The mechanical behaviour and physical ageing of semicrystalline polymers: 2.

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The model of an extended glass transition in semicrystalline polymers (see Part 1[1]) has been further evaluated. It is shown that the model can explain the effect of ageing on the dynamic mechanical properties and also the effect of the quenching temperature on volume relaxation. It is further shown that, for semicrystalline and amorphous polymers, the ageing after complicated thermal histories is strikingly similar. It is finally demonstrated that, above T_g, filled rubbers show the same (physical) ageing effects as semicrystalline polymers.

(**Keywords:** semicrystalline polymers; filled rubbers; extended glass transition; T_g distribution; physical ageing; dynamic mechanical properties; creep properties)

INTRODUCTION

In Part 1[1] of this series of papers, we discussed the model for semicrystalline polymers outlined in *Figure 1*. The main feature of this model is that the crystals disturb the amorphous phase and reduce segmental mobility. This reduction will be at its maximum in the immediate vicinity of the crystals, and only at large distances from the crystals will the properties of the amorphous phase become equal to those of the bulk amorphous material. This picture was derived from a similar and well-known model for filled rubbers[2-4], in which the carbon black particles restrict the mobility of parts of the rubbery phase.

The main consequence of this immobilization is that the glass transition will be extended towards the high-temperature side. Above the T_g of the bulk amorphous material, some parts of the amorphous phase are rubbery, other parts are glassy, and still other parts will just be passing through their glass transitions. Therefore, in a semicrystalline polymer, the amorphous phase will not have a single T_g, but a T_g-distribution. The lowest glass temperature, T_g^L, will be equal to the T_g of the bulk amorphous material (or higher, when the amorphous phase is totally disturbed (see *Figure 1*)), the highest, T_g^U, will depend on the interaction between the crystalline and amorphous phases. The loss peak ($\tan\delta$) at T_g will be broadened, i.e. extended towards the high-temperature side (*Figure 1*).

Concerning physical ageing[5], the model predicts the following: below T_g, the amorphous phase will be completely glassy and suffer from the same ageing effects as a purely amorphous polymer. Above T_g, part of the amorphous phase of the semicrystalline polymer is still glassy. Therefore, for such materials, ageing will persist at temperatures above T_g, a behaviour not shown by purely amorphous polymers.

The effect of physical ageing on creep properties has been described in detail in Part 1[1]. It was shown that the temperature range can be divided in four characteristic regions: Region 1 ($T < T_g^L$), Region 2 ($T \sim T_g^L$), Region 3 (($T_g^L < T < T_g^U$) and Region 4 ($T \geqslant T_g^U$). Details about the behaviour in these four regions is given in Part 1[1], where it is also shown that the model predictions agree with the experimental findings.

The present paper gives the results of some additional experiments, dealing with dynamic mechanical properties and complicated thermal histories. We will also consider the following point: the model of an extended glass transition in semicrystalline polymers has been borrowed from the rubber literature. Therefore, if our explanation for the ageing effects in semicrystalline polymers above their T_g has some ground, the same ageing effects *must* be found in carbon black-filled rubbers and above their T_g, the behaviour of these materials *must* be of type 3 (see ref. 1) and as will be shown this is indeed the case.

The spirit of the discussion is as in Part 1; where we simply start from the assumptions that the crystalline phase acts as an inert filler and that the amorphous phase has a T_g-distribution. We then investigate to what extent these assumptions can explain the behaviour of the material. We do not at all deny that there may be (secondary) crystallization effects; we simply ignore such effects and look how we can arrive at an explanation based on phenomena occurring only in the amorphous phase.

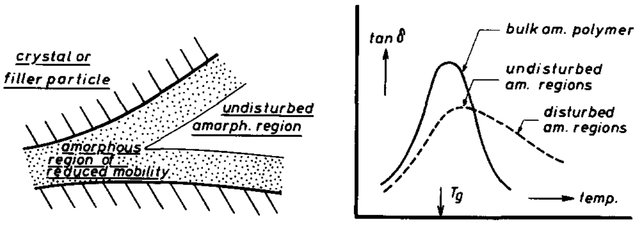

Figure 1 Extended glass transition in semicrystalline polymers and filled rubbers. [Reproduced from Struik, L. C. E., 'Physical Aging of Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978, by permission of Elsevier Science Publishers ©]

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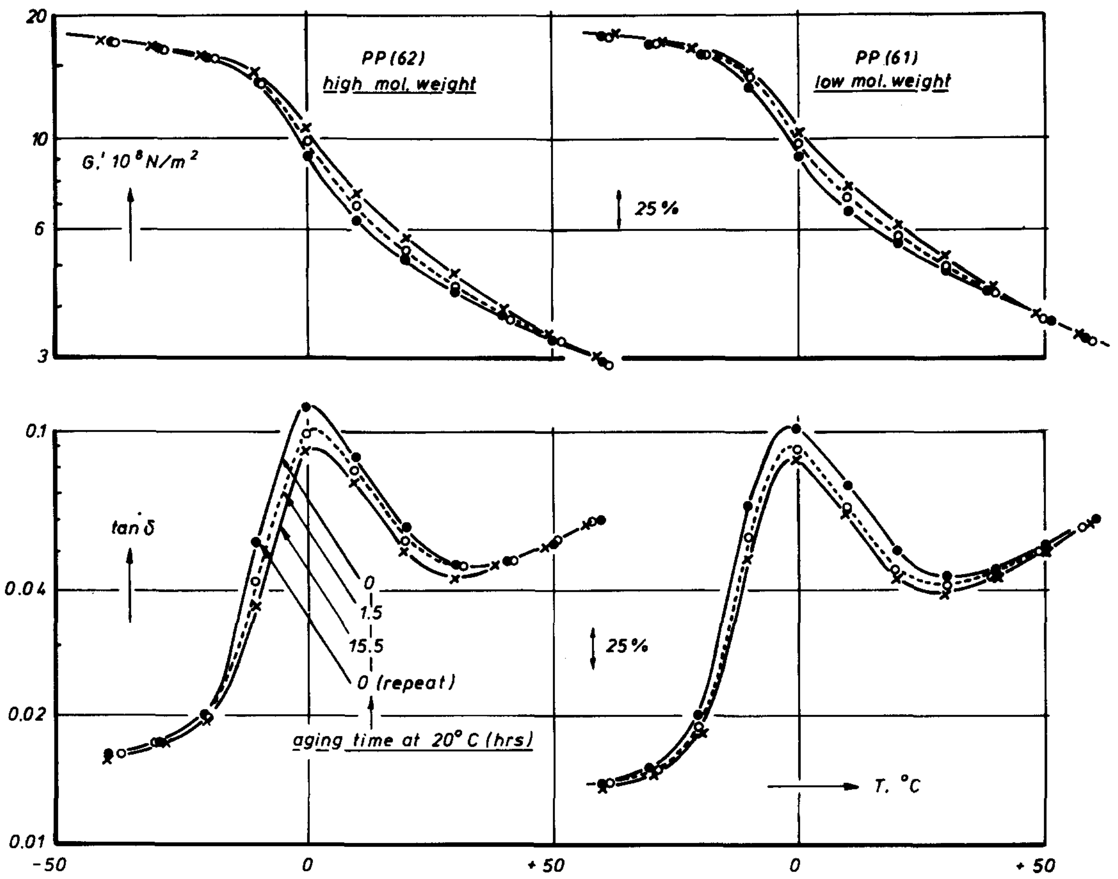

