Polymer 44 (2003) 1171–1179

polymer

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# Kinetics of ageing and re-embrittlement of mechanically rejuvenated polystyrene

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**Abstract**

Pre-deforming polystyrene by rolling results in elimination of strain softening and induces ductile deformation behaviour in a subsequent tensile test. However, both yield stress and strain softening recover in time as a result of ageing, resulting in renewed brittle failure behaviour. The kinetics of this process is addressed in this paper. Although the process of recovery of yield stress and strain softening shows no molecular weight dependence, the time-scale of renewed brittle fracture after rejuvenation does. Any localisation of strain can only be stabilised if the molecular network can transfer sufficient load. For relatively low molecular-weight polystyrene, the load bearing capacity is already exceeded at short ageing times, whereas for higher molecular-weight grades this takes longer. Since the creep compliance and shift-rate of mechanically rejuvenated polystyrene shows a pronounced increase as compared to thermally rejuvenated polystyrene, the segmental mobility in the mechanically rejuvenated samples has increased, despite a lower free volume. This indicates that a new explanation for ageing should be postulated, which is discussed.

*Keywords:* Mechanical rejuvenation; Ageing kinetics; Polystyrene

## 1. Introduction

Crazing, shear yielding, and necking are the mechanisms that generally dominate the macroscopic deformation behaviour of glassy polymers. Which of these localisation phenomena prevails is determined by the post-yield behaviour of the polymer, i.e. the strain softening and the strain hardening. Most striking example here is the difference in macroscopic behaviour of polystyrene and polycarbonate. Polystyrene exhibits substantial strain softening and only a weak contribution of the strain hardening. Localisations of strain, induced during the initial stage of deformation, cannot be stabilised and evolve almost without limits. As a result this extreme strain localisation leads to the initiation of crazes, as postulated by Kramer [1] and, ultimately, macroscopic failure. Polycarbonate, on the other hand, exhibits only a moderate amount of strain softening and a stronger contribution of the strain hardening. Localised plastic deformation zones, induced by strain softening, can be stabilised and transfer deformation to other regions in the material. As a result a larger volume participates in the deformation and shear yielding and stable necking are observed in a tensile test. Despite this, also polycarbonate will initiate crazes if a more severe localisation is introduced by changing the geometry of the test, e.g. by adding a notch.

The amount of strain softening can be altered by thermal treatments, like quenching and annealing. Small changes in yield stress can have major consequences for the macroscopic deformation behaviour. For instance, a subtle increase in strain softening, induced by annealing, leads to severe localisation of strain and brittle fracture in a relatively low molecular weight polycarbonate [2,3]. Other examples include the observations of Cross and Haward [4], who showed that by rapid cooling of PVC a reduction in the strain softening results in homogeneous deformation in a subsequent tensile test, whereas slowly cooled samples exhibit necking.

The most effective way to influence strain softening is by pre-deformation. Bauwens [5] demonstrated that by alternating bending of PVC samples, prior to tensile testing, necking was suppressed. Similar experimental observations were reported by G'Sell [6] for epoxy and Aboulfaraj et al. [7] for polycarbonate, respectively. Mechanical pre-conditioning of polycarbonate was also performed by Govaert

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PII: S0032-3861(02)00863-7

et al. [8] and Tervoort et al. [9]. Cylindrical tensile bars were torqued to and fro, and subsequently subjected to a tensile test. The original moderate amount of strain softening was virtually eliminated by this pre-conditioning and localisation of strain was prevented, resulting in homogeneous deformation without neck-formation. Pre-deformation can also be performed by rolling, as was reported first by Gruenwald [10], who observed a remarkable increase in toughness for polycarbonate, which could again be erased upon annealing at temperatures below $T_g$. Broutman and co-workers adapted this procedure and performed similar studies on a number of amorphous polymers [11–13], excluding polystyrene. In these studies a sharp increase in Izod impact strength was found at an optimum degree of thickness reduction (PC $\approx$ 5%, PVC $\approx$ 30%), while at larger reductions, the impact strength decreased again. The authors claimed the slight molecular orientation and the residual stresses induced to be the origin of this toughness enhancement. However, the fact that annealing well below the glass transition temperature did erase the toughness enhancement whereas the molecular orientation did not disappear [13], questions their explanation. The influence of residual stresses remained unclear since during annealing a correlation between the relaxation of the residual stresses and the sudden transition from ductile to renewed brittle fracture was not observed.

