to see whether the tan δ peaks have their counterparts in the plots of *r* vs. *T*. In such a comparison, the time scales should be similar, since relaxation peaks shift to higher temperatures with increasing frequency (decreasing time). Since the volume relaxation data refer to times of 2000–10000 s, we took tan δ at low frequencies. For the methacrylates, data below 10^{-3} Hz $[t = (2\pi\nu)^{-1} = 160\,\mathrm{s}]$ were not available; for the

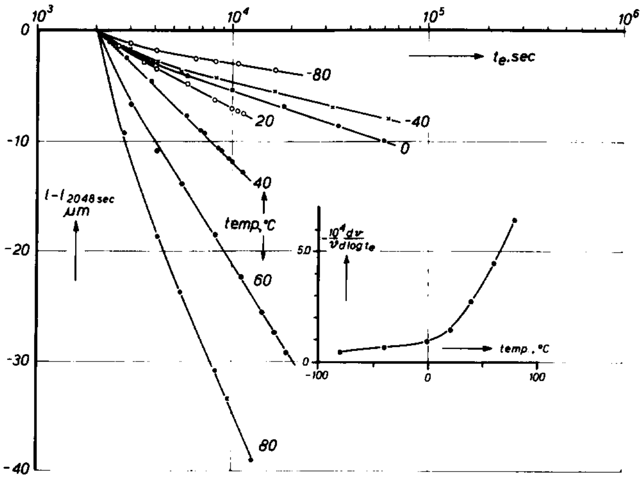

Figure 1 Volume (length) relaxation of SAN quenched from 105°C to various temperatures; l_{2048} (about 190 mm) denotes the length at $t_e = 2048$ s. [Reproduced from Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978, by permission of Elsevier Science Publishers©]

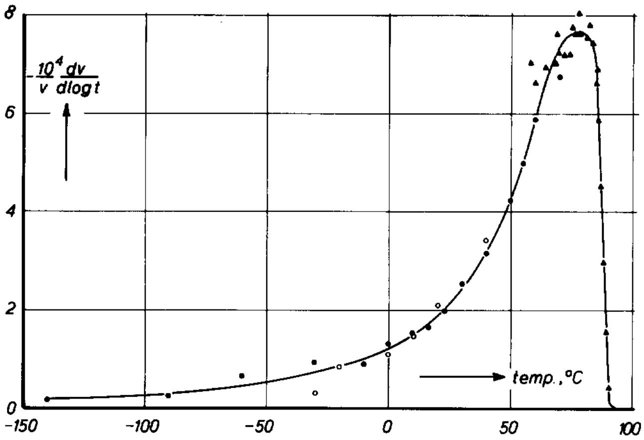

Figure 2 Volume relaxation rate vs. temperature for PS; maximum t_e about 1 day. Comparison of various measuring techniques: ●, length dilatometry; ▲, volume dilatometry in oil baths; ○, volume dilatometry, but with dilatometers quenched in a gas thermostat similar to the one described in Appendix A11 of ref. 2. [Reproduced from Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978, by permission of Elsevier Science Publishers©]

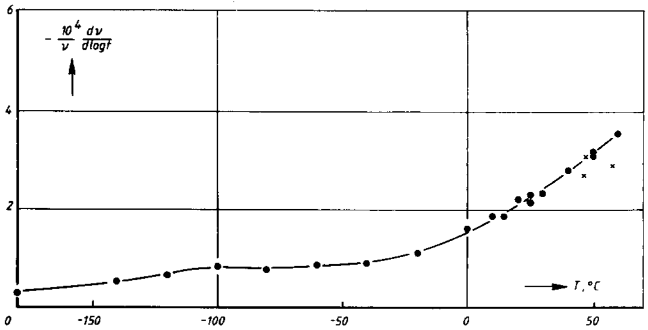

Figure 3 As *Figure 2*, but for rigid PVC. ●, length dilatometry, rigid PVC I, $T_0 = 80$°C; ×, volume (mercury) dilatometry, rigid PVC III