Figure 2 Effect of ageing at 20°C on the 1 Hz modulus and damping of PP. After annealing at 130°C, the sample was subjected to the following successive tests: test 1 (———) 120↓20°C (0 h), data points not shown; test 2 (– –○– –) 120↓20°C (1.5 h); test 3 (——×——) 120↓20°C (15 h); test 4 (●) 120↓20°C (0 h), repeat of test 1. After each ageing history, the sample was cooled to -120°C and then measured during during heating in steps of 10°C which lasted about 25 min. No ageing effects were found for $T < -50$°C; the low-temperature data were therefore omitted

Details of experimental techniques and materials are not given in this paper; see Part 1[1].

EFFECT OF AGEING ON THE DYNAMIC MECHANICAL PROPERTIES

Modulus and damping at 1 Hz

Suppose that a semicrystalline polymer is quenched from a high temperature T_0, and aged during a time t_1 at a temperature T_1 between T_g^L and T_g^U. During this ageing, the amount of material that is glassy at T_1 increases. Therefore, the fraction of the amorphous phase that has its glass transition below T_1 decreases, which will manifest itself in, e.g. plots of modulus and damping vs. temperature measured after ageing at T_1. Below T_1, the damping will decrease and the modulus increase with increasing ageing time t_1, and only at temperatures considerably above T_1 will the ageing that occurred at T_1 be erased.

Experimental results illustrating this behaviour are summarized in *Figures 2–7*. *Figure 2* concerns high- and low-molecular weight polypropylene. Ageing at 20°C for 15 h reduces the tan δ peak at 0°C by about 30%, and increases the modulus by at most 18%. The ageing effects are completely erased by a short heating period to 120°C (see test 4), and furthermore the effects of room temperature ageing disappear for $T > 50$°C.

Figure 2 shows that the effect of molecular weight is small. For the low-molecular weight material, the T_g and the height of the tan δ peak are slightly lower. The same was found from the creep data (not shown).

Much larger effects than those seen in *Figure 2* are obtained when the ageing time is increased to 6000 h. Some data, presented earlier[6], are given in *Figures 3* and *4*. The material was polypropylene PP (43) which has a similar molecular weight to the PP (61) shown in *Figure 6* (see Table 1 in ref. 1).

The results for PET, nylon-6 and nylon-12 are given in *Figures 5* and *6*. Their behaviour resembles that of PP, but the effects are smaller. This might be due to the fact that in the nylons and in PET, the lower glass transition is more pronounced and better separated from the transition of the immobilized amorphous regions; the same was suggested by the creep data[1].

Figure 7 gives some results for HDPE. Considerable changes in G' and tan δ are observed after ageing at -50°C and 0°C, and as for PP, the effects are repeatable (compare tests 1 and 6) and the changes disappear at temperatures over the range 20°C–40°C above the ageing temperature T_1. In agreement with expectations, the effects are only seen when T_1 lies near or somewhat above T_g^L (~ -40°C, see ref. 1); no effects are observed after ageing at -100°C or $+50$°C.

Damping at very low frequencies (1.6×10^{-4} Hz)

Below T_g^L (Region 1), the creep curves obey the same formula as those of amorphous polymers below their T_g

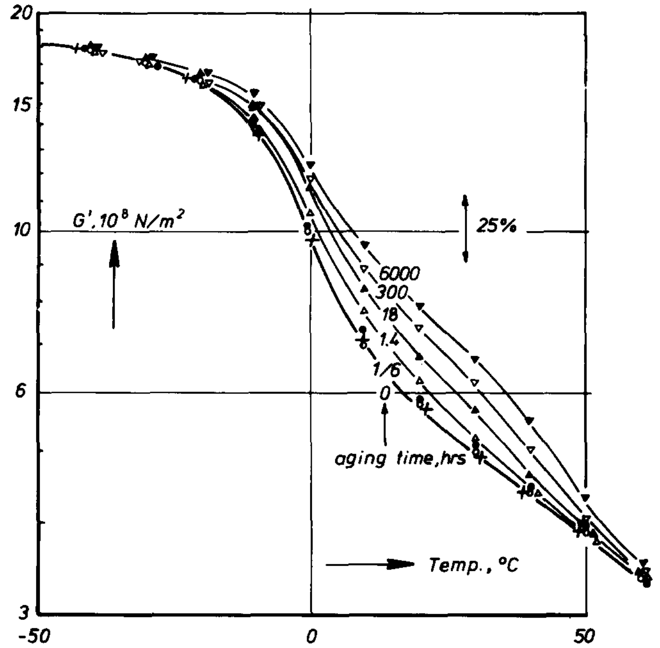

Figure 3 Dynamic shear modulus G' at 1 Hz for PP (43), measured after the following ageing histories: (○ ● △ ▲ ▽ ▼): 120↓23°C (t_e in hours) with t_e values of, respectively, 0, 1/6, 1.4, 18, 300 and 6000 h; (×): 120↓23 (1000 h)↑120↓23°C (18 h); (+): 120↓23 (6000 h)↑120↓23°C (0 h). [Reproduced from Struik, L. C. E. *Plastics and Rubber Processing and Applications* 1982, **2**, 41–50, by permission of Elsevier Science Publishers©]

