

# On McCrum's sequential aging theory

L. C. E. Struik

DSM Research, PO Box 18, 6160 MD, Geleen, The Netherlands

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For amorphous polymers McCrum's theory of sequential aging is shown to disagree with experiment.  
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## 1. INTRODUCTION

In a series of papers<sup>1–3</sup>, McCrum *et al.* criticized the author's explanation of physical aging in amorphous polymers. An illustration is given in *Figure 1*. We consider a quench from  $T_0 > T_g$  to final temperature  $T < T_g$ . The time elapsed after the quench is denoted by  $t_e$ . After quenching, the specific volume gradually decreases with time<sup>4,5</sup>. It is assumed that this is accompanied by a gradual decrease in free-volume,  $v_f$ , and a simultaneous decrease in molecular mobility  $M$ . It is further assumed that the rate of small-strain mechanical creep is determined by  $M$ .

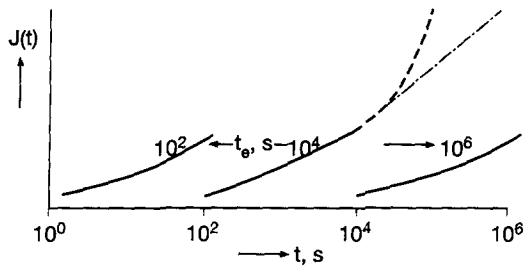
The gradual change in mobility,  $M$ , naturally leads to a distinction between the so called short- and long-term creep compliances (see Chap. 10 of ref. 5). Let  $t_e$  be the aging time at the start of the creep test. The aging time at creep time  $t$  will be  $t_e + t$ . Since the material continues to age,  $M$  at  $t > 0$  will differ from that at  $t = 0$ . Thus, to get a 'snapshot' of the properties at aging time  $t_e$ , creep time  $t$  should remain much less than  $t_e$ . The resulting creep curves were called short-time or momentary creep curves. Examples are given in *Figure 1* (full curves). Each curve is determined by the mobility,  $M$ , at the moment (aging time  $t_e$ ) of loading; since  $t \ll t_e$ , the mobility remains about the same during each test. If, between  $t_{e1}$  and  $t_{e2} > t_{e1}$  mobility,  $M$ , has decreased by a factor of  $x$ , the creep at  $t_{e2}$  is delayed compared to that at  $t_{e1}$  by the same factor. On a log-time scale, the creep curves at  $t_{e1}$  and  $t_{e2}$  will be mutually shifted by a factor  $\log x$  (full curves in *Figure 1*).

The so called *long-term creep* is defined as the creep for creep times  $t$  comparable to or greater than  $t_e$ ; it is affected by the continued aging during the creep test. To obtain a clear distinction we introduced the symbols  $J(t)$  for momentary and  $\bar{J}(t)$  for long-term creep. In *Figure 1*, the long-term creep curve is indicated by the dashed-dotted curve; it has a sound physical meaning. For long-term creep, changes in  $t_e$  no longer necessarily lead to uniform shifting along the  $\log t$  scale; as shown in Figure 107 of ref. 5, this only holds if  $M$  decreases in inverse proportion with  $t_e$  ( $\mu = 1$ ).

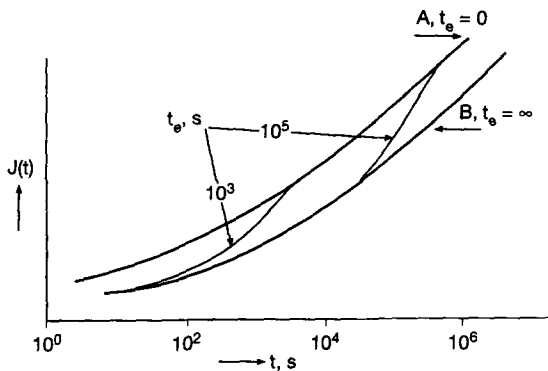
*Figure 1* also shows the momentary creep curve extrapolated to  $t > t_e$  (dashed). By definition, the momentary curve can only be measured for  $t \ll t_e$ , so,

this extrapolated curve is hypothetical and may have no physical meaning. However, as shown in Chap. 10 of ref. 5, the extrapolated part can be obtained unambiguously and accurately by time-temperature superposition of momentary creep-curves measured at different temperatures. Therefore, in the long-term creep theory (Chap. 10 of ref. 5), we used the *additional assumption* that the momentary creep curve, extrapolated to  $t > t_e$ , has physical meaning and can be used to calculate the long-term from the short-term creep. This additional assumption has been applied only in that particular context; it was not used to explain the effect of aging on short-time creep. So, in contrast to McCrum's theory (see below), the author's explanation of the aging effects on short-term creep did not contain speculations about hypothetical curves.