A similar rolling procedure was followed by Govaert et al. [8] to pre-deform glassy polystyrene. Consistent with the previous studies, a remarkable increase in ductility was observed after a thickness reduction of approximately 30%. The tremendous reduction in strain softening, observed after rolling, was made responsible for the prevention of strain localisation in a subsequent tensile test. This interpretation is consistent with observations of pre-conditioning of polycarbonate by torquing [8,9] and the observations of Broutman that the ratio yield stress (maximum in stress) and draw stress (stress at which the polymer is drawn) approaches unity after a certain degree of rolling [11].

A common factor in these studies is the transient nature of the toughness enhancement. In time, either at room temperature or at elevated temperatures (below $T_g$), the ductility or impact strength decreases again. Govaert et al. [14] showed that the renewed brittle fracture in polystyrene occurred at the same time scale as the recovery of the yield stress and strain softening. For polycarbonate a similar recovery was observed although on a much longer time-scale [15,16]. Since the factors that influence this transient behaviour are unknown, the actual study was designed. Tensile bars of polystyrene were pre-deformed by rolling and, subsequently, subjected to a uniaxial tensile test after certain periods in time (ageing times) after mechanical rejuvenation, allowing examining the kinetics of the recovery of the yield stress and strain softening. At each ageing time step, 50 tensile tests were performed to determine the probability to failure as function of the ageing time.

Moreover, to investigate any differences in the state after thermal rejuvenation and mechanical rejuvenation by rolling, the creep behaviour was studied.

## 2. Experimental section

### 2.1. Materials

The materials used were three commercial grades of polystyrene, N5000 (Shell), Styron™ 648 and 660 (Dow Chemical). Gel permeation chromatography (GPC) was performed to determined their molecular weights and molecular-weight distributions. In Fig. 1 the weight fraction of the log(molecular weight) is given as function of the molecular weight.

The weight-averaged and number-averaged molecular weights, given in Table 1, increase in the sequence of Styron™ 660, N5000 and Styron™ 648. The dispersities of the Styron™ grades are similar, around 3, whereas for the N5000 grade it is slightly higher: 3.5.

For the uniaxial compression tests, cylindrical samples (∅6 mm × 6 mm) were machined from plates ($160 \times 160 \times 9\ \mathrm{mm}^3$), which were compression moulded from granular material at a temperature of 190 °C. First, the materials were heated for 15 min and next compressed during 5 min in five steps of increasing force, up to 300 kN. In between the steps, the force was released to allow for degassing. Afterwards the mould was placed in a cold press and cooled to room temperature at a moderate force (100 kN). All tensile specimens were prepared via injection moulding, shaped according to ISO 527.

### 2.2. Treatments

Quenching of tensile bars was performed after heating of the samples in an oven at 110 °C (just above $T_g$) for half an hour and, subsequently, rapid cooling in liquid nitrogen. Mechanical pre-deformation of the tensile bars was performed by rolling, along the length axis, on a two-roll mill (diameter of 45 mm), more extensively described in

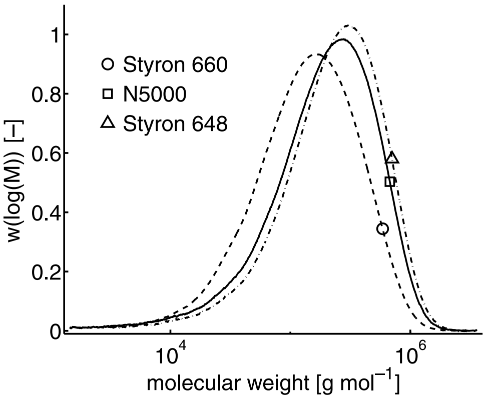

Fig. 1. Molecular-weight distribution of the PS grades used in this study.

Table 1
Weight-averaged and number-averaged molecular weights of the PS grades used in this study

| | $M_w$ (g mol$^{-1}$) | $M_w$ (g mol$^{-1}$) | $M_w/M_n$ |
|---|---|---|---|
| Styron™ 660 | 203 401 | 65 822 | 3.09 |
| N5000 | 281 461 | 79 968 | 3.52 |
| Styron™ 648 | 318 490 | 107 215 | 2.97 |

Govaert et al. [14]. During rolling, a thickness reduction of approximately 32% was achieved while the length of the tensile bars increased by 36%. Since the rolling procedure induced a temperature rise of approximately 35 °C, cooling of the samples to room temperature was allowed prior to testing.

### 2.3. Mechanical testing

In uniaxial compression, performed on a servo-hydraulic MTS Elastomer Testing System 810, cylindrical specimens were compressed, under strain control, at a constant logarithmic strain rate of $10^{-2}$ s$^{-1}$ between two parallel, flat steel plates. The friction between the sample and steel plates was reduced by an empirically optimised method. Onto the sample a thin film of PTFE tape (3M 5480, PTFE skived film tape) was applied and the surface between steel and tape was lubricated with a soap-water mixture. During the test no bulging or buckling of the sample was observed, indicating that the friction was sufficiently reduced.