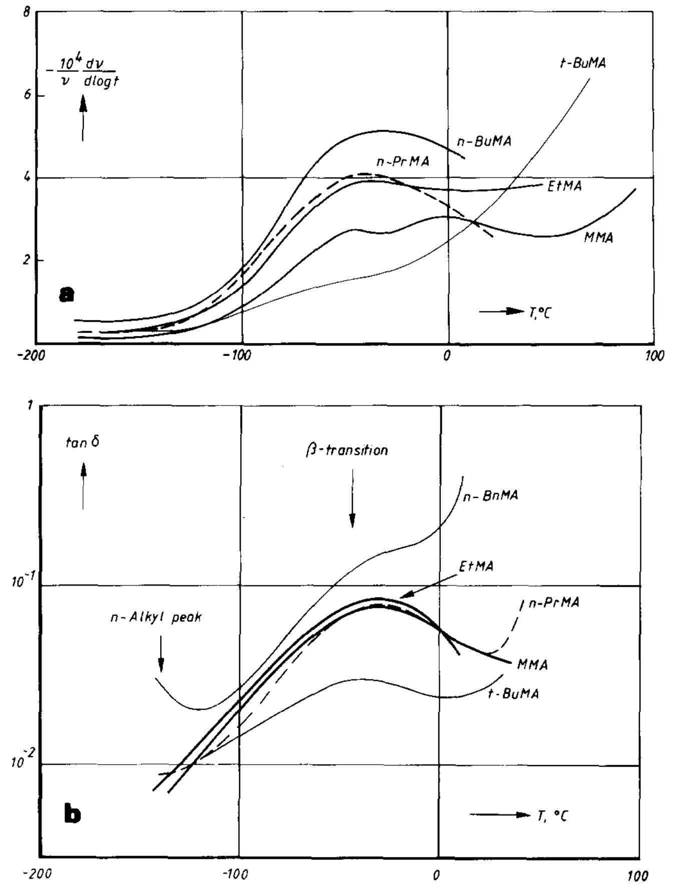

Figure 4 Volume relaxation rate r for times t_e, elapsed after quenching from above T_g, of 2000–10000 s (upper) and mechanical damping tan δ at a frequency ν of 10^{-3} Hz $[t=(2\pi\nu)^{-1}=159$ s$]$ for a group of polymers in *Table 1*. For the damping measurements the thermal history of the sample was not known exactly; the samples were taken from the stock (long storage at 20°C in a desiccator over P_2O_5) and were tested, starting at the lowest temperature. The uncertainty about the thermal history is not important; thermal history hardly affects the secondary tan δ peaks[5]