McCrums explanation of the aging effects is shown in *Figure 2*. The effect is interpreted as a transition from the initial curve A ( $t_e = 0$ ) to the final curve B ( $t_e = \infty$ ). Both curves are hypothetical and cannot be measured over the full time scale. McCrum further assumes that the shift between curves A and B is only small (order of one decade, i.e. much smaller than the shifts seen in *Figure 1*). McCrum finally assumes (assumption c of legend to *Figure 2*) that the transition occurs for creep times  $t$  about equal to  $t_e$ . It is the transition that features the effect of aging on creep; far left or right from the transition, the creep follows curves A or B which are independent of age. Assumption c implies that the transition shifts to longer times when  $t_e$  increases, in fact in proportion to  $t_e$ . So, a double-logarithmic shift rate,  $\mu = d \log(\text{transition time}) / d \log t_e$  of unity<sup>5</sup> is contained in assumption c from the very beginning. McCrum's detailed calculations<sup>1</sup> show that the creep curve around the transition shifts without change in shape when curves A and B are flat<sup>1</sup> (in fact when the retardation spectrum is a wide box); shift rate  $\mu$  is then well defined and equal to unity. When A and B are strongly curved, the short-time creep curves (thin in *Figure 2*) no longer superimpose perfectly and the (ill-defined) approximate shift rate becomes considerably less than unity<sup>1</sup>. This ingenious construction seriously contradicts the author's explanation of the aging effects. In fact, the large effects of aging on mobility and creep rate are denied. The large (apparent) shifts of



**Figure 1** Effect of aging on the small-strain creep compliance  $J(t)$  of an amorphous polymer; conventional picture<sup>5</sup>. (—) Short-time (momentary) compliance; (---) extrapolated momentary compliance; (- · -) long-term compliance. For further explanation see text



**Figure 2** McCrum's explanation of the effect of aging on short-time creep<sup>1</sup>. Curve A refers to the initial state at  $t_e = 0$  (just after quenching), curve B to the equilibrium state at  $t_e = \infty$ . The shift between A and B is only small, as explicitly stated by McCrum it is of the order of 1 decade, i.e. much smaller than the shifts in Figure 1. McCrum further assumes that at aging time  $t_e$ : (a) the creep for times  $t \ll t_e$  follows curve B; the units with short retardation times are already at the new equilibrium; (b) the creep for times  $t \gg t_e$  follows curve A; the units with long retardation times are still in the original state; (c) for creep times  $t$  comparable to  $t_e$ , the creep curve shows a transition from the lower (B) to the higher curve (A)

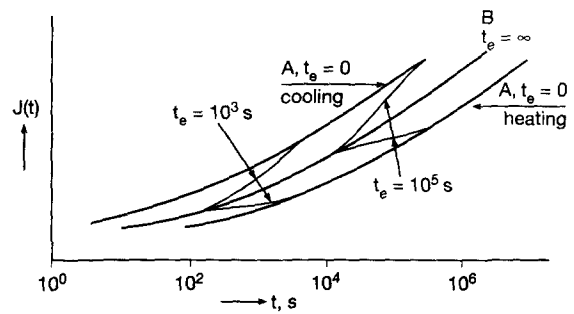
the short-time creep curves are considered as artefacts<sup>1</sup> which arise because, for different values of  $t_e$ , the creep tests (focusing on the transition) refer to different parts of the retardation spectrum. In view of the serious discrepancies with the conventional theory, we investigate to what extent McCrum's theory agrees with experimental facts not considered in refs 1-3.

## 2. COMPARISON OF MCCRUM'S THEORY WITH EXPERIMENT

### 2.1. Retrograde shifting after an up-jump from thermodynamic equilibrium

For a sample heated instead of being cooled, the volume increases with  $t_e$ <sup>4</sup>. The conventional picture then predicts that the creep curves will shift to shorter times, i.e. to the left. This prediction agrees with experimental data obtained after up-quenches from *thermodynamic equilibrium*. Data for amorphous polymers are given in Section 9.2. of ref. 5 and in ref. 6. Retrograde shifting was also found for the semi-crystalline PP (Figure 13 of ref. 7) but in that case, the up-quench most probably did not start from thermodynamic equilibrium.