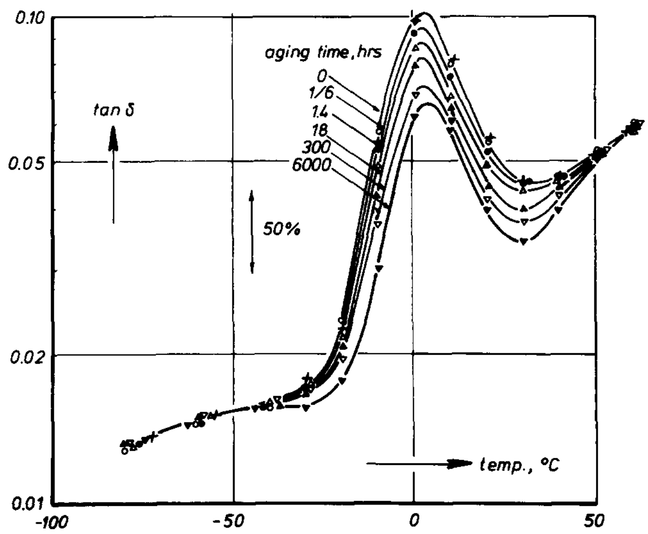

Figure 4 As *Figure 3* but now for the 1 Hz dynamic damping tan δ. [Reproduced from Struik, L. C. E. *Plastics and Rubber Processing and Applications* 1982, **2**, 41–50, by permission of Elsevier Science Publishers©]

(c.f. Figure 16 of ref. 1):

$$J(t)=J_0 e^{(t/t_0)^{\gamma}} \qquad \gamma\sim 1/3 \qquad (1)$$

The creep curves have a positive curvature and the slope $m=\mathrm{d}\ln J(t)/\mathrm{d}\ln t$ increases with t according to:

$$m=\mathrm{d}\ln J(t)/\mathrm{d}\ln t=\gamma(t/t_0)^{\gamma} \qquad (2)$$

During ageing, the creep curves will shift to longer times which means that t_0 in equation (1) increases with elapsed ageing time t_e. If the horizontal shift rate (see ref. 1) is denoted by μ, we have:

$$\mathrm{d}\ln t_0/\mathrm{d}\ln t_e=\mu \qquad (3)$$

The low-frequency damping tan δ at angular frequency ω can be expressed in terms of m:

$$\tan\delta(\omega)\simeq\frac{\pi}{2}m=\frac{\pi}{2}\gamma(t/t_0)^{\gamma}; \qquad \omega=1/t \qquad (4)$$

Therefore, an increase in t_e will cause an increase in t_0 (equation (3)) and a decrease in tan δ:

$$\mathrm{d}\ln\tan\delta/\mathrm{d}\ln t_e\simeq-\gamma\frac{\mathrm{d}\ln t_0}{\mathrm{d}\ln t_e}=-\gamma\mu\sim-1/3\mu \qquad (5)$$

Equation (5) shows that for a shift rate μ of unity, the damping decreases by a factor of 2 for each increase in ageing time t_e. These are the changes to be expected in Region 1. In Regions 2–4, the curvature of the ln J vs. ln t plot of semicrystalline polymers will be (much) less than in Region 1[1] and therefore the changes in tan δ will be (much) smaller. An example of such ageing effects in tan δ, for HDPE, is given in *Figure 8*. Around −60°C the effects

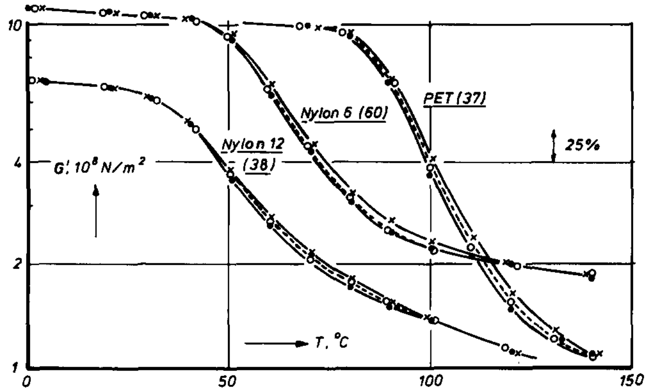

Figure 5 As for *Figure 2*, but now for nylon-12 (38), quenched from 150°C and aged at 80°C; nylon-6 (60), quenched from 150°C and aged at 90°C, and PET (37), quenched from 160°C and aged at 120°C. Symbols and curves as for *Figure 2*

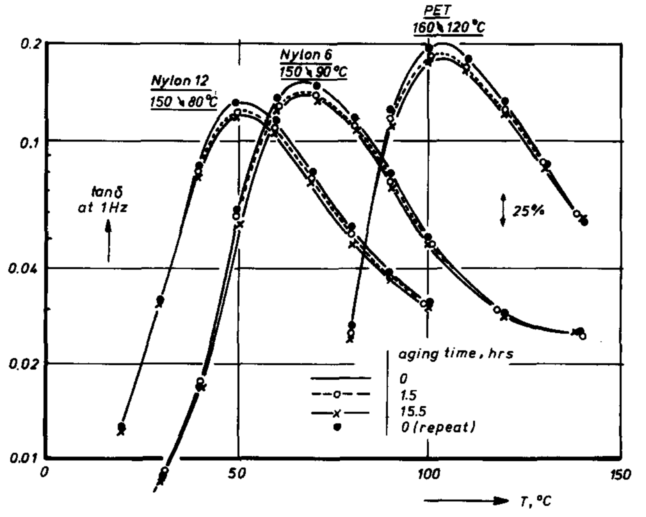

Figure 6 As for *Figure 5*, but now for the 1 Hz damping

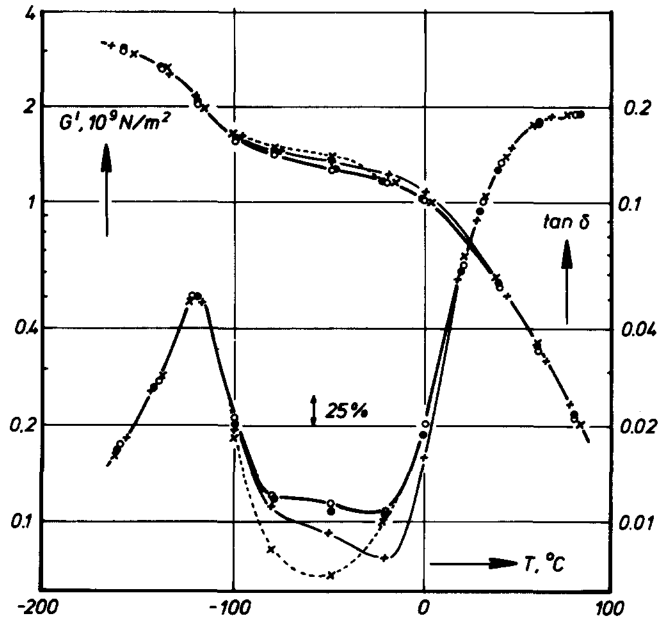

Figure 7 Modulus and damping at 1 Hz of HDPE (40). After annealing at 110°C, the sample was subjected to the following six successive tests: (○) test 1 100°C↓ − 160°C; test 2 100°C↓ − 100°C (16 h); (×) test 3 100°C↓ −50°C (16 h); (+) test 4 100°C↓0°C (16 h); test 5 100°C↓50°C (16 h); (●) test 6 repeat of test 1. After each ageing history, the sample was measured during heating from −160°C to 80°C in steps of 20°C each lasting 25 min. The results of tests 2 and 5 are not shown since they closely resemble those from tests 1 and 6