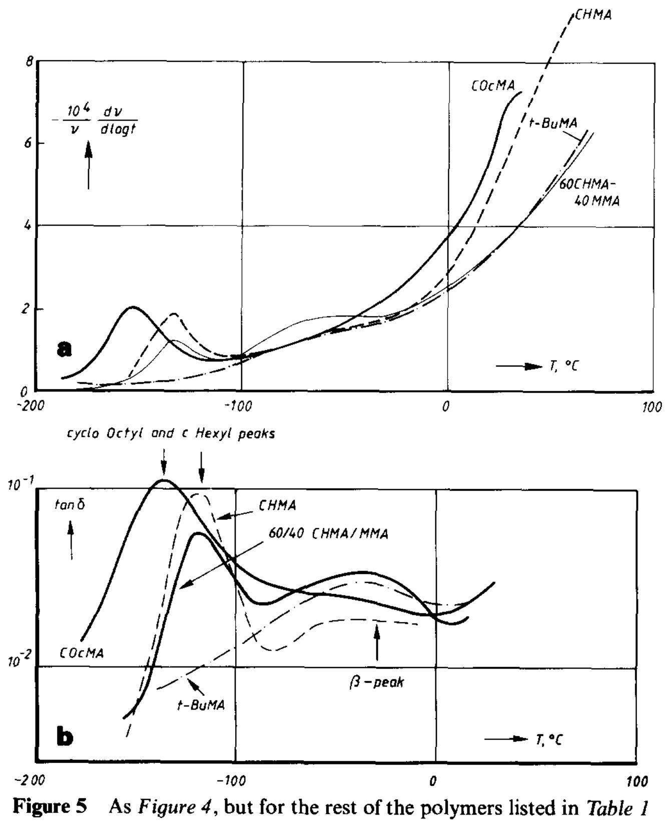

Figure 5 As *Figure 4*, but for the rest of the polymers listed in *Table 1*

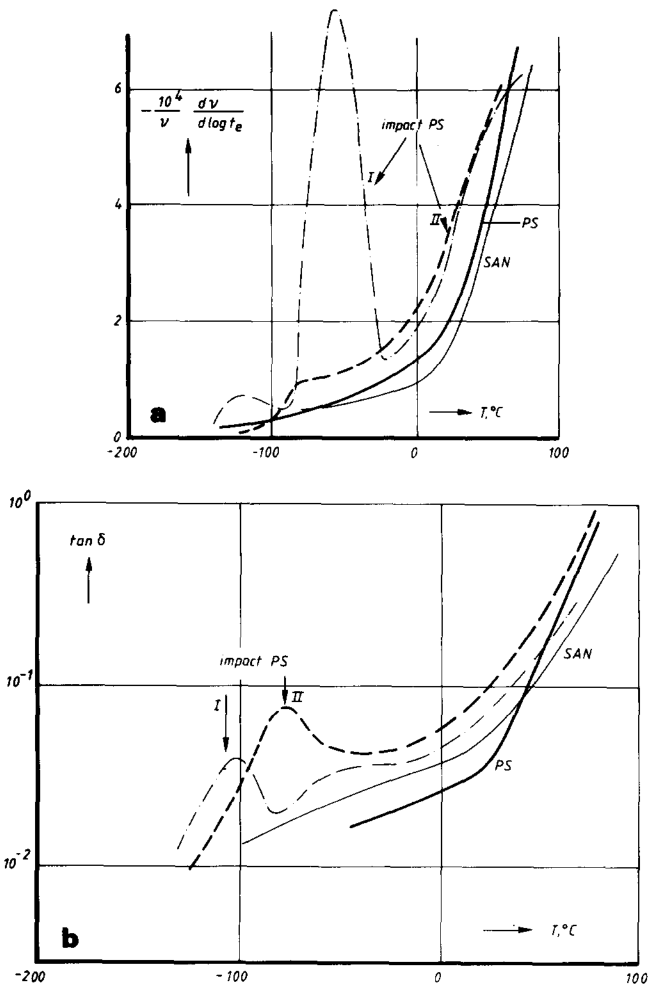

Figure 6 As *Figure 4*, but for the PS, impact PS I and II and SAN listed in *Table 2*. The tan δ data are now at 10^{-4} Hz; they refer to an elapsed time, t_e of 3 h for PS and SAN and 2.2 h for the impact polystyrenes after quenches from above T_g to the measuring temperature

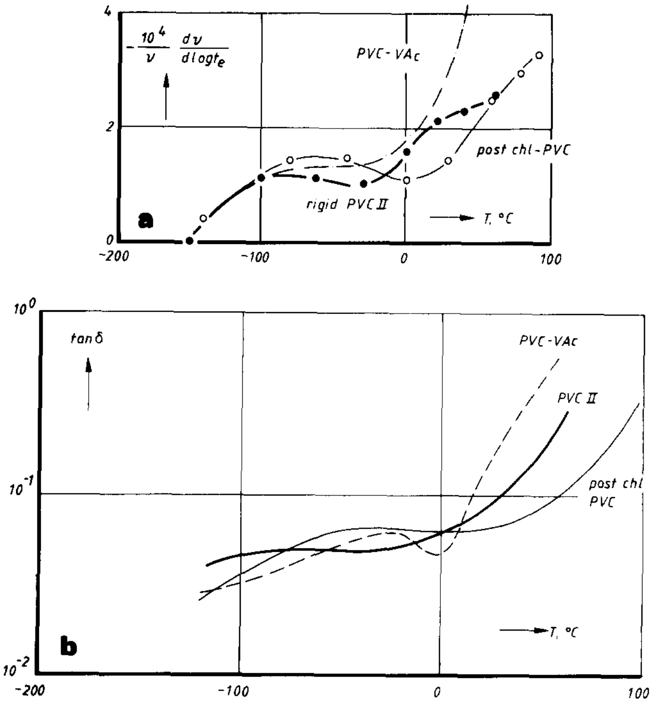

Figure 7 As *Figure 6*, but for three types of PVC. The tan δ data refer to t_e values of 3 h for PVC-VAc and post-chl. PVC and 2.2 h for rigid PVC II