Tensile test were performed on a Zwick Z010 tensile tester, at a constant linear strain rate of $10^{-3}$ s$^{-1}$, at distinct ageing times after pre-deformation. At each ageing time, 50 tensile tests were performed for each grade to obtain statistically relevant data. Besides the stress–strain curve, the yield stress and draw ratio at which fracture (ductile or brittle) occurred, were recorded. In this respect 'ductile' is defined when a tensile bar exceeding 6% macroscopic strain (well beyond the yield point). The tensile creep experiments were performed at TNO Industrial Technology on an in-house built tester [17]. Since the requirements for the tensile creep specimens differ from ISO standards, only the waisted sections of the pre-deformed tensile bars were used. Loading, following the procedure described by Struik [17], was performed at distinct ageing times after mechanical or thermal rejuvenation. The shortest ageing time was 1350 s, doubled every next ageing time till 21600 s in the last time step. During the tests the creep compliance was measured at a constant temperature of 40 °C.

### 2.4. Density measurements

The density of the materials was measured before and after the pre-deformation on a Davenport density gradient column filled with a NaBr/water solution kept at a temperature of 23 °C. Calibration spheres were used and the density gradient over the column was 0.020 g cm$^{-3}$ (ranging from 1.040 to 1.060 g cm$^{-3}$) over a length of 700 mm. Since the reading accuracy is at least 1 mm, the resolution on the density measurements is $3 \times 10^{-5}$ g cm$^{-3}$. The samples used for these measurements were cut from the tensile bars and polished to prevent adhesion of air bubbles to the surface, which could influence the results.

## 3. Results

### 3.1. Intrinsic behaviour

In uniaxial compression the intrinsic deformation behaviour, i.e. deformation without localisation phenomena like shear banding, necking and crazing, was determined. As expected, see Fig. 2, the molecular-weight (distribution) has no significant influence on the intrinsic behaviour. However, properties that are influenced by the molecular weight are related to failure. Following Flory's [18] approach, Merz et al. [19] and McCormick et al. [20] reported that the tensile strength of polystyrene increases with increasing $M_n$. Since fracture phenomena are absent in uniaxial compression tests, this influence could not be observed.

### 3.2. Pre-deformation

Pre-conditioning or pre-deformation has major consequences on both the intrinsic properties and macroscopic deformation behaviour of amorphous polymers [10,11,14]. In Fig. 3, the deformation behaviour of polystyrene N5000 in tension, compression, and after rolling are presented. In this figure the absolute values of the stress and strain are plotted on the axis to enable comparison of both tensile and compression tests. When injection-moulded bars of polystyrene are subjected to a uniaxial tensile test, they exhibit crazing and brittle macroscopic fracture already in the apparent elastic region. Strains and stresses, which are typically reached in such a test, are in the order of 1–2% and 40–50 MPa. The intrinsic behaviour of polystyrene,

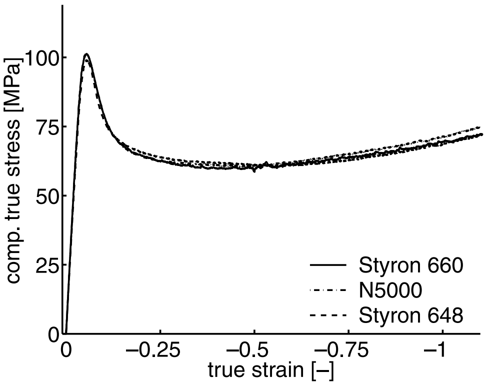

Fig. 2. Intrinsic deformation behaviour of the three PS grades, measured in compression.

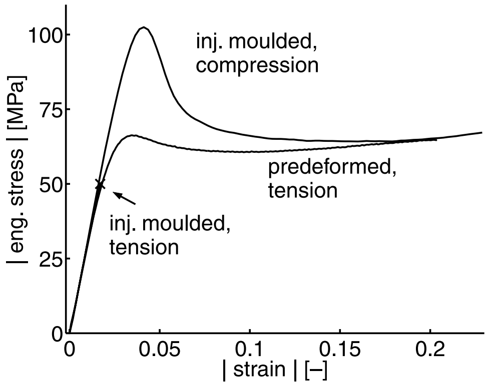

Fig. 3. Deformation of PS in tension, compression and pre-deformed in tension.

represented by the compression curve, is characterised by a high yield stress, a pronounced strain softening and weak strain hardening. The effect of pre-deformation is quite clear from Fig. 3: strain softening is virtually eliminated and ductile deformation behaviour is observed, even in a tensile test, reaching macroscopic strains of 30%.

