

# Effect of high stress on the ageing behaviour of high density polyethylene

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The influence of large applied stress on the tensile creep and stress relaxation properties of high density polyethylene (HDPE), quenched from 100°C and aged for various times at room temperature, has been investigated. From the creep experiments it was concluded that physical ageing effects persisted up to at least an applied stress of 20 MPa when a new sample was used for each creep experiment. However, the effects of the ageing appeared to be partially diminished at the highest stress levels used here. A high stress pulse was found partially to erase previous ageing and reactivate the ageing process. In the stress relaxation tests attention was focused on the internal stress level,  $\sigma_i$ . It has earlier been observed that  $\sigma_i$  increases with ageing time. This dependence of the internal stress on ageing time was found to persist up to high deformations. Only at very high initial stresses, well beyond the yield point, was  $\sigma_i$  unaffected by the ageing time. The influence of physical ageing on the stress relaxation behaviour was also studied for HDPE filled with glass spheres.

(Keywords: polyethylene; creep; stress relaxation; physical ageing; high deformations)

## INTRODUCTION

Today it is well known that physical ageing can have a substantial influence on the mechanical and other properties of polymers<sup>1-6</sup>. The physical ageing process has been studied in greatest detail for amorphous polymers, but is also considered to be of importance in semicrystalline polymers like polyethylene and polypropylene<sup>1,7-9</sup>. Although considerable knowledge concerning the physical ageing process has emanated from the above mentioned studies as well as from other work, and a sufficient description of the process is at hand in many cases, the basic mechanisms involved do not appear to be fully understood or agreed upon.

According to Struik<sup>1</sup> the main effect of physical ageing is to shift the relaxation or retardation spectrum along the time axis without changing its shape. For semicrystalline polymers above the usual glass transition temperature, he suggested that the amorphous phase could be viewed as consisting of two parts<sup>8</sup>. One part, close to the crystallite surfaces, may still be glassy and age in the same way as an amorphous polymer below the glass transition temperature. The other part, further away from the crystallites, has undergone its glass transition and consequently does not age.

Chai and McCrum have a different view on ageing<sup>7,10,11</sup>. They proposed that physical ageing distorts the relaxation or retardation spectrum due to sequential relaxation. Only relaxation times shorter than or equal to the ageing time shift to longer times. Furthermore, they proposed that the limiting compliances change with ageing time. These two mechanisms would then make it difficult or impossible to construct a master curve by shifting flow curves obtained at different ageing times horizontally and vertically.

Based on Struik's work on physical ageing in semi-crystalline polymers<sup>8</sup>, a model describing the effect of physical ageing on the stress relaxation behaviour of

high density polyethylene (HDPE) at room temperature was developed<sup>12</sup>. It was predicted that the superposition of relaxation curves obtained at different ageing times would fail, which is in agreement with experimental results at this temperature. If the results of that investigation are generalized, they indicate that the relaxed limiting modulus value increases with ageing time. This supports the suggestion by Chai and McCrum, but on the other hand it is not in conflict with Struik's hypothesis. Another complicating factor when discussing possible mechanisms in conjunction with physical ageing is that relaxation of thermal residual stresses might affect the process<sup>9,13,14</sup>.

When investigating the effect of physical ageing on creep and stress relaxation behaviour, the experiments have usually been restricted to small strains. However, Struik<sup>1,15</sup> has examined the ageing of amorphous polymers at higher stresses and concluded that the shift rate decreased with increasing applied stress when a new sample was used for each creep curve. He suggested that the mechanical deformations imposed generated free volume which counteracted the spontaneous decrease in free volume during ageing and thus retarded the ageing process. The purpose of the present work is to investigate to what extent this also occurs for a semicrystalline polymer like HDPE at room temperature. Both the creep and the stress relaxation behaviours at larger deformations are included in this study. The stress relaxation behaviour of HDPE filled with glass spheres is also included.

## EXPERIMENTAL

### Materials

The HDPE grade used was Stamylen 9089F, DSM with a nominal density of 0.963 g cm<sup>-3</sup>, a melt flow index of 8 g (10 min)<sup>-1</sup> (MFI 190/2) and a weight average

molecular mass ( $\bar{M}_w$ ) of  $6 \times 10^4 \text{ g mol}^{-1}$ . In some experiments the polymer was filled with 20 vol% glass spheres (3000 CP00, Potters Industries) with an average diameter of  $30 \mu\text{m}$ .