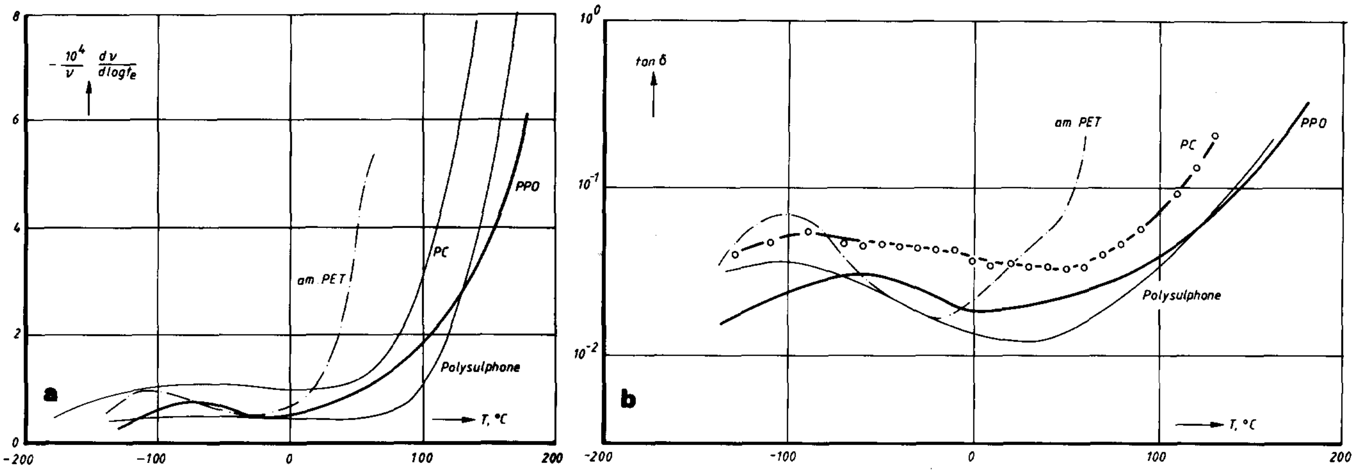

Figure 8 As *Figure 6* but for PC ($t_e = 5.3$ h), polysulphone, amorphous PET and PPO ($t_e = 2.2$ h). These t_e values refer to the tan δ data

commercial polymers, the time corresponding to the frequency of 10^{-4} Hz $[t = (2\pi\nu)^{-1} = 1600\,\mathrm{s}]$ comes closer to that of the volume relaxation tests.

It should be realized that the time scales in the two subfigures have a different character. For volume relaxation, the driving force is the temperature jump, and so the characteristic time for the relaxation is the time t_e elapsed after the jump. For mechanical creep, the driving force is the applied mechanical stress and therefore the characteristic time is the creep time t elapsed after application of the stress.

To avoid overcrowded figures, data points were generally omitted. To get an impression of the experimental accuracy, data points for r vs. T are given in *Figure 7a* for post-chl. PVC and rigid PVC (compare also *Figures 1–3*); for tan δ points are given in *Figure 8b* (PC). For the other materials the scatter around the curves was similar.

DISCUSSION

Volume relaxation peaks at secondary transitions

Inspection of *Figures 4–8* immediately reveals that the secondary tan δ peaks have their counterparts in volume relaxation. We now consider the figures one by one.

Methacrylate polymers, Figure 4. Figure 4b shows a broad loss peak around -30°C and this tan δ peak has its counterpart in volume relaxation (*Figure 4a*). We here deal with the well known[3,7,8] secondary relaxation in methacrylates which is due to the rotation of the carbonyl side group (–COOR) around the C–C link which connects the side group with the main chain (R stands for methyl, ethyl, n-propyl, etc.). At 1 Hz the peak is usually found around 25°C[7,8] and the activation energy is known to be 18 kcal mol^{-1} (ref. 9). So, at 10^{-3} Hz the peak is expected at -30°C, just as found in *Figure 4b*. For volume relaxation, the times (2000–10000 s) are 13–60 times longer than the 160 s corresponding to the frequency of 10^{-3} Hz. In view of this, it is not surprising that volume relaxation rate r peaks at -40 to -50°C (*Figure 4a*). It is further well known[7,8] that the secondary peak of methacrylates is strongly suppressed when R is a tert-butyl group (steric hindrance). This effect is clearly observed both in *Figure 4a* and *4b*.

Another well known loss peak in methacrylate polymers is the n-alkyl peak, found when R is an n-alkyl side chain longer than two units[10]. For n-PrMA and n-BuMA this peak is usually found at about -180°C for 1 Hz[11]. From the activation energy of 5.4 kcal mol^{-1} (ref. 11), we calculate a peak temperature of -198°C at 10^{-3} Hz. This peak is not observed in *Figure 4* because the measuring temperatures were not sufficiently low. Only for n-BuMA in *Figure 4b* is there a high-temperature tail of the peak.

Methacrylate polymers containing saturated rings, Figure 5. Figure 5b shows the well known peaks due to the motions of the cyclohexyl and cyclooctyl side groups[4]. These loss peaks have their counterparts in volume relaxation (*Figure 5a*); due to the difference in frequency (see above) the peaks in r lay at a somewhat lower temperature than those in tan δ. It is also known[4] that cyclohexyl and cyclooctyl side groups suppress the β-peak discussed in connection with *Figure 4*. This is clearly visible in *Figure 5a* (compare with *Figure 4a*) but similarly in *Figure 5b* (compare with *Figure 4b*). Interestingly, the β-peak reappears again in the 60/40 copolymer of cyclohexylmethacrylate (CHMA) and methylmethacrylate (MMA), both in tan δ (*Figure 5b*) and in r (*Figure 5a*).