If the temperature is first lowered and after some time raised to final temperature  $T$ , the volume-relaxation curve may show a peak and indeed, the shifts are then to the left for short times (increasing volume) and to the



**Figure 3** McCrum's theory for aging after stepwise cooling or heating from thermodynamic equilibrium; for explanation see text

right for long times (decreasing volume)<sup>5,6</sup>. Such peaks are observed when the period at the lower temperature  $T_2$  is too short for reaching thermodynamic equilibrium at  $T_2$  (see Section 2.4).

Altogether, the conventional picture gives an excellent explanation of the experimental facts.

The consequences of McCrum's theory are shown in Figure 3. After cooling, we have a transition from a *lower to a higher* curve (B to A); after heating, we have the reverse (transition from *higher to lower* curve). Consequently, the shape of the creep curves after heating will differ drastically from that after cooling and in both cases, the shapes will differ from that of the creep curve at equilibrium (curve B). In fact, McCrum's theory predicts that for  $t \approx t_e$ , the curves after quenching will move upwards and those after heating downwards compared to the equilibrium curve B. The experimental evidence given in Figure 84 of ref. 5 and ref. 6 disproves McCrum's theory. The curves measured after cooling and heating from equilibrium states have the same shape and can be superimposed on the curve measured at equilibrium.

It may be objected that we stretched McCrum's theory to a range (heating) outside that (cooling) for which it was designed. Admitting this, we restrict ourselves to cooling. McCrum's theory predicts that the short-time creep curves measured during aging have another shape than the equilibrium curve; as said before this disagrees with experiment. So, even for cooling, the theory does not work.

### 2.2. Long-term creep

According to McCrum's theory, any real creep curve, including long-term ones, should lie between the extremes A and B of Figure 2. These curves are mutually shifted by only a decade or so<sup>1</sup>. Consequently, long-term creep curves measured at different values of aging time  $t_e$  can only differ slightly (shifts of a decade at most). The conventional picture predicts that the shifts for long-term and short-term creep will be similar and may become much larger than one decade. Experimental data (Figures 108 and 111 of ref. 5) confirm this.

### 2.3. The $\mu = 1$ case

According to McCrum's theory, the shift rate  $\mu$  will be about unity when the creep retardation spectrum is flat (zero slope) whilst  $\mu$  progressively decreases when the slope/curvature of the spectrum increases<sup>1</sup>. This follows from his basic equation (4)<sup>1</sup>. Experiments on amorphous polymers<sup>5</sup> reveal that  $\mu$  is about unity for the low-temperature tail of the glass transition where

the (short-time) creep curves show high upward curvature and the spectrum is certainly not constant or flat (cf. equation (10) and Figure 34 of ref. 5). Much flatter creep curves (and thus spectra) are found at temperatures further below  $T_g$ , but exactly at such temperatures,  $\mu$  drops to values far below unity<sup>5</sup>. So, again McCrum's predictions do not agree with the experimental data on amorphous polymers. McCrum's argument about  $\mu \approx 1$  appears to focus on the centre of the glass transition where the spectrum peaks (zero slope). However, such peaks occur at temperatures so close to  $T_g$  that aging has most probably disappeared; almost all aging data reported in ref. 5 pertain to retardation times left from the peak.

#### 2.4. The thermo-stimulated creep (TSC) evidence

The picture of sequential aging originally resulted from TSC-experiments on PP<sup>3</sup> and an amorphous polymer<sup>2</sup>. The latter was deformed at  $T_g - 2^\circ\text{C}$  for 360 s. Next it was unloaded for 60 s and subsequently quenched to  $-29^\circ\text{C}$  and aged there for various times  $t_a$ . If the creep properties were measured at  $-29^\circ\text{C}$ , McCrum observed the usual aging effects (large shifts). However, if the creep-recovery is measured around  $T_g$ , hardly any effect of the aging period at  $-29^\circ\text{C}$  is observed. So, the mechanical relaxation times just below  $T_g$  are not influenced by the aging period at  $-29^\circ\text{C}$ . McCrum's interpretation is that the 'package of retardation times' which are affected by the aging at  $-29^\circ\text{C}$  is the very short-time tail of the spectrum at temperatures  $T_1$  close to  $T_g$ . At  $T_1$ , this package is almost immediately in equilibrium and no effect of the aging at  $-29^\circ\text{C}$  is observed.