The preparation of the HDPE-glass sphere composites is described in Reference 16. Some of the glass spheres were surface modified with an azide functional alkoxysilane (AZ-CUP™ MC, Hercules Inc.) as part of another investigation<sup>16</sup>. This silane provides a covalent bond between glass and polyethylene<sup>17</sup>. Two amounts of silane were used: 0.0214 and 0.206 wt% of the spheres.

Rectangular samples with a width of 5–6 mm were cut from 1 mm thick compression moulded sheets. The samples were then heat treated at  $110^\circ\text{C}$  for 16 h and slowly cooled ( $1^\circ\text{C min}^{-1}$ ) to room temperature. This was done to eliminate any residual stresses from the processing and to achieve a stable morphology. The specimens for the ageing experiments were heated again to  $100^\circ\text{C}$  for 1 h and then quenched in ice-water.

### Methods

A mechanical analyser, Dynastat, IMASS was used for the creep experiments, with a loading time of approximately 20 ms. The gauge length was 50 mm at stresses up to 8 MPa, 40 mm at 12 MPa and 30 mm at 16 MPa or more. The shorter gauge length at high applied loads is due to the limited elongation allowed in the Dynastat. The stress relaxation experiments were performed using relaxometers similar to one described earlier<sup>18</sup>. The initial strain rate was  $0.0125 \text{ s}^{-1}$  and the gauge length was 80 mm. All experiments were performed in tension at  $25 \pm 0.2^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Stress-strain behaviour

Figure 1 shows stress-strain relationships for HDPE up to a strain of 5% and for the composites up to break. These curves were obtained with the relaxometers and they reflect the behaviour of slowly cooled specimens. Very small effects from the quenching and subsequent ageing could be noticed with regard to the stress-strain behaviour. The initial tensile modulus increased with the

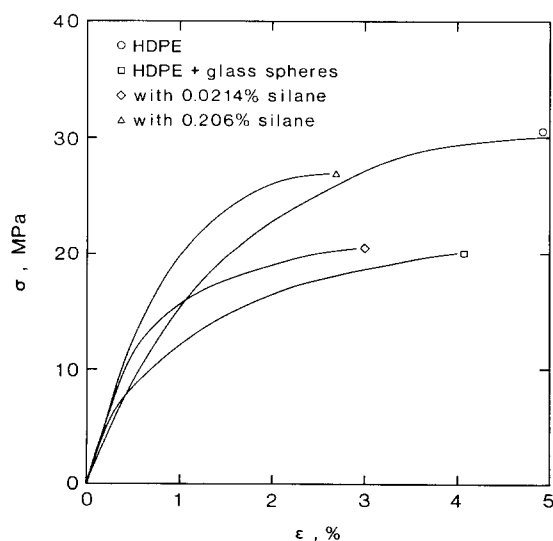


Figure 1 Stress-strain curves for slowly cooled samples of the composites. The strain rate was  $0.0125 \text{ s}^{-1}$

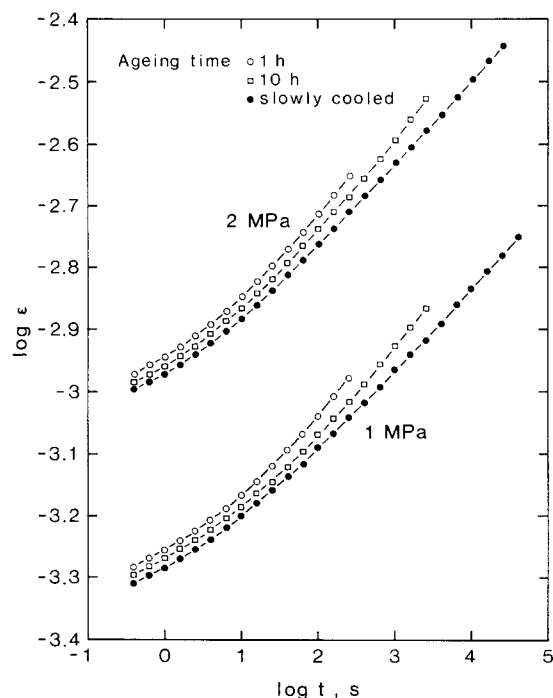


Figure 2 Creep curves for HDPE at applied stresses of 1 and 2 MPa. The specimens were quenched and aged for 1 or 10 h or slowly cooled

addition of glass spheres, but if the spheres were not silane treated the stress attained at larger strains was low, probably due to premature debonding at the glass/HDPE interface. Improving the bonding between the filler and the matrix by the silane treatment improved the stress-strain behaviour, but the composites then became more brittle. The best combination of strength and stiffness of the composite is achieved when the larger amount of silane (0.206 wt% filler) was used for the surface treatment. A corresponding improvement in creep resistance has been reported earlier<sup>19</sup>.