Polystyrenes and SAN, Figure 6. For straight PS and SAN, no sign of a secondary maximum is observed both in tan δ and volume relaxation rate r (*Figures 6a* and *6b*). It is known that PS has a weak secondary loss peak located around 40°C at 1 Hz[5]. This peak is best observed in slowly cooled (annealed) samples; it is generally obscured by the low-temperature tail of the glass transition in quenched samples[5]. This explains the absence of the secondary peaks in *Figure 6*. The impact polystyrenes show a tan δ peak at -100°C (PS I) and -80°C (PS II); these peaks are due to the glass transition of the rubber component of these impact modified materials. For PS I, the peak is also seen in volume relaxation rate r (around -115°C); for PS II, the plot of r vs. T only shows a shoulder at -80°C. The intense peak in r vs. T for PS I at about -60°C is not observed in tan δ; it has been shown[5] that this peak is an artefact due to crystallization of the rubber components of PS I.

Rigid PVC, PVC-VAc and post-chl. PVC, Figure 7. As is well known[3,5,12], rigid PVC possesses a secondary transition located at about -40°C for 1 Hz. This peak is observed in *Figure 7a* and, although weak, in *Figure 7b*. The temperature location is as expected: from the activation energy of about 15 kcal mol^{-1} (ref. 9), we calculate a shift from -40 to -95°C when the frequency drops from 1 to 10^{-4} Hz. It is also known[5,12] that for post-chl. PVC, the peak is broader and shifted to a higher temperature; both effects are seen in *Figures 7a* and *7b*. for PVC-VAc, the situation is less conclusive; T_g has decreased considerably and the secondary loss peak is overlapped by the low-temperature tail of the glass transition (*Figure 7a*).

PC, polysulphone, amorphous PET and PPO, Figure 8. For amorphous poly(ethylene terephthalate) (PET) and PPO, the secondary peaks[8] in tan δ are well pronounced and have their counterparts in volume relaxation rate r. For PC and polysulphone, the situation is less conclusive: the tan δ peaks are very broad particularly for PC, and the plots of r vs. T only show a broad weak peak (PC) or a shoulder (polysulphone).

Intensity of the secondary volume relaxation peaks

For the mechanical damping in shear, the secondary loss peaks have a height tan δ_{max} of 0.01–0.1 (cf. *Figures 4–8*). The peak at the glass–rubber transition has a height of about 1 or more[6,8]. So, for tan δ in shear, the height of secondary peaks is 1–2 orders of magnitude lower than that of the T_g peak. Such a big difference certainly does not exist for volume relaxation rate r. As shown by *Figures 4–8*, the secondary peaks in r have a height of $1–4 \times 10^{-4}$. *Figure 1* shows that for PS, the maximum value for r at T_g is about 8×10^{-4}, and this is a typical value for r at T_g (see ref. 13). So, for volume relaxation, the secondary peaks are much higher compared to the T_g peak than for relaxation in shear. This is not surprising: volume relaxation is a bulk phenomenon and also for the bulk modulus K the changes at secondary transitions and at T_g are much closer to one another than for shear or uniaxial extension. In fact, at secondary transitions the relative changes in shear modulus G and bulk modulus K are about the same. At T_g, however, G drops by 2–3 orders of magnitude, whilst the changes in K are limited to a factor of 2–4 (ref. 14).

Long-term volume relaxation

The data of *Figures 4–8* give volume relaxation rate r for times between 2000 and 10000 s. These data cannot be used to predict the volume relaxation over much longer periods of time. Strong (experimental) indications exist[13] that r will slowly increase with time, particularly for temperatures not too far below T_g.

Thermal expansion behaviour

The presence of secondary peaks in r suggests that the thermal expansivity α will change at the secondary transition temperature T_β. Above T_β, the volume relaxation rate connected to the secondary process is high and the process can follow the changes in temperature. Below T_β, this is no longer the case and α will be smaller than at temperatures above T_β.

Thermal expansivity α was measured for most of the polymers of *Tables 1* and *2*. We used the same length dilatometer as described above. The samples were cooled in steps of 10°C (sometimes 20°C) and α was simply calculated from:

$$\alpha = \frac{1}{l}\frac{\Delta l}{\Delta T} \tag{3}$$

where l = sample length; ΔT = temperature step; Δl = change in length per step ΔT.