Although the samples are slightly oriented as a result of the pre-deformation, the observed ductility of polystyrene originates from the reduction in strain softening and not from the molecular orientation. This conclusion is substantiated by two facts. First, Broutman et al. [11,12] showed, using an identical rolling procedure on polycarbonate, that the improved impact toughness is only slightly influenced by the relative angle of the rolling direction and the test direction. Second, the enhanced ductility is of transient nature, see below, whereas the induced molecular orientation is permanent at room temperature on this time scale.

To investigate the transient behaviour of this ductility, tensile tests are performed at distinct ageing times, see Fig. 4. In these tests, apart from the stress–strain curve, the yield stress and strain to break are recorded. In time, the yield stress increases, see Fig. 4, and strain softening is, consequently, restored, whereas the large strain behaviour remains unchanged. Approximately 2 days after pre-deformation, renewed brittle fracture is observed for the PS N5000 grade.

The yield stress increases linearly on a logarithmic time-scale with ageing time, see Fig. 5. Each marker represents the average value of 50 tensile tests. Since recovery of the yield stress, and thus of strain softening, displays a behaviour similar to physical ageing and proves to be independent of molecular weight, it can be ascribed to relaxation of the polymer chains on a segmental scale.

The obtainable draw ratio is strongly dependent on the ageing time, shown in Fig. 6 for PS N5000. The majority of the tensile bars exhibits ductile deformation behaviour ($\lambda > 1.06$) up to 5 h after pre-deformation, whereas after 48 h every single tensile bar fractures in a brittle manner.

From Fig. 6(a), the fraction of brittle fractures (defined here as the fraction of bars with a draw ratio smaller than 1.06) observed, are determined at each ageing time. Following an identical procedure for the other grades, and representing these data versus the ageing times, gives the probability to brittle fracture as function of ageing time (Fig. 6(b)). This probability to failure proves to be dependent on the molecular weight. For the low molecular weight grade, the majority of the tensile bars display brittle fracture at relative short ageing times, i.e. after 1 h. With increasing molecular weight, the renewed brittle fracture is postponed: it takes 2 days for N5000 and 1 week for Styron™ 648, respectively.

Since the intrinsic behaviour, Fig. 2, and the kinetics of yield stress and strain softening recovery with ageing, Fig. 5, are identical for all grades, the difference in macroscopic deformation behaviour after ageing must originate from the influence of molecular-weight, more specifically $M_n$ on the breaking stress, Merz et al. [19] and McCormick et al. [20]. In Fig. 7 the influence of $M_n$ on the deformation behaviour is illustrated.

Localisations of strain, induced by an increased strain softening, evolve in the same way for all materials. Strain localisation can only be stabilised if the stress, or the force, which can be transferred by the polymer network in the localised plastic zone is sufficiently high in order to exceed the yield stress of the surrounding material. However, the

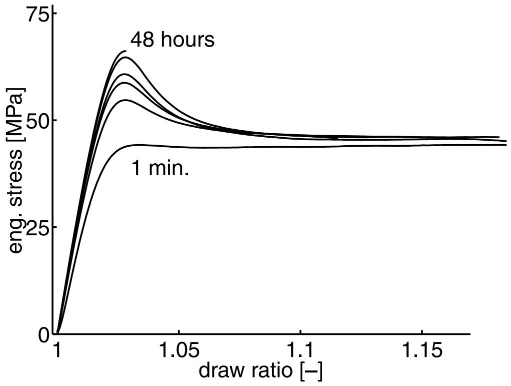

Fig. 4. Sequence of tensile tests on PS N5000 at distinct ageing times after rolling: renewed brittle fracture after 48 h is observed.

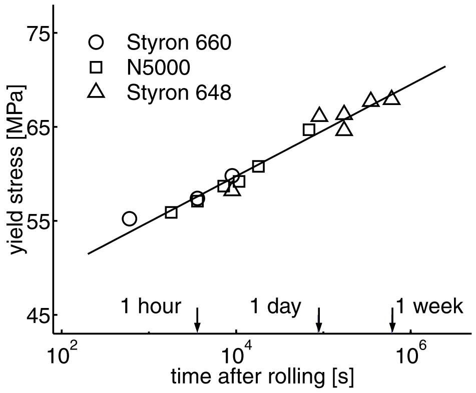

Fig. 5. Kinetics of the yield stress recovery after pre-deformation.