Several years earlier, the author found exactly the same effect (see Figure 96 of ref. 5) but explained it differently, viz. from the volume-recovery peaks found by Kovacs<sup>4</sup> (see also pp. 97–111 of ref. 5 and ref. 6). During aging at  $-29^\circ\text{C}$  there will be a decrease in volume. However, on heating to a temperature  $T_1$  close to  $T_g$ , this densification recovers rapidly and during the subsequent measuring period at  $T_1$ , the volume recovery develops as if the material were directly quenched to  $T_1$  and had never been aged at  $-29^\circ\text{C}$ . Thus, at  $T_1$  there is no remembrance of the aging period at  $-29^\circ\text{C}$ . In conclusion, the result of McCrum's TSC experiment can be explained by both theories.

### 3. DISCUSSION

Section 2 shows that three of the four predictions of McCrum's theory disagree with experiment whilst the conventional theory works in all cases; for the fourth prediction (TSC) we cannot discriminate between the two theories. The obvious conclusion is that the sequential aging hypothesis does not work.

Two remarks seem appropriate:

(a) *Effect of aging on DMTA (dynamic mechanical thermal analysis)*. McCrum argued that 'if thermal history could change spectra so drastically (shifts of many decades as reported by the author) it is doubtful if DMTA and DETA could play the highly significant analytical role they do in polymer research and development'<sup>1</sup>. In his theory, this role was 'saved' by interpreting the large shifts, found by the author, as artefacts.

This argument is incorrect and confusing. First, for

small strains (linear viscoelastic behaviour), DMTA and creep behaviour are determined by the same retardation spectrum and one-to-one related<sup>8</sup>. Thus, it is impossible that the effect of aging on creep is an artefact and that on DMTA real, or vice versa.

In practice, DMTA data are indeed less sensitive to aging than creep data. In view of the above, such differences cannot be intrinsic and must be due to differences in the experimental conditions. The most relevant difference lies in the frequency which is generally much higher for DMTA than for creep. For amorphous polymers, two consequences of this frequency difference can be mentioned. The first was discussed in ref. 9: aging is due to shifts (changes in mobility,  $M$ ) and the effect of a shift is proportional to the slope of the creep or dynamic modulus vs frequency curve. Aging further refers to the low-temperature tail of the glass transition and the slope of this tail decreases with increasing distance from the centre of the transition. Thus, for measuring temperatures below  $T_g$ , the high frequency DMTA test (e.g. done at 1 Hz) focuses on a part of the tail that is further removed from the centre than the part seen in creep (frequencies of  $10^{-6}$ – $10^{-3}$  Hz); consequently, the aging effects will be less (for details, see Figure 4 of ref. 9). The second point refers to DMTA experiments in which the glass transition is forced to be seen at higher frequencies, e.g. at 10 Hz or 1 MHz. This is possible by raising the temperature to values considerably above the (structural)  $T_g$ ; however, at such high temperatures, the (structural) aging effects necessarily disappear ( $T > T_g$ ).

(b) *Temperatures far below  $T_g$* . The arguments against McCrum's theory came from aging data measured at temperatures not too far below  $T_g$ . It is only for such temperatures that we have reliable data on retrograde shifting and can compare the creep curves with those at equilibrium (Section 2.1.). So, it cannot be excluded that McCrum's sequential aging theory might be applicable at low temperatures (where aging and creep are rather unimportant).

### 4. CONCLUSION

For amorphous polymers, McCrum's theory of sequential aging is disproved by experiment.

### ACKNOWLEDGEMENT

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N. G. McCRUM COMMENTS ON PAPER BY  
L. C. E. STRUIK ENTITLED: 'ON McCRUM'S  
SEQUENTIAL AGING THEORY'

The method of time/elapsed time superposition pioneered by Struik is unsuitable for fundamental research. The method is fatally flawed: all statements derived from time/elapsed-time superposition are subjective. The operator must first decide to plot compliances on a log or on a linear scale: then an arbitrary combination of horizontal and vertical shifts is imposed to produce a superposition. But what is a satisfactory superposition? One that is satisfactory to one observer will be unsatisfactory to another. Scanning methods are far superior for studying the effects of aging on discrete portions of the spectrum. Chai and I formed the hypothesis that aging proceeds sequentially: short aging times do not affect long retardation times. This is a simple hypothesis testable by scanning. It is to be hoped that with the availability of good commercial equipment more extensive experiments will be undertaken.

Hertford College,  
Oxford OX1 3BW, UK

L. C. E. STRUIK'S REPLY TO N. G. McCRUM'S  
COMMENTS

Obviously, Dr. McCrum does not react upon the arguments against his theory. He merely criticizes the superposition methods of Ref. 5 (1977) which have not been used in the present paper.