The results are shown in *Figures 9–11*. It is obvious that α shows clear transitions for the cyclohexyl and cyclooctyl substituted methacrylates (*Figure 10*); for the other polymers the transitions are more gradual and obscured by the general (slow) increase of α with temperature. So, in this respect we disagree with Simha and coworkers[15]: the secondary transitions are much better revealed by tan δ or volume relaxation rate r than by α, and measurements of α are not very suitable for detecting secondary transitions.

Theoretical implications

To explain the secondary volume-relaxation peaks, we can follow two lines:

(a) *Explanation from the kinetics and temperature dependence of the secondary relaxation process itself* (cf. ref. 23). Secondary relaxations are usually described with the two-potential well model[3,4]. The molecule has two stable states (I and II), separated by a high energy barrier (*Figure 12*). The potential energy curve is changed by applying an external stress σ. Therefore, upon application of σ, one state becomes favoured with respect to the other; a number of molecules jump from the unfavoured to the favoured state and macroscopically, we observe a relaxation effect.

To have relaxation in shear, the motion from state I to II must have a shearing effect on the environment of the molecule; to have relaxation in bulk (hydrostatic compression) the motion from I to II must be accompanied by a volume effect[17]. Experiment

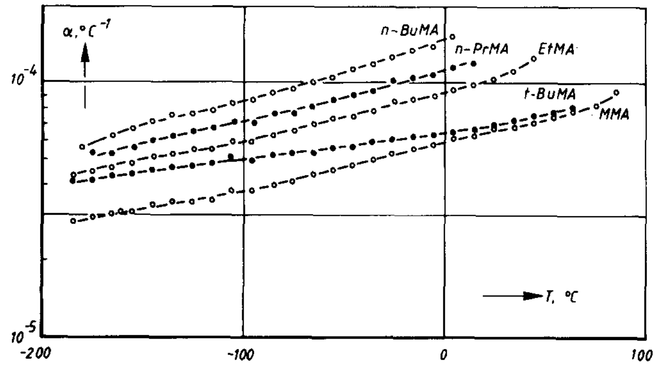

Figure 9 Linear thermal expansivity α vs. temperature for the same polymers as in *Figure 4* (notice that the α-scale is logarithmic)

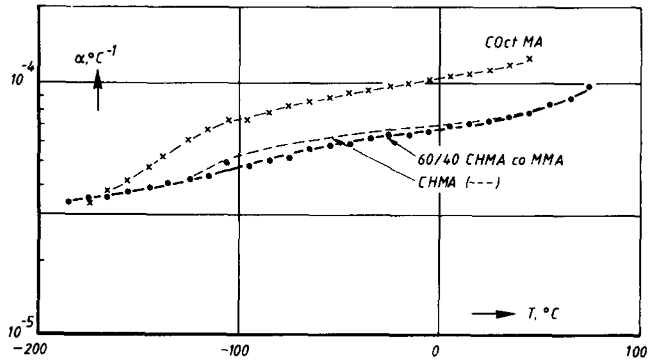

Figure 10 As *Figure 9*, but for the cyclohexyl and cyclooctyl methacrylates of *Figure 5*. [CHMA data are due to Dr J. de Jong of TPD-TNO (1955)]

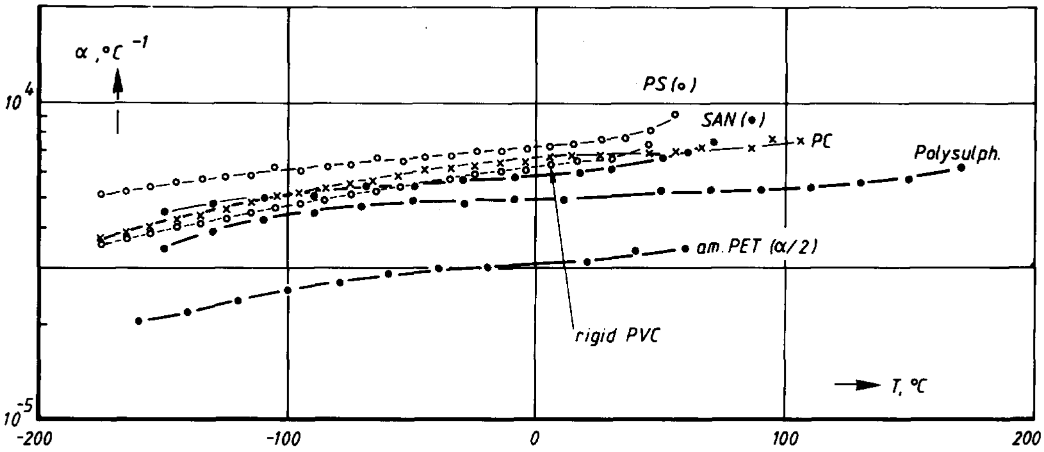

Figure 11 As *Figure 9*, but now for some commercial polymers. The rigid PVC sample differs from those of *Table 2*: it was taken from a 200 mm pipe produced by Wavin before 1969. The other materials are described in *Table 2*