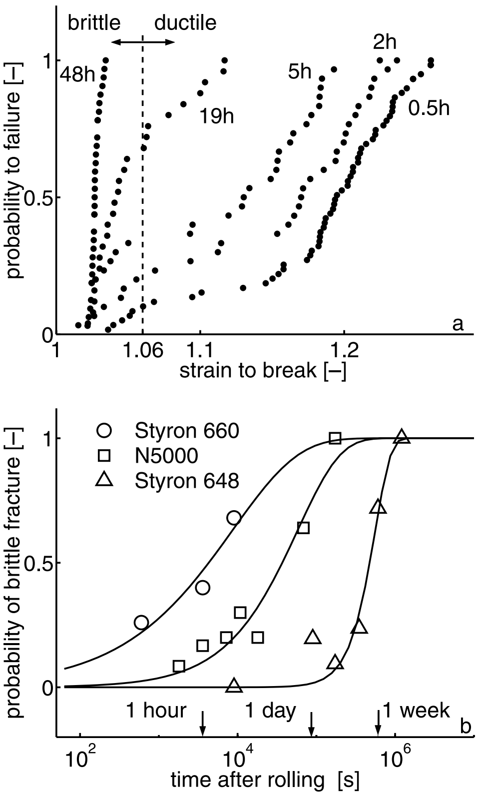

Fig. 6. Probability to brittle failure: decreasing strain to break for N5000 with increasing ageing time (a) and influence of molecular weight (b).

polymer network can only be loaded up to a limited stress, the tensile strength. Hence, after a certain ageing time, the stress in the local plastically deformed zone required to surpass the recovered yield stress in the, yet, hardly deformed regions, exceeds the tensile strength. Since this tensile strength is related to $M_n$, both the recovering yield stress and the time-scale, at which fracture occurs, are dependent on $M_n$.

That intrinsic strain softening is dominant in the macroscopic response of polymers, provides another verification possibility, since strain softening is rate dependent [15,21]. Therefore, also a rate dependency of the ductile-to-brittle transition is expected, see Fig. 8. At 10 min after rolling, the specimen deformed at a strain rate of $10^{-4}\,s^{-1}$ exhibits no strain softening. Increasing the strain rate by 1 and 2 decades, results in an increase of yield stress and strain softening with 10 and 20 MPa, respectively, see Fig. 8(a).

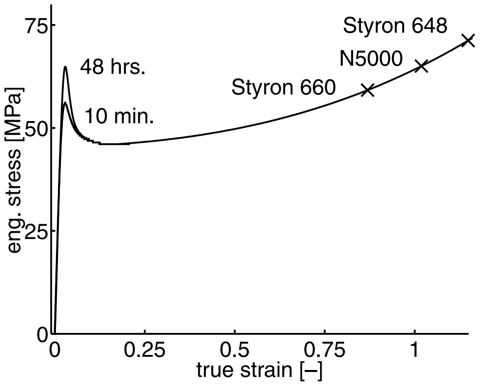

Fig. 7. Schematic representation of the intrinsic tensile response of the three PS grades at 10 min and 48 h after rolling.

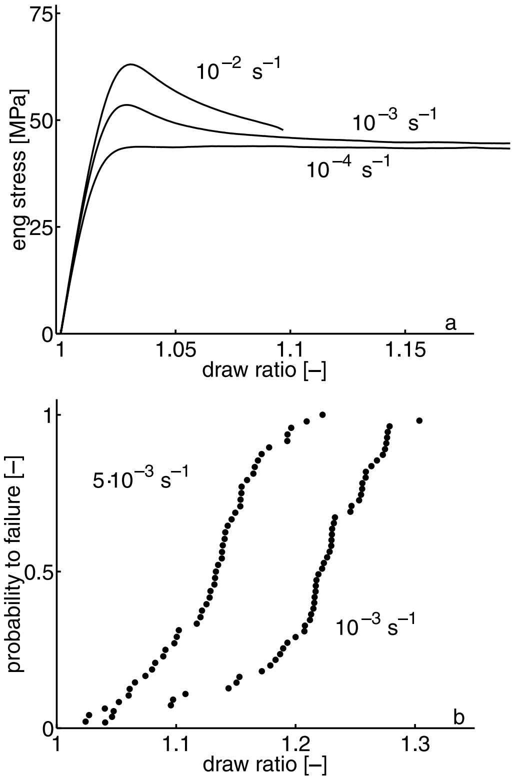

Fig. 8. PS N5000: influence of strain rate on the tensile behaviour at 10 min after rolling (a) and the accompanying distribution of draw ratios (b).