### The effect of ageing time on creep behaviour at higher stresses

When evaluating the effect of ageing time at higher stresses a separate specimen was used for each experiment to avoid the influence of any earlier deformation<sup>15</sup>. The maximum load possible in the Dynastat is 100 N. With a sample thickness of 1 mm and a width of 5 mm, the maximum stress attained was 20 MPa. Only unfilled HDPE was used for the creep tests.

Figure 2 shows the creep behaviour at applied stresses of 1 and 2 MPa while Figure 3 shows the creep curves at higher stresses, 16 and 20 MPa. The specimens had been aged at room temperature ( $25^\circ\text{C}$ ) for 1 and 10 h after the quench. Creep curves for slowly cooled specimens are also included in these figures. At all the investigated stresses, some effect of ageing time on creep behaviour can be observed. However, the change due to ageing is not the same at low and high applied stresses. In the low stress region the curves are shifted to longer times with increasing ageing time, as described earlier<sup>19</sup>. Superposition using horizontal and vertical shifts to obtain a master creep curve can only be accomplished with difficulty. At high stresses the effect of ageing time is apparently erased to a significant extent after a very short creep time, which is in line with the results obtained for amorphous polymers<sup>1</sup>. However, the strain at very short

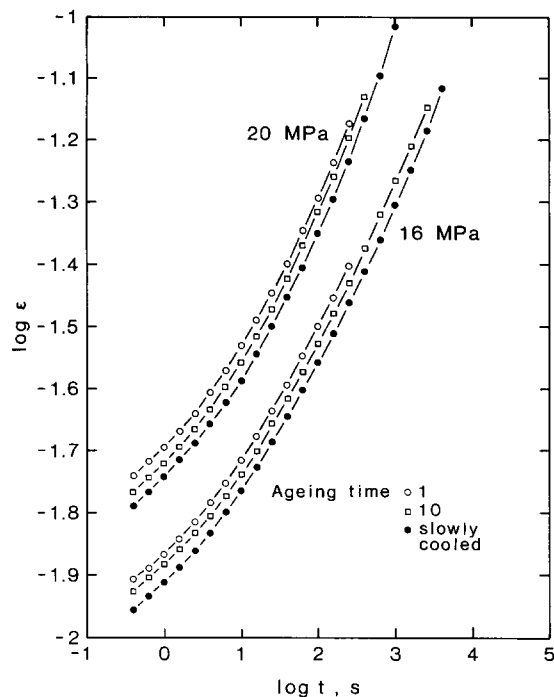


Figure 3 As for Figure 2 but for applied stresses of 16 and 20 MPa

times (at constant high stress) decreases with increasing ageing time. This can possibly be traced to a decrease in the limiting compliance  $J_U$  at  $t=0$  with increasing ageing time; see below and Reference 10. The effect of a decreasing limiting compliance  $J_U$  is expected to be more evident at higher stresses, partly due to the nonlinear viscoelastic character of HDPE (see below).

In Figure 4 the creep compliance  $J(t) = \epsilon(t)/\sigma_0$  is shown as a function of the applied stress  $\sigma_0$  at different loading times. Here the strain is denoted by  $\epsilon$ , and  $t$  is the creep time. The nonlinear viscoelastic character of HDPE, manifested through the stress dependence of  $J(t)$  even at low  $\sigma_0$ , is evident here. With increasing ageing time the compliance at a given stress and loading time decreases of course (Figures 2 and 3).