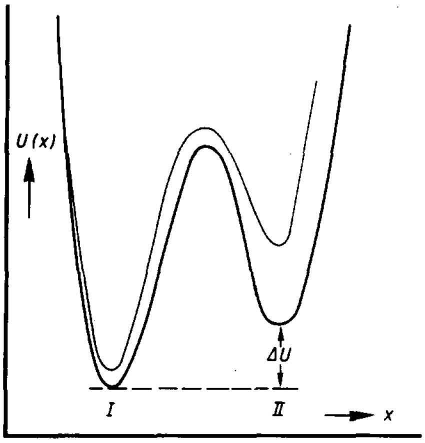

Figure 12 Illustration of the two-potential well model; potential energy U is given for zero stress (——) and for stress $\sigma \neq 0$ (——)

shows[18-20] that for amorphous polymers, secondary peaks are usually found both in shear and in bulk*. Consequently, we can safely assume that the molecular motions responsible for secondary relaxation usually have a volume effect.

Such a volume effect, however, is not sufficient to have volume relaxation after temperature jumps. When such a jump is the driving force for relaxation, there will only be an effect if the two states (I and II) have different energies so that on cooling more and more molecules flow into the deepest well. So, to have secondary volume-relaxation peaks, ΔU (see *Figure 12*) must be non-zero. Moreover, to have volume contraction the low-energy well must have the lowest volume.

We now encounter the problem that volume relaxation peaks are observed for polymers (e.g. CHMA, *Figure 5*) for which we know that ΔU is zero or small[4]. Furthermore, in a recent theory[17], the present author showed that in the glassy state secondary relaxations must be characterized by zero ΔU values to understand the temperature dependence of the relaxation strength. The theory takes into account the mechanical coupling of the relaxing molecular group with its environment. Due to this coupling, the two energy levels split in six. In fact, there are three types of molecules. For two types, the energy difference between states I and II is very large (5–10 kcal mol^{-1}) and these molecules hardly contribute to the relaxation process (the molecule is blocked in the lowest state (I or II)). For the third type, the energy difference is zero and the molecules of this type almost exclusively contribute to mechanical or dielectric relaxation. Since the energy difference is zero, these molecules will not contribute to the volume relaxation process as produced by temperature jumps. Consequently, the secondary volume relaxation peaks cannot be explained in this way.

(b) *Volume relaxation as a bulk creep process produced by changes in internal pressure.* Thermal expansion and volume relaxation can also be explained from the concept of an internal pressure P_i that changes (increases) with temperature and that produces volume changes in exactly the same way as an external (negative) hydrostatic pressure (cf. refs. 21 and 22). To illustrate this, consider a material without relaxation and characterized by a bulk compliance $B = 1/K$ (K = bulk modulus). The cubical, thermal expansion coefficient α_c is then given by:

$$\alpha_c(T) = B(T)\mathrm{d}P_i/\mathrm{d}T \tag{4}$$

in which α_c and $B(T)$ are assumed to vary with temperature but not with time.

Suppose now that we deal with a real material with a bulk creep compliance $B_T(t)$. The material is ideally quenched (infinite cooling rates) from temperature T_0 to T. If we write ΔP_i for the change in internal pressure $P_i(T_0) - P_i(T)$, we find:

$$-[v_T(t) - v_{T_0}]/v_{T_0} = \Delta P_i B_T(t) \tag{5}$$

where v_{T_0} stands for the original equilibrium volume at T_0. Differentiation with respect to $\log t$ yields:

$$-\frac{1}{v_{T_0}}\frac{\mathrm{d}v_T}{\mathrm{d}\log t} = \Delta P_i \frac{\mathrm{d}B_T(t)}{\mathrm{d}\log t} \tag{6}$$

In glassy polymers, the volume changes due to changes in temperature will be limited to a few per cent. So, we can replace v_{T_0} in equation (6) by the momentary volume v at

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* In papers[19,20] only complex modulus G^* and complex Poisson ratio μ^* are given. Using the formula $K^* = \frac{2}{3}G^*(1+\mu^*)/(1-2\mu^*)$ we can calculate the complex bulk modulus K^* from the data in refs. 19 and 20. We then find loss peaks in $\tan \delta_K = K''/K'$.

final temperature T. Using the definition of equation (1), we thus find:

$$r = -\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}\log t} = \Delta P_i \frac{\mathrm{d}B_T(t)}{\mathrm{d}\log t} \qquad (7)$$

where t is the time elapsed at final temperature T [t_e in equation (1)].