Fig. 8(b) shows that the probability to failure at lower draw ratios is unambiguously higher at a strain rate of $5 \times 10^{-3}\,s^{-1}$ compared to $10^{-3}\,s^{-1}$ at an ageing time of 10 min. This can be rationalised by the fact that at a higher strain rate, resulting in more strain softening, the maximum tensile strength of the polymer network is earlier exceeded, confirming the explanation given above.

## 4. Creep tests

The kinetics of recovery of the yield stress and strain softening are independent of the molecular weight and resembles the kinetics of an ageing process. The question rises whether the typical time-scale of this progressive ageing equals that of physical ageing after thermal rejuvenation and whether mechanical rejuvenation can be interpreted as an ultimate quenching procedure.

It is well known that physical ageing, and the accompanying structural rearrangements of the molecules, have consequences for the small-strain visco-elastic and time-dependent behaviour of amorphous polymers [17,22].

Therefore, creep tests are performed at distinct ageing times after rejuvenation (both thermal and mechanical).

During the creep tests, the compliance of the samples is measured. For creeping materials, the compliance rises as time passes. The evolution of this compliance was described by a stretched exponent [17] and reads

$$D(t) = D_0 \exp\left(\frac{t}{a_e \tau}\right)^{\gamma} \tag{1}$$

where $D_0$ is the initial compliance, $t$ the creep time, $\tau$ the relaxation time and $a_e$ the shift factor. As shown by Struik [17], the creep curves are super-imposable and hence the shape of the curves is not influenced by physical ageing. This super-imposability and the fact that the creep curves stretch over many decades, suggest that the process of creep can be described by a spectrum of relaxation times. This has led to the introduction of a shift factor ($a_e$) by which the relaxation time is multiplied. It was shown that many polymers age in a similar way and that ageing can be characterised by a double-logarithmic shift rate, $\mu$, which is defined as

$$\mu = -\frac{\mathrm{d}\log a_e}{\mathrm{d}\log t_e} \tag{2}$$

where $t_e$ is the ageing time.

Fig. 9(a) and (b) shows the creep behaviour of thermally and mechanically rejuvenated polystyrene (N5000), respectively. During creep at constant force, the strain increases in time resulting in an increase in creep compliance. For the quenched material the creep compliance increases slightly from 0.396 to 0.465 GPa$^{-1}$, for the shortest ageing time, i.e. 1350 s after quenching. As the ageing time rises, a shift along the logarithmic time axis to longer creep times is observed, consistent with observations reported in literature for many amorphous polymers [17].

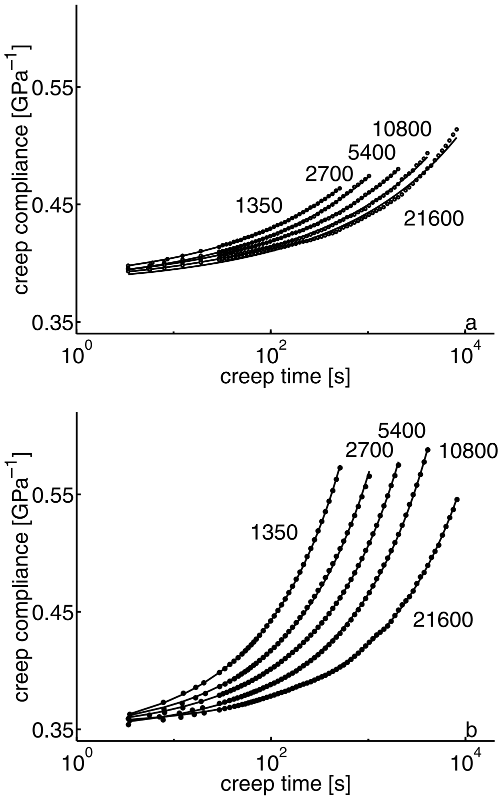

Fig. 9. Creep compliance of PS N5000 as function of creep time at distinct ageing times (in s) for thermally rejuvenated PS (a) and mechanically rejuvenated PS (b).

The creep compliance curves for rolled polystyrene, shown in Fig. 9(b), deviate considerably from the curves of the quenched material. Initially a lower creep compliance is measured, indicating that the stiffness for the samples after pre-deformation was initially higher, which can be rationalised by the fact that slight orientation of the polystyrene molecules during the rolling procedure occurred. Moreover, as was shown by Broutman et al. [11,12] and will also be shown later in this paper, the macroscopic density increased after rolling, resulting in a closer packing of the chains.