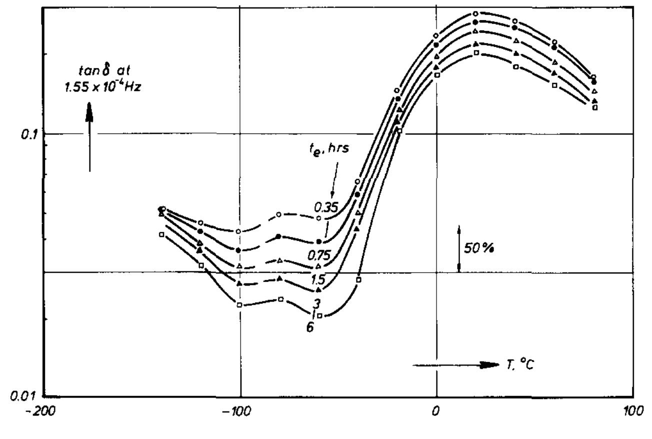

Figure 8 Damping tan δ at 1.55×10^{-4} Hz as calculated from the creep rate at 1024 s. The material, HDPE (40), was quenched from 100°C to various temperatures T; the different curves refer to different ageing times t_e elapsed at T

are of the expected order of magnitude, whereas at higher temperatures (in Regions 2 and 3, compare with Figure 19 of ref. 1) they indeed become smaller.

The impossibility of time–temperature superposition in Region 3

In Part 1 we showed that in Region 3, an increase in temperature will scarcely change the position of the creep curve on the time scale; the main effect will be a shift in an upward direction and a change in shape (see Figure 9 of ref. 1). Since dynamic properties are intimately related to creep properties (see equations (4) and (5) of ref. 1), this result can be used to understand the effect of temperature on modulus and damping. The damping is related to d ln J/d ln t; consequently, an increase in temperature will only slightly shift (horizontally) the curve of tan δ vs. the logarithm of frequency. On the other hand, the modulus will decrease considerably (upward shifts of creep curves), much more so than might be attributed to the horizontal shifts in the tan δ curves.

Some experimental data on PP which support this conclusion are given in *Figure 9*; similar results were obtained on other polymers. Clearly, if it were attempted to superimpose the data of *Figure 9* by horizontal shifts, the shifts of G' would be much larger than those for tan δ.

EFFECT OF AGEING ON CREEP PROPERTIES AND VOLUME RELAXATION

Influence of the quenching temperature

Suppose that we quench a semicrystalline polymer from an initial temperature T_0 to some final temperature T. If T_0 lies between T_g^L and T_g^U, the amount of polymer that is rubbery at the moment of quenching will increase with T_0. Therefore, at constant T and increasing T_0, the volume relaxation and the ageing effects at T will become larger, and the value of the modulus just after quenching will become smaller. This dependence on T_0 will be pronounced for temperatures T lying in Regions 2 and 3 and will become smaller when T lies below T_g^L (all amorphous material then freezes into the glassy state by cooling through T_g^L and the effect of changes in T_0 disappears). On the other hand, if T_0 lies above T_g^U, the amorphous phase is entirely rubbery at the moment of quenching, and as in amorphous polymers, the dependence on T_0 will be slight.

Experimental results supporting these deductions are presented in *Figures 10* and *11*. *Figure 10a* concerns PP, a material for which Region 3 covers the entire range between 20°C and 100°C (see ref. 1). Rate β depends strongly on quenching temperature T_0. The same holds for nylon-12 (*Figure 10b*); the initial temperature of 80°C certainly lies below Region 4; consequently, β increases when T_0 is raised from 80°C to 140°C. For LDPE (*Figure 11*), all three T_0 values lie near to or in Region 4 (see Figure 20 of ref. 1) and as expected, the dependence on T_0 is only slight. Similar effects as for volume relaxation were found for the effect of ageing on creep (data not shown here).

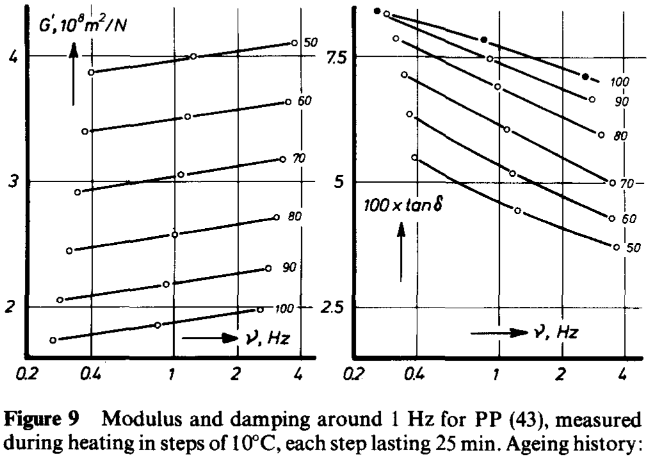

Figure 9 Modulus and damping around 1 Hz for PP (43), measured during heating in steps of 10°C, each step lasting 25 min. Ageing history: sample as received