Regardless of the applied stress and the ageing time the logarithmic creep rate,  $\log(d\epsilon/dt)$ , decreased linearly with  $\log t$ , at least for creep times up to 1000 s. The slope of the line depends both on the applied stress and the ageing time. Using this observation, the limiting compliance  $J_U$  at time  $t=0$  can be estimated<sup>10</sup> and it is also included in Figure 4. The limiting compliance  $J_U$  decreased with increasing ageing time at all stresses which is in line with the ageing hypothesis of Chai and McCrum<sup>10</sup>. This may then contribute to the physical ageing process as reflected in the change in the creep behaviour.

#### Reactivation of the ageing process by application of a high stress

Struik proposed that a high stress pulse will produce an increase of free volume when applied to an amorphous polymer below the glass transition temperature. This means that the ageing process can be reactivated by applying a stress pulse of sufficient magnitude to a previously aged sample<sup>1</sup>. To investigate this for HDPE, slowly cooled samples were subjected to a stress 'pulse' of 20, 24 or 28 MPa with a duration of 11 s. The corresponding creep strains at the end of this period were

2.6, 4.2 and 6.6%, respectively. For these experiments, thinner samples (0.65 mm) had to be used to make the high applied stresses possible. Figure 5 shows the creep behaviour of HDPE at a low applied stress (1 MPa) before the high stress pulse and also the corresponding creep curves at the same stress at various elapsed times after removal of the high stress. When evaluating the creep the preceding recovery curves were extrapolated

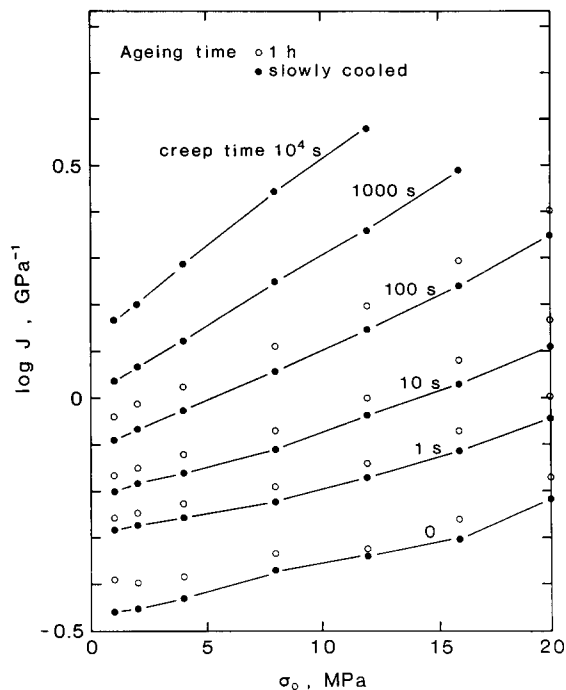


Figure 4 Creep compliance  $J = \epsilon/\sigma_0$  versus applied stress  $\sigma_0$  at different creep times for slowly cooled samples and specimens quenched and aged for 1 h

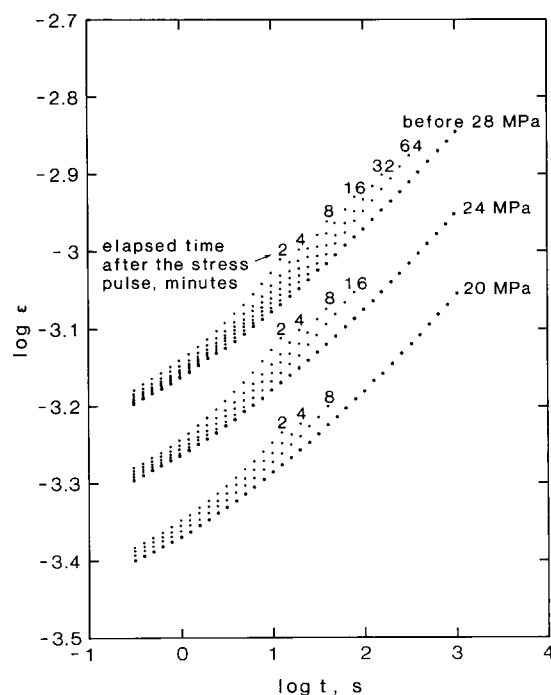


Figure 5 Effect of a high stress 'pulse' of intensity 20, 24 or 28 MPa and duration 11 s on creep behaviour at an applied stress of 1 MPa. The larger dots refer to the creep behaviour before the stress pulse and the smaller dots to the creep properties at different elapsed times after the high stress. The upper curve family is displaced 1/10 decade upwards and the lower curves are displaced 1/10 decade downwards