The creep compliance of the pre-deformed samples increases faster with creep time; for the shortest ageing time an increase from 0.363 to 0.573 GPa$^{-1}$ is observed, which is three times as much than for the quenched material. This pronounced creep behaviour indicates that the segmental mobility of the polymer chains in the mechanically rejuvenated material is relatively large compared to that of the quenched material. This does not necessarily imply that rejuvenated state of both materials is different, since it is expected that the elimination of strain softening is accompanied by a higher degree of segmental mobility.

A characteristic feature of creep curves is the horizontal shift factor by which they can be shifted along the logarithmic time axes to form a master curve. As shown in Fig. 10, these shift factors prove to be quite different for the thermally and mechanically rejuvenated materials. The shift factor is proportional to the ageing time for both materials but their slopes, a characteristic measure for creep, differ quite remarkably. The shift rate for the pre-deformed material is 50% larger than for the quenched material, that has a shift rate of 0.69, consistent with values reported by Struik [17].

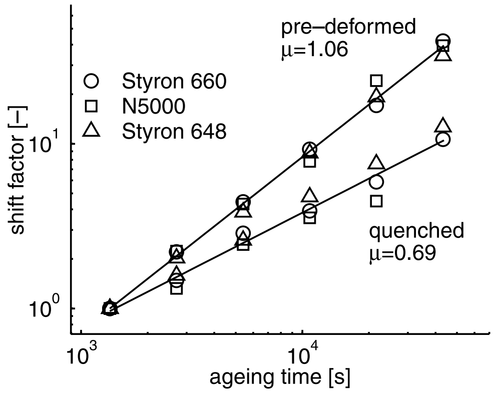

Fig. 10. Shift factor of thermally rejuvenated and mechanically rejuvenated PS N5000 as function of ageing time.

These results suggest that the mechanically rejuvenated state achieved by pre-deformation is quite different from the state reached after thermal quenching. This also gives rise to the question whether the relaxations on a molecular scale, involved in progressive ageing after pre-deformation, are different from those after quenching. Answering this question, requires knowledge of the processes active on a molecular scale while strain softening evolves during ageing.

## 5. Density measurements

Classically the process of physical ageing, and the accompanying changes in properties, are attributed to changes in free volume. This is explained by the fact that a reduced free volume lowers the mobility on segmental scale, and results in, for instance, an increased modulus and yield stress [17]. Since yield stress and strain softening are inherently coupled, this would imply that in a rejuvenated state of reduced strain softening the free volume should be higher and thus the macroscopic density should be lower. To investigate this, the densities of the PS grades are measured, before and after mechanical rejuvenation. Interestingly, these measurements show an opposite effect, summarised in Table 2, and the density after mechanical rejuvenation is higher than prior to this treatment for all grades. Although the differences are small, they are certainly significant taking into account the accuracy of the density gradient column used (the differences are 10 to 40 times as large as the accuracy of the measurement).

Similar observations were done by Broutman et al. [11, 12]. They applied an identical procedure for the pre-deformation of various other polymers, like PC, ABS and PVC, and reported an increase in density after rolling of their specimens. Consistent in this respect are the results reported by Xie et al. [23], who found an increased density, measured by means of positron annihilation lifetime spectroscopy (PALS), during uniaxial compression tests. For such a test it is known that the strain softening is strongly reduced and even eliminated [24].

## 6. Discussion

During processing of polymers, generally rapid cooling from above the rubbery to the glassy state takes place. When passing the glass transition temperature, the segmental mobility of the polymer chains is drastically reduced and hence molecules are not in thermal equilibrium anymore and their occupied volume is larger than the actual equilibrium volume. In time, with ageing of the material, the limited segmental mobility, which the molecules possess, causes volume relaxation and thus reduction of the free volume. Due to physical ageing also an increase in the yield stress and concurrent strain softening is observed. The question is, however, whether the classical free volume theory can account for all these effects.

Table 2
Density of PS grades before and after pre-deformation

| | Density before (g cm$^{-3}$) | Density after (g cm$^{-3}$) |
|---|---|---|
| Styron™ 660 | 1.05112 | 1.05145 |
| N5000 | 1.05118 | 1.05137 |
| Styron™ 648 | 1.04968 | 1.05080 |

If with physical ageing the reduction in free volume leads to a reduced segmental mobility and, consequently, changes in properties, this would imply that in a rejuvenated state the mobility is enhanced and the density decreased due to an increase in free volume. The density measurements presented here, which are consistent with similar experiments of Broutman et al. [11,12], show an increased density after mechanical rejuvenation, the treatment that results in the most extreme, reversible reduction of the yield stress. These observations are supported by those of Xie et al. [23] and Hasan et al. [24]. These experimental observations question the mechanism proposed by Struik that free volume is the governing parameter in physical ageing [17].