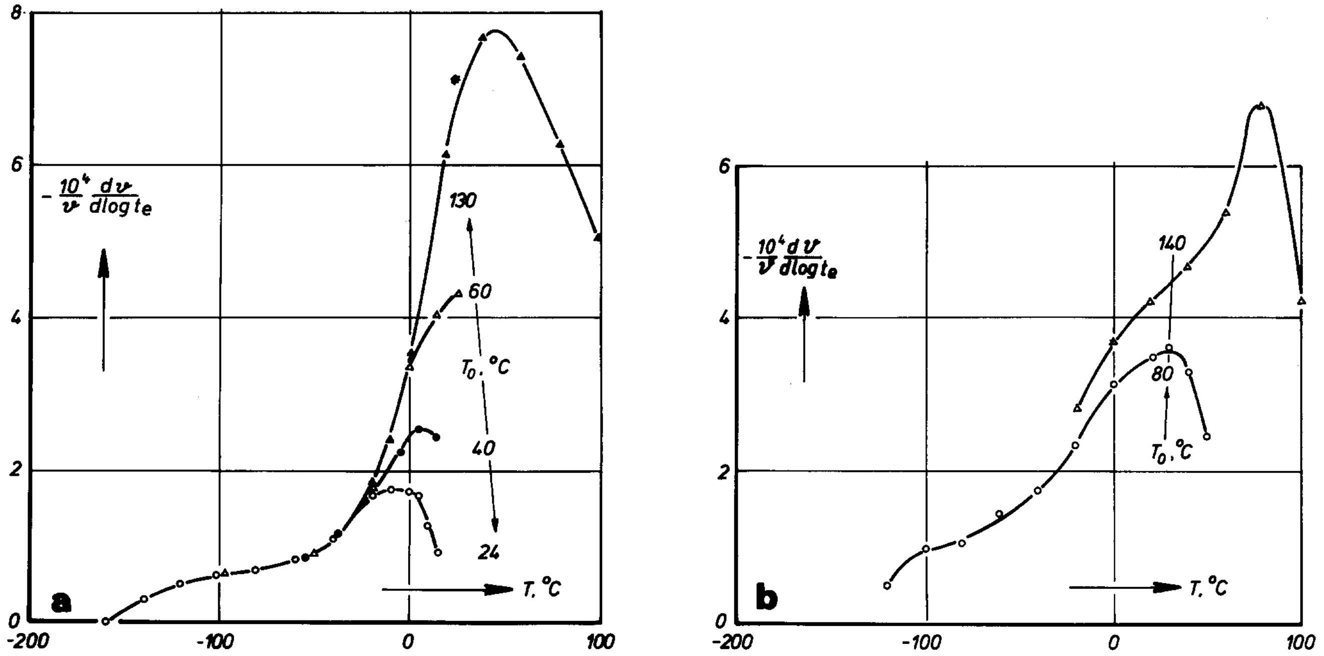

Figure 10 (a) Volume relaxation rate $\beta = -\frac{1}{v}\frac{dv}{d\log t_e}$ for PP (43) annealed at 135°C and quenched from different initial temperatures T_0 (residence time at T_0: 30 min). The data points indicated in *Figures 10a* and *11* by an asterisk were obtained by measuring the density changes (by hydrostatic weighing) during 1–6000 h after quenching from 120°C (PP) and 80°C (LDPE). (b) Nylon-12 (38) annealed at 90°C ($T_0 = 80$°C) or 160°C ($T_0 = 140$°C)

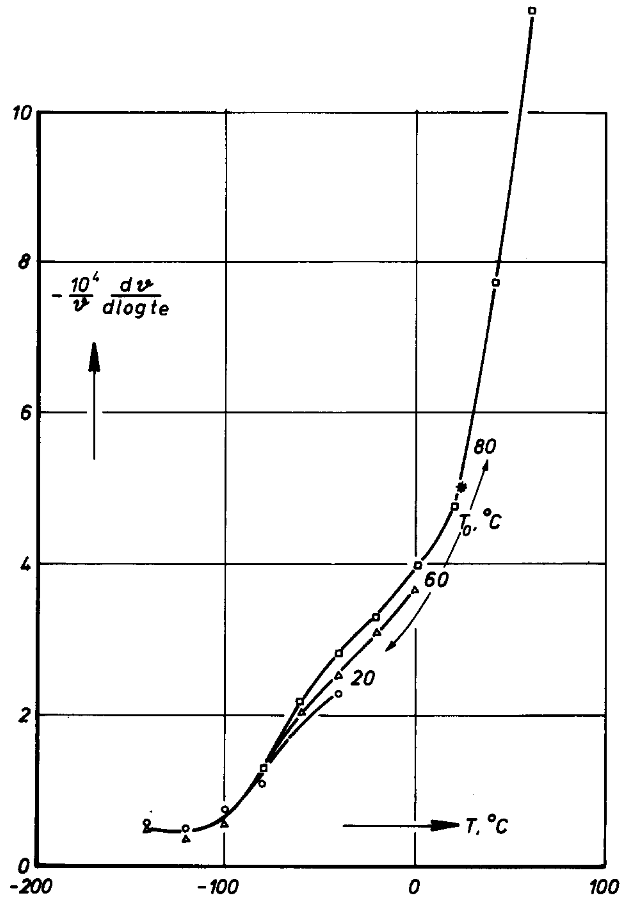

Figure 11 As for *Figure 10*, but now for LDPE (41). The samples had previously been annealed at 20 ($T_0 = 20$°C); 80 ($T_0 = 60$°C) and 90°C ($T_0 = 80$°C)

Complicated thermal histories

Until now, we have considered the ageing and volume relaxation after simple quenching from T_0 to T. For amorphous polymers, more complicated thermal histories have been investigated, e.g. $T_0{\downarrow}T_1(t_1){\downarrow}T$ (pre-anneal at T_1) or $T_0{\downarrow}T_1(t_1){\uparrow}T$ (intermediate temperature T_1 lower than final ageing temperature T). The pertinent data for rigid PVC are given in Figures 93 and 86 of ref. 5. It is interesting to see whether the peculiar effects found for amorphous polymers are also revealed by the semicrystalline materials above their T_gs.

Some experimental results for PP are presented in *Figures 12* and *13*. *Figure 12* concerns the effect of pre-annealing at $T_1 = 40$°C on the ageing $T = 20$°C. As for PVC (Figure 93 of ref. 5) the ageing at 20°C cannot be very much reduced by pre-annealing at 40°C.