and subtracted from the apparent creep strain according to the procedure in Reference 15. As shown in *Figure 5*, the application of the stress 'pulse' seems to erase some of the previous ageing in the sense that the curves are shifted to shorter times after removal of the high stress. Increasing ageing time after the stress pulse then shifts the curves to the right, i.e. the ageing is reactivated. *Figure 5* shows that the highest stress (28 MPa) gave a slightly larger shift of the curves to the left after the stress pulse. HDPE thus behaves similarly to amorphous polymers, although the magnitude of the reactivation appears to be smaller at these stresses. Note that the same type of reactivation as shown in *Figure 5* for slowly cooled samples was also observed for specimens that had been aged for 2000 s at room temperature after the quench in ice-water.

From the results given in *Figure 5* it is not possible to conclude that the apparent reactivation of ageing is due *only* to an increased amount of free volume in the amorphous phase due to the imposed deformation. It is possible that the high stresses (or deformations) cause a time-dependent change in the structure of the material and that this change manifests itself as shown above. After all, the deformations attained are significant (*Figure 1*). However, the similarity between the behaviour of HDPE and the amorphous polymers<sup>1</sup> in this respect leads us to favour the free volume explanation by Struik, at least as a working hypothesis.

The results presented in this section do show that the change in viscoelastic properties with increasing time after a thermal quench are to a significant degree likely to be associated with a physical ageing process. When merely investigating the effect of ageing time on the flow process at small strains it cannot be excluded that the effect of ageing time is due to relaxation of thermal residual stresses caused by the quenching of the specimens<sup>9</sup>. However, such a relaxation can hardly produce any reactivation of the ageing process, as depicted in *Figure 5*.

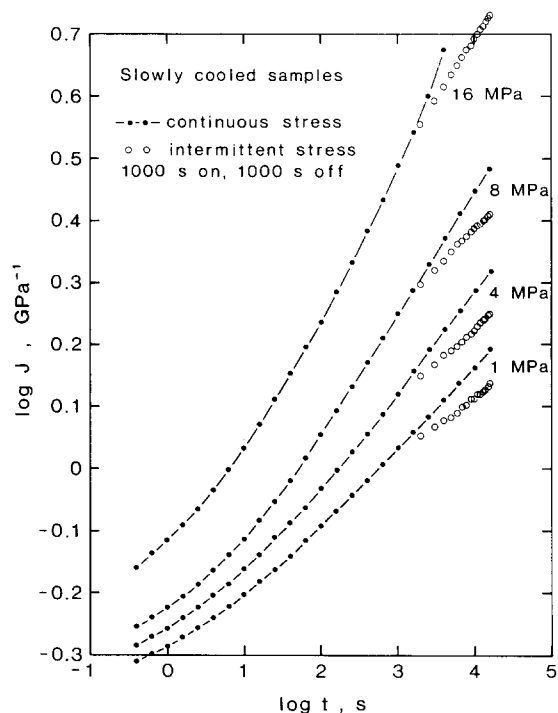
#### Intermittent creep behaviour

Struik<sup>1</sup> pointed out that the decrease in free volume during the ageing process can be retarded or even arrested by an intermittent loading sequence. This resulted in a higher creep strain at 20°C for poly(vinyl chloride) (PVC) when subjected to a periodic high stress than the strain resulting from continuously applied stress of the same magnitude<sup>1</sup>. The PVC samples had been aged for 1 h at 20°C after a quench from 90°C.