The question remains what the physical origin of strain softening is and how it relates to physical ageing. Therefore, a possible explanation that could account for the experimental observations is discussed. Since glassy polymers are in a non-equilibrium state after rapid cooling, in time these materials will pursuit a state closer to the equilibrium state. This drive for an energetically more favourable state, driven by primary and secondary interactions of the polymer chains, is accompanied by changes in physical properties. The interactions of the inter and intra-molecular forces between the polymer molecules can be captured in a concept of a potential energy landscape [25]. This potential energy landscape is defined as a distribution of valleys (energy minima), mountains (energy maxima) and mountain passes (saddle points) [26]. Since polymer chains still possess a certain degree of mobility on a segmental scale in the glassy state, this landscape is not static, but subject to dynamic processes dominated by vibrations within local minima and relaxation between local minima [26]. These dynamic processes lead to local reconfigurations of chain segments and, consequently, a slow loss of energy, deepening the valleys already present in the landscape. Malandro and Lacks [26] investigated by molecular dynamics simulation the influence of shear stress on this potential energy landscape of ductile glasses. They concluded that changes in the potential energy landscape, induced by shear, implied the disappearance of local energy minima, resulting in mechanical instabilities and discontinuous local stress drops. On a macroscopic level this stress drop becomes continuous and can be identified as intrinsic strain softening. Despite the simplicity of the model, it can account for the macroscopic stress–strain response of an amorphous glass in a qualitative way, including its temperature dependence.

Atomistic simulations of Utz et al. [27] confirmed this view point and showed that by ageing the macroscopic stress-drop increases. Moreover, they showed that plastic deformation can 'reverse' these ageing effects. Straining of an aged polymer glass therefore requires more energy than all the minima in the potential energy have to be overcome. Since by ageing these minima become deeper, more energy is required to establish yielding and hence the material exhibits more strain softening. The energy required to draw the material at large strains remains of course identical, as was shown in these atomistic simulations. After this 'pre-deformation' a renewed process of relaxation and strive for local minimisation of potential energy takes place and local minima in potential energy evolve again.

The enhanced mobility, observed in the creep experiments of Fig. 9, can be rationalised by the fact that by pre-deformation the material is taken to a higher energy state. If the minima in the potential energy landscape are levelled out, the chains possess more mobility and creep is facilitated. With ageing, the drive for minimisation of energy reduces the mobility and increases the yield stress and automatically the strain softening. Therefore, considering the intrinsic behaviour of amorphous polymers, a fair view point could be that the stress at which the network contribution takes over during deformation, observed in rapidly quenched samples (PVC) [4] or mechanically rejuvenated samples (see Fig. 3), can be regarded as the natural response of polymers. Thus, in time increasing yield stress, and, consequently, strain softening, should be regarded as the natural increase in resistance to flow of the polymer chains due to an increasing number of deeper energy minima in the potential energy landscape.

The drive for local energy minimisation must be interrelated to structural rearrangements of polymer chains. Since crystallisation is an effective way to reduce potential energy, some degree of local order in non-crystallisable polymers is not beyond imagination. From the early scattering studies, local order in glassy polymers is subject of controversy. Although the scattering patterns of glassy polymers like polystyrene and polycarbonate are very distinct, Mitchell and co-workers stated that any parallelism between chain segments must be minimal [28,29]. Recent studies, employing techniques like NMR, (FT)IR and atomistic simulations, do suggest the presence of some local order, however, on a much smaller scale [30–39]. It was shown by NMR studies that a preferential packing of molecules exists for glassy polycarbonate which consists of planar alignments of phenylene groups and parallel or perpendicular alignment of carbonate groups [33]. The presence of small-scale order in polystyrene is less well documented and most studies on NMR for polystyrene involve conformation changes [34,35,40–43].

Considering the structure of the polymer chains, a local order would certainly involve the (re-)arrangement of phenylene rings. As these rings in the side groups of polystyrene are quite mobile compared to the rings situated in the backbone of polycarbonate, this possibly accounts for the differences in kinetics of the yield stress and strain softening recovery between polystyrene and polycarbonate, see Ref. [15].

Further studies, using molecular modelling and the application of these experimental techniques on extreme materials, such as the mechanically rejuvenated polystyrene presented in this study, will be needed to substantiate the present discussion.

## Acknowledgements

The authors wish to acknowledge the financial support provided by the Dutch Technology Foundation (STW) (Grant EWT.3766).

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