Let us now consider the experiment $T_0{\downarrow}T_1(t_1){\uparrow}T$, in which the sample is first quenched from an initial temperature T_0 to an intermediate temperature T_1, next stored at T_1 during a time t_1 insufficient for reaching thermodynamic equilibrium, and finally heated to temperature T. When such an experiment is done with an amorphous polymer (see pages 97–101 of ref. 5), the volume relaxation cuve at final temperature T will show a maximum that is reached at some time $t_e = t_{max}$. Time t_{max} is roughly proportional to storage time t_1, and the ratio t_{max}/t_1 strongly decreases with increasing temperature difference $T - T_1$ (Figure 102 of ref. 5). The ageing behaves correspondingly: for $t_e < t_{max}$ the retardation times are decreasing, and for $t_e > t_{max}$ they are increasing with t_e. Our model suggests that the same behaviour must be expected for semicrystalline polymers. Some data confirming this are given in *Figure 13*. In agreement with expectation, the creep curves shift monotonically to the

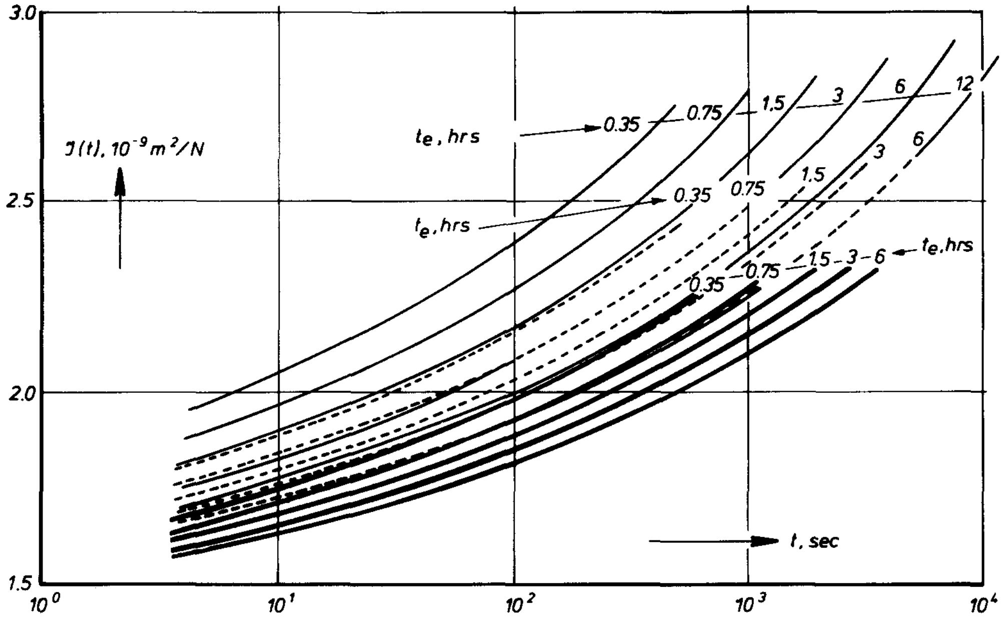

Figure 12 Effect of ageing on the small-strain torsional creep of PP (43) at 20°C. The three families of curves were obtained after the following histories: (———) 120 (1 h) ↓ 20°C; (-----) 120 (1 h) ↓ 40°C (1 h) ↓ 20°C; (———) 120 (1 h) ↓ 40°C (16 h) ↓ 20°C. [Reproduced from Struik, L. C. E. *Plastics and Rubber Processing and Applications* 1982, **2**, 41–50, by permission of Elsevier Science Publishers ©]

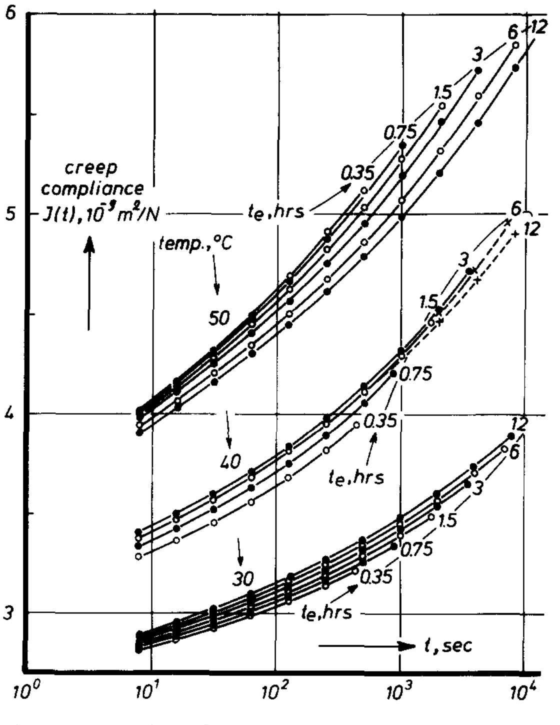

Figure 13 Ageing of PP (43) at $T = 30$°C, 40°C and 50°C after 130°C ↓ 20°C (1500 h) ↑ T; t_e is the time elapsed at final temperature T. [Reproduced from Struik, L. C. E. *Plastics and Rubber Processing and Applications* 1982, **2**, 41–50, by permission of Elsevier Science Publishers ©]

left when $T = 30$°C ($t_{max} > 12$ h); they first shift to the left and then to the right at $T = 40$°C ($t_{max} \sim 1.5$ h), and at $T = 50$°C they continuously shift to the right ($t_{max} < 0.35$ h). The volume relaxation behaviour was not measured, but that volume maxima indeed occur is known from Davis's work[7].

PHYSICAL AGEING OF FILLED RUBBERS

Since the model of an extended glass transition was actually taken from the rubber literature (see the Introduction), a check on whether filled rubbers indeed show physical ageing above T_g was considered to be of crucial importance. Our model predicts that at temperatures above the T_g of a well-vulcanized non-crystallizing rubber, we will observe the following:

(1) There will be little creep and no ageing in the unfilled rubber.

(2) There will be much more creep and a considerable ageing in the filled material, the more so the smaller the particle size (for a constant volume fraction of filler, the contact area between rubber and filler, i.e. the disturbance of the rubbery phase, increases with decreasing particle size).

(3) The creep and ageing behaviour will be of type 3.

(4) The damping and temperature dependence of the modulus will be larger the smaller the particles are.

The experiments were done on an unfilled SBR, and on two identical SBR's filled with 30 vol% HAF black or $BaSO_4$. The ageing after quenching from +70°C was measured at temperatures between −40°C and +50°C ($T_g \sim -60$°C). Some typical results are presented in *Figures 14–17*.

Figure 14 shows that the filled rubber suffers much more creep and ageing than does the unfilled rubber. The same holds for the creep rate (damping tan δ) and the temperature dependence of the modulus (see *Figure 15*). That the effect of particle size is as expected is shown in *Figures 15* and *16* and that the ageing is indeed of type 3 becomes clear from *Figure 14*. Thus points (1)–(4) are confirmed by experiment, except for some unexplained ageing in the unfilled rubber (see *Figure 14*). It was found over the entire temperature range between −40°C and +50°C (see *Figure 16*), and similar small ageing effects were found in other unfilled rubbery materials such as crosslinked PUR, PMMA at $T > 120$°C, etc.