For the logarithmic creep rate $\mathrm{d}B_T(t)/\mathrm{d}\log t$, we have a formula similar to equation (2):

$$\tan\delta_K(\omega) \simeq \frac{\pi}{2}\frac{\mathrm{d}\ln B_T(t)}{\mathrm{d}\ln t} = \frac{\pi}{2}\frac{1}{B_T(t)}\frac{\mathrm{d}B}{\mathrm{d}\ln t}; \quad \omega = 1/t \qquad (8)$$

So equation (7) can be written as:

$$r = \frac{4.606}{\pi}\Delta P_i B_T(t)\tan\delta_K; \quad \omega = 1/t \qquad (9)$$

in which the factor $4.606 = 2 \times 2.303$ originates from the change from $\log t$ to $\ln t$.

This equation immediately explains the secondary volume relaxation peaks. In glassy polymers, $\tan\delta$ peaks in shear (***Figures 4b–8b***) will be accompanied by $\tan\delta$ peaks in bulk compression. So, $\tan\delta_K$ in equation (9) and therefore also volume relaxation rate, r, will peak at about the same temperatures as $\tan\delta_G$ in shear.

Let us now show that equation (9) predicts the right order of magnitude of the volume relaxation effects. First, we should realize that practical quenches are not ideal; in fact, the sample is rapidly cooled (in 10–20 min) from T_0 to T. During cooling the secondary processes will be very quick (short relaxation times) as long as the temperature is above T_β (secondary transition temperature, now defined as the temperature of the $\tan\delta_G$ peak at 1 Hz)†. So, these secondary processes can follow the changes in P_i produced by cooling as long as the temperature exceeds T_β. Consequently, the secondary processes are in 'equilibrium' with P_i for $T > T_\beta$ which means that for the behaviour at final temperature T, it is the change in P_i between T_β and T that counts. In view of this, we have to write

$$\Delta P_i \sim (T_\beta - T)\partial P_i/\partial T \qquad (10)$$

in equation (9).

We further have [cf. equation (4) and note that the relaxation effects are only weak ($\tan\delta \ll 1$)]:

$$\frac{\partial P_i}{\partial T}B_T(t) \sim \alpha_c(T) \qquad (11)$$

Combining equations (9)–(11) we find:

$$r \sim \frac{4.606}{\pi}\alpha_c(T)(T_\beta - T)\tan\delta_G\,(\omega = 1/t) \qquad (12)$$

in which we used the assumption $\tan\delta_G = \tan\delta_K$ (actually, $\tan\delta_K$ is considerably smaller than $\tan\delta_G$).

As an example, consider the CHMA polymer of *Figure 5*. We have $\tan\delta_{G\max} \sim 0.1$ and $\alpha_c = 3\alpha \sim 1.2 \times 10^{-4}/°\mathrm{C}$ (***Figure 10***). Taking $T_\beta - T = 10$–$20°\mathrm{C}$, we find r values of 1.8–3.6×10^{-4} which is of the correct order of magnitude (see *Figure 5a*).

It should finally be realized that the explanations (a) and (b) are fundamentally different. In (a) we tried to explain the volume relaxation from the effect of temperature on the population over the two wells; we only considered the relaxing group itself and therefore concluded that volume relaxation effects will be absent if $\Delta U = 0$. In (b) we actually assume that the (normal) thermal contraction of the environment of the relaxing group is the driving force for volume relaxation. This contraction (due to cooling) produces a hydrostatic pressure upon the relaxing group and, provided that the two positions of the group have unequal volumes, this pressure will cause a volume relaxation effect, even when $\Delta U = 0$ (i.e. when ΔU of the isolated relaxing group equals zero).

CONCLUSIONS

In glassy polymers quenched from above to below T_g, the isothermal volume relaxation rate r shows similar peaks as the mechanical damping $\tan\delta$. The peaks are much better resolved than the corresponding 'steps' in thermal expansivity α.

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† This choice is somewhat arbitrary. The characteristic frequency at T_β, here taken as 1 Hz, depends on the reciprocal cooling rate.