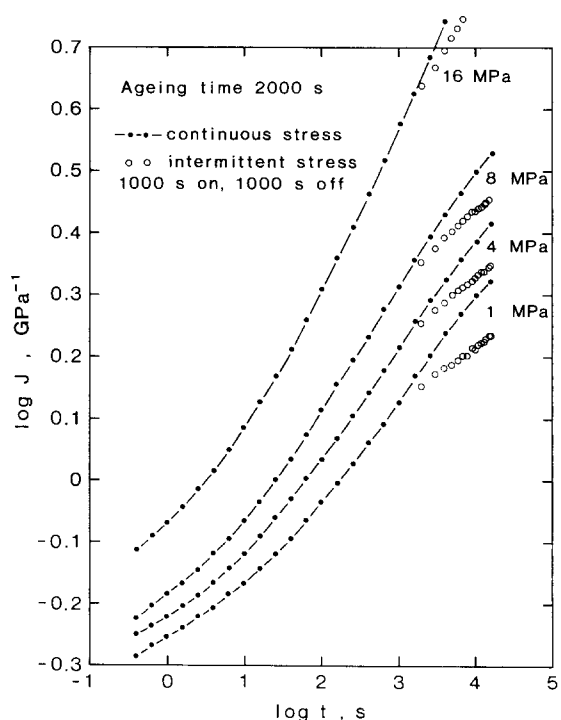
In *Figures 6* and *7* the creep compliance of HDPE obtained from continuous creep experiments and that from intermittent loading sequences are compared. The stress applied was increased from 1 to 16 MPa. For the samples that were periodically loaded, the load was removed after 1000 s and then applied again after another 1000 s and so on. The time axis in *Figures 6* and *7* refers to the time under stress, not the total time<sup>1</sup>. *Figure 6* shows the results for slowly cooled samples and *Figure 7* the corresponding curves for quenched specimens aged for 2000 s before the first loading. At all the stresses investigated the intermittent loading resulted in a lower creep deformation and a lower creep rate than obtained with continuous loading. Up to a stress of 16 MPa, the difference between the continuous creep and the intermittent creep seems to be independent of the stress.

This is true for the quenched as well as for the slowly cooled specimens.

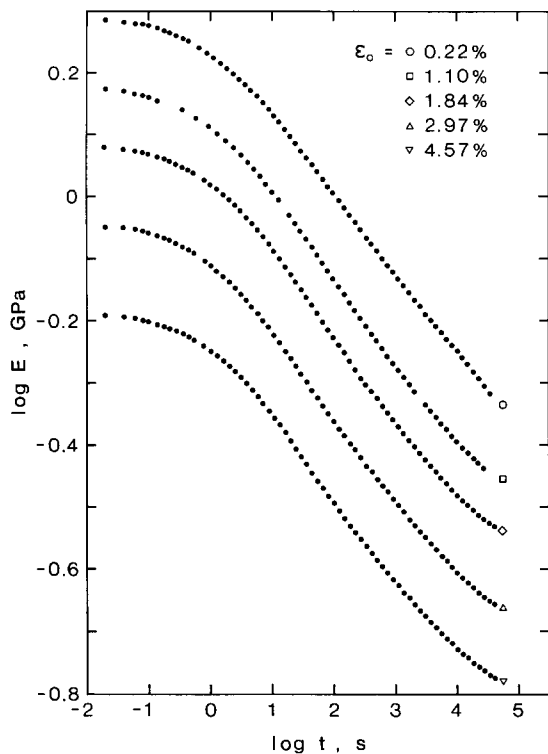
As mentioned above, Struik<sup>1</sup> showed that an intermittent loading with a sufficiently high stress may give a higher creep rate than the same stress applied continuously. The conclusion from our experiments is that an applied stress of 16 MPa is not sufficient to reduce the decrease in free volume for HDPE to the extent that



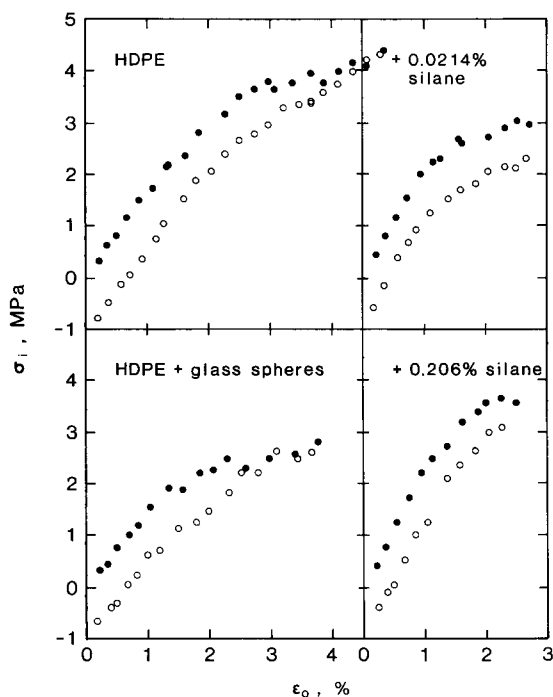
**Figure 6** Creep compliance versus time for slowly cooled HDPE at various stresses. The apparent compliance for the intermittent curve was calculated as total strain/stress at the ends of the stress periods. The time scale refers to time under stress