As for amorphous and semicrystalline polymers, the ageing effects in the filled rubbers are reversible (c.f. Figure 10 of ref. 1). As illustrated in *Figure 17*, they can be reproduced several times in the same sample. *Figure 17* also shows that the ageing is not some non-linear effect caused by the sequential creep testing on one and the same sample[8].

For filled rubbers we can analyse the effects of temperature and ageing time in some more detail than for semicrystalline polymers. Since we know the creep properties of the matrix, i.e. the unfilled rubber, we can separate the total creep of the material into the contributions from, on the one hand, the undisturbed rubbery matrix, and on the other, the immobilized shells around the filler particles. This can be done by considering the relative compliance, i.e. the ratio of the compliances of the filled and unfilled rubber at the same temperature, ageing time and creep time.

Some results are given in *Figure 18*. We observe that the creep curves now shift horizontally and that the shift rate is of the order of unity (0.7). For the SBR–HAF black vulcanizate, a similar behaviour was observed over the entire range between $-20°C$ and $+50°C$, and over this range shift rate μ varied between 0.7 and 1.0. The behaviour of the SBR–$BaSO_4$ was less ideal. The effects are smaller and the experimental scatter is larger with no perfect superposition, as in *Figure 18*, being observed.

As regards the shapes of the creep curves and the effects of temperature, we can reason as follows. If the adhesion between filler and rubber is sufficiently strong, the immobilized shell will remain intact up to very high temperatures. Region 4 is not easily reached, and as

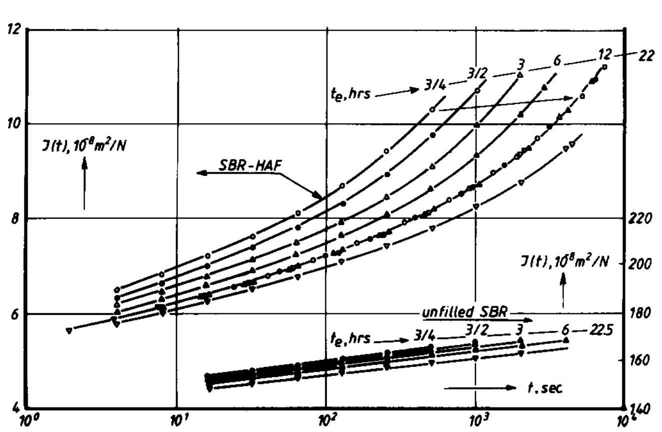

Figure 14 Small-strain torsional creep of unfilled SBR (55) and SBR–HAF (56) both at 20°C and at various times t_e after a quench from $+70°C$. Note that the two vertical scales are different (the compliance of the unfilled rubber is of course much larger than that of the filled rubber), but that the scale sensitivity, i.e. the percentage change in J per cm is about the same. The master curve was obtained by horizontal and vertical shifts; the arrow indicates the shifting direction

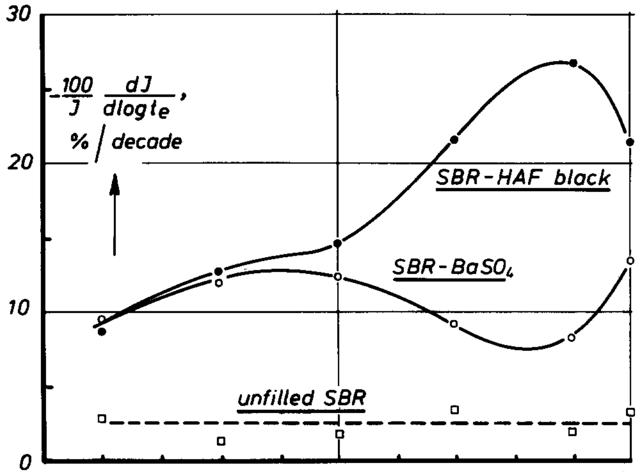

Figure 16 Percentage decrease in the 1000 s compliance per tenfold increase in elapsed time for filled and unfilled SBR's quenched from 70°C to various temperatures T, and measured between ageing times t_e of 1.5 to 23 h

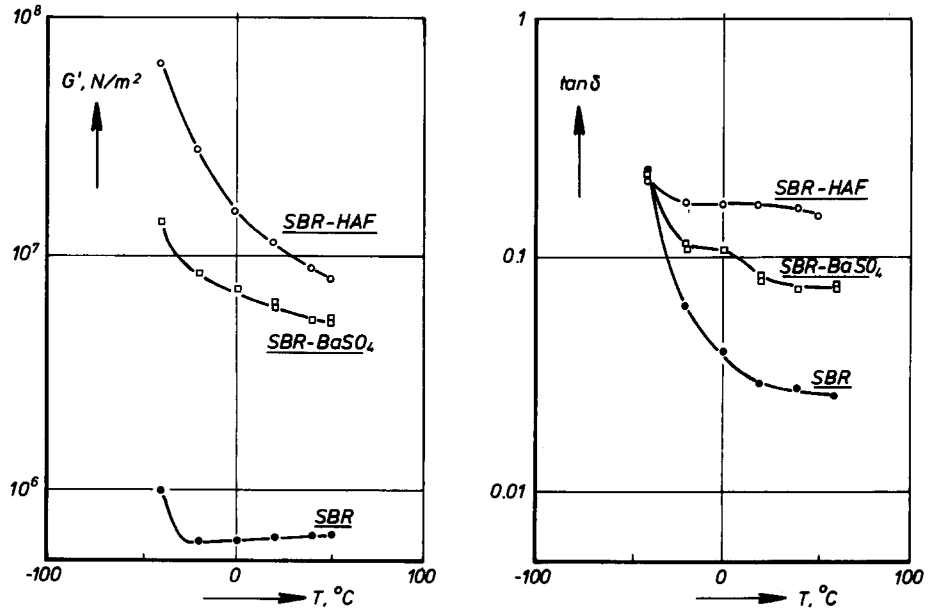

Figure 15 Modulus and damping at 1.55×10^{-4} Hz of filled and unfilled SBR as calculated from the creep compliance and its rate at 1024 s. The creep data were obtained 6 h after quenches from 70°C to T

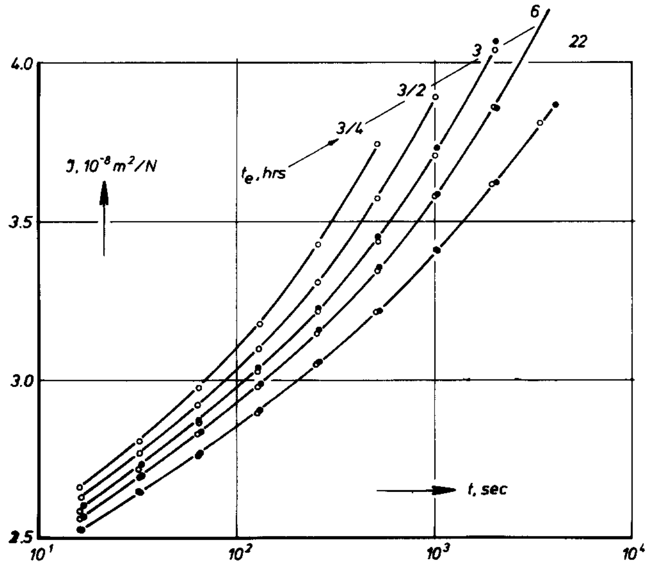

Figure 17 Small-strain torsional creep of SBR–HAF (56) at various times, t_e, elapsed after a quench from 70°C to −20°C. (○) First series of tests at t_e's of 3/4, 3/2, 3, 6 and 22 h. (●) Second series on the same sample, but only at t_e's of 3, 6 and 22 h (the tests at 3/4 and 3/2 h were not done)

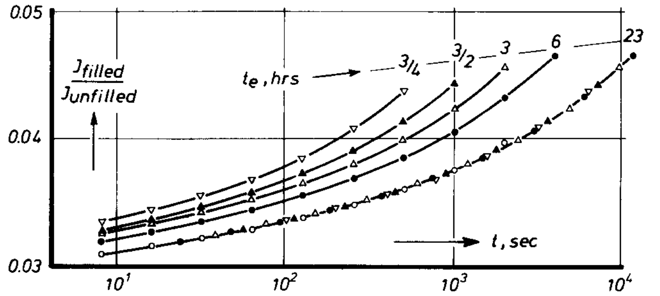

Figure 18 Relative compliance of SBR–HAF (56) at various times after a quench from 70°C to 0°C. The master curve was obtained by *purely horizontal* shifting ($\mu \sim 0.7$)

shown by *Figures 16* and *19*, this is indeed the case. With increasing temperature, the glassy shells around the filler particles will decrease in thickness, and since the material is soft, only those layers which are just entering the glass transition will significantly contribute to the creep. Therefore, the creep curves will show a marked curvature, although it is less than that of the creep curves of amorphous polymers below their T_gs (see *Figure 19*). Furthermore, an increase in temperature will hardly change the position of the creep curve on the time scale (reasons for this were given in Part 1). Therefore, if creep curves measured at different temperatures are superimposable, the shifts will be mainly vertical (compare *Figure 19* with Figure 9 in ref. 1).

A final point about the filled rubbers is illustrated in *Figure 20*. As expected, these materials show volume relaxation effects at temperatures above T_g. In *Figure 20*, the peak at −70°C is the normal peak at the T_g of the SBR; the surprisingly large peak around −20°C may be attributed to the layers with reduced mobility.

DISCUSSION

As stated in the Introduction of Part 1[1], the general discussion of the results is postponed to Part 4 of this series of papers. Here it suffices to say that the deductions from the model with respect to dynamic mechanical properties, complicated thermal histories and the ageing of filled rubbers are in good agreement with the experimental findings.

CONCLUSIONS

(1) The model of an extended glass transition qualitatively explains the effect of ageing on the dynamic mechanical properties of semicrystalline polymers.

(2) The effect of complicated thermal histories on the creep properties is strikingly similar for a semicrystalline material such as PP at 20°C–40°C and an amorphous polymer such as PVC.

(3) At temperatures above T_g, filled rubbers show the same ageing effects as semicrystalline polymers.

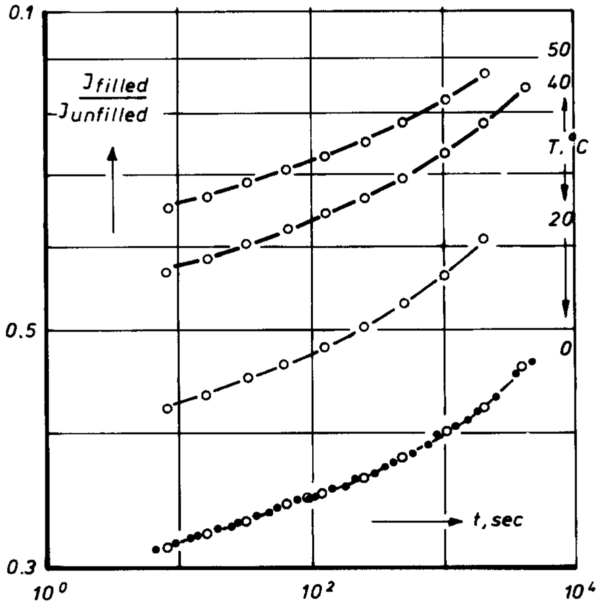

Figure 19 Relative creep compliance of SBR–HAF (56) 6 h after quenches from 70°C to various temperatures *T*. The master curve was obtained by vertical shifts combined with small horizontal shifts (< 0.2 decade)

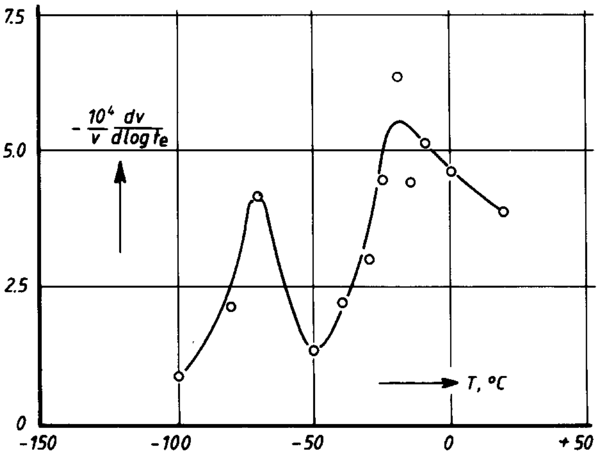

Figure 20 Volume relaxation rate β as measured by length dilatometry (see ref. 1) for SBR–HAF rubber (49) quenched from 40°C to different temperatures *T*

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