**Figure 7** As for *Figure 6*, but for quenched samples aged for 2000 seconds before testing



**Figure 8** Stress relaxation modulus  $E = \sigma/\epsilon_0$  versus  $\log t$  for slowly cooled samples of HDPE at different applied strains  $\epsilon_0$



**Figure 9** The internal stress  $\sigma_i$  versus applied strain  $\epsilon_0$  for unfilled HDPE and HDPE filled with glass spheres, untreated or with a thin or a thick silane layer: ●, slowly cooled samples; ○, specimens aged for 10h after the quench

the difference between the two types of creep curves in Figures 6 and 7 diminishes markedly.

#### *Influence of ageing on the stress relaxation behaviour at high initial stresses*

Figure 8 shows stress relaxation curves for unfilled HDPE (slowly cooled samples), plotted as  $\log E$  versus

$\log t$ , where  $E = \sigma/\epsilon_0$ , obtained at different values of the applied strain  $\epsilon_0$ . The nonlinearity of the material is clear; at higher applied strains the curves seem to move to shorter times. The glass-filled composites behave in the same way.

Of primary interest here was the internal stress  $\sigma_i$  and how it was affected by ageing time. The internal stress is here defined as the stress approached after very long times in a stress relaxation experiment. The determination of  $\sigma_i$  is based on an extrapolation procedure devised by Li<sup>20</sup> and its application to polymers has been outlined in detail earlier<sup>9,18</sup>. It is known<sup>9,12,18</sup> that the internal stress  $\sigma_i$ , as defined above, increases with ageing time at lower initial stresses, which is the reason for concentrating on this parameter.

Figure 9 shows the internal stress  $\sigma_i$  versus the applied strain  $\epsilon_0$  for HDPE and the composites, aged for 10h or slowly cooled. The corresponding curve for samples aged for 100h lies between the two curves shown. An ageing time of 1000h gave  $\sigma_i$  values very close to the curve for slowly cooled samples. Clearly, the internal stress  $\sigma_i$  increased with increasing ageing time. As mentioned in the Introduction, this can be explained by the hypothesis that the amorphous phase of HDPE near the crystallites is still glassy at room temperature<sup>12</sup>. It is also clear from Figure 9 that addition of untreated glass spheres reduces  $\sigma_i$  compared to  $\sigma_i$  for unfilled HDPE, while the silane treatment increases  $\sigma_i$ , due to improved adhesion between the two phases. This has been discussed in detail elsewhere<sup>19</sup>.

The most striking feature of the curves shown in Figure 9 is that for unfilled HDPE the  $\sigma_i(\epsilon_0)$  curves coincide at strains above 4% irrespective of the ageing time. In this sense the ageing is erased by a high deformation (or a high initial stress). This is in line with the effect of the stress on the creep curves, i.e. only at high applied stresses is an effect on ageing behaviour noted. Note that with regard to the stress-strain behaviour (Figure 1) this certainly is high deformation. The curves are well beyond any initial linear part of the  $\sigma(\epsilon)$  curve for HDPE. For HDPE containing untreated glass spheres the  $\sigma_i(\epsilon_0)$  curves for different ageing times coincide at a lower strain,  $\approx 2.5\%$ . Thus, in this case also, an erasing of the ageing effect by high stresses is expected. When the glass spheres are silane treated, the composites become more brittle and the strains attained here appear to be too low for the different  $\sigma_i(\epsilon_0)$  curves to coincide.

## CONCLUSION

A high applied stress appears to erase the effect of ageing time on the creep and stress relaxation behaviour of HDPE. This is analogous to the observation made for amorphous polymers. However, only at quite high stresses do the stresses applied markedly retard the ageing process, i.e. at deformations significantly beyond any approximately linear initial part of the stress-strain curve. Due to the similarity to the results obtained for amorphous polymers the results obtained here can be interpreted in terms of the free volume hypothesis<sup>1</sup>. However, this does not preclude the possibility that changes in the relaxation strength can occur during ageing. On the contrary, this can be expected for a semicrystalline polymer like polyethylene<sup>12</sup>.

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