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Temporary toughening of polystyrene through mechanical pre-conditioning

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Abstract

The post-yield behaviour of glassy polymers is governed by intrinsic strain softening followed by strain hardening. Intrinsic softening is the dominant factor in the initiation of plastic localisation phenomena like necking, shear band formation or crazing. Removal, or a significant reduction, of intrinsic softening can be achieved by mechanical or thermal pre-conditioning, and is known to suppress necking in tough amorphous polymers like polycarbonate and polyvinylchloride. Here, the effect of mechanical pre-conditioning on the macroscopic deformation of a brittle polymer, notably polystyrene, is studied. As a result of mechanical pre-conditioning, a 30% thickness reduction by rolling, the yield stress is decreased and the intrinsic softening drastically reduced, resulting in a more stable deformation behaviour yielding an increase in the macroscopic strain to break to approx. 20% as compared to 2% in the untreated samples. The effect observed is of a temporary nature, as, due to progressive ageing, the yield stress increases and intrinsic softening is restored on a time-scale of minutes. This indicates that the toughening is indeed caused by the removal of intrinsic softening, and not due to enhanced strain hardening related to molecular orientation induced by the rolling treatment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanical pre-conditioning; Intrinsic softening; Tensile behaviour

1. Introduction

The macroscopic deformation behaviour of glassy polymers is generally dominated by localisation phenomena like necking, shear band formation or crazing. This susceptibility to localisation is directly related to their intrinsic large strain behaviour, which can be studied in loading conditions that suppress localisation, e.g. uniaxial compression [1,2], or by using special experimental techniques that control the growth of localised deformation zones, e.g. a video-controlled tensile test [3].

The yield behaviour of glassy polymers is known to depend significantly on strain rate, temperature and pressure [4]. These influences are, however, less significant in the post-yield behaviour which is governed by two characteristic phenomena [3,5]. Immediately after the yield point the (true) stress tends to decrease with increasing deformation, an effect that is usually referred to as ‘intrinsic strain softening’. At large deformations, the softening effect is saturated and the true stress starts to rise again with increasing deformation. This ‘strain hardening effect’ has been subject of a number of studies in the past, e.g. [1,6,7], and is generally interpreted as a rubber elastic contribution by the molecular entanglement network.

Intrinsic strain softening is important in the initiation of strain localisation. As during softening the deformation is allowed to proceed at a decreasing level of the (true) stress, small stress variations will inherently lead to large differences in the local strain rate, thus forming nuclei for localised plastic deformation zones. In the absence of intrinsic softening, the deformation will be homogeneous if the strain hardening behaviour is large enough to compensate for the geometrical softening during a tensile test (Considère construction) [4,7]. Another theoretical, but numerical, study was performed on neck formation in plane strain extension by Wu and van der Giessen [8]. They showed that intrinsic strain softening always leads to strain localisation, whereas in the absence of softening strain localisation can be suppressed if the amount of strain hardening is sufficient. Experimental evidence is also available, Cross and Haward [9] used samples of quenched polyvinylchloride (PVC), that display no intrinsic softening, and observed uniform deformation in a tensile test whereas slowly cooled samples necked. An alternative method to remove the strain softening effect is based on the saturation of intrinsic softening by application of plastic pre-deformation (mechanical pre-conditioning). A classical example is the alternated

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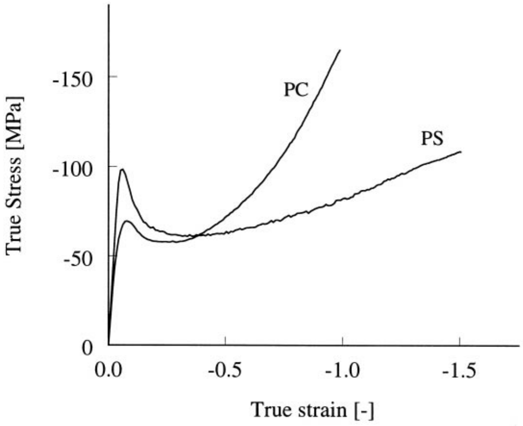

Fig. 1. Uniaxial compression curves of PC and PS at a strain rate of $10^{-2}\,s^{-1}$. True stress as a function of true strain ($\ln(\lambda)$).

bending procedure applied on PVC samples by Bauwens [10] that suppressed necking in a subsequent tensile test. Similar results were achieved by G'Sell [11] after plastic cycling in simple shear on polycarbonate (PC) samples, while in our laboratory axi-symmetrical samples were plastically cycled in torsion [12,13]. Subsequent mechanical testing on these 'rejuvenated' samples resulted in homogeneous deformation in both tensile and torsion loading. The application of this technique allowed for an accurate characterisation of the strain-hardening behaviour of PC [14].

All these experimental and numerical findings clearly indicate the dominant role of intrinsic softening in the localisation behaviour of glassy polymers. However, the experimental work was limited to polymers that are macroscopically tough and display necking, a moderate form of localisation. The question rises whether the same applies to amorphous polymers that are macroscopically brittle; e.g. polystyrene (PS) that shows much stronger localisation in the form of crazes. Although the exact conditions for craze formation are not yet completely understood, it is well established that craze initiation involves the unstable growth of a strongly localised plastic deformation zone leading to lateral stress-build-up and incipient cavitation [15–17]. Here we investigate whether this strong localisation behaviour, displayed by PS, can be rationalised by its intrinsic post-yield behaviour, and, furthermore, whether the macroscopic behaviour can be influenced by modification of the post-yield behaviour using mechanical pre-conditioning in the glassy state.

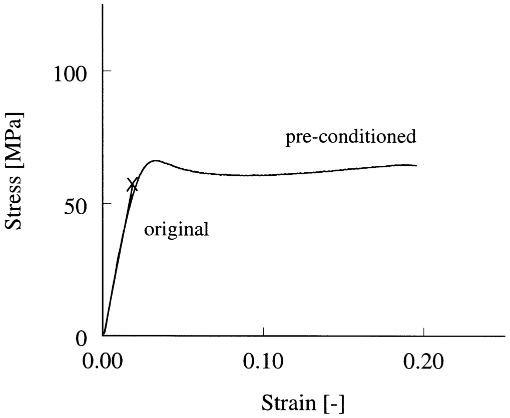

Fig. 2. Uniaxial tensile curves of untreated and mechanically preconditioned PS obtained at a strain rate of $10^{-2}\,s^{-1}$.

2. Experimental

The materials used were a general purpose polystyrene (PS, N5000), supplied by Shell and polycarbonate (PC, Lexan 161R) supplied by GE. Cylindrical samples for the compression tests, with a diameter of 6 mm and a height of 6 mm, were machined from compression moulded sheets. Tensile specimens were injection moulded, shaped according to ASTM D638.

Compression tests were performed on a MTS servo-hydraulic tensile/compression tester at room temperature and a strain rate of $10^{-2}\,s^{-1}$. In order to avoid barrelling of the compression samples, Teflon tape and liquid soap were applied between sample and compression plates. Tensile tests were performed on the same machine at a strain rate of $10^{-2}\,s^{-1}$. All tests were performed at room temperature.

The mechanical pre-conditioning treatment for PS consisted of rolling the tensile bars along the length axis, on a two-roll mill of 45-mm diameter. A thickness reduction of 32% resulted, and the length of the tensile bar increased with approximately 36%. Since rolling resulted in a rise in temperature of the specimens to approximately 35°C, they were allowed to cool down for a period of 10 min. Subsequent tensile tests were performed at time intervals of 10 min, after the mechanical pre-conditioning, to investigate the influence of progressive physical ageing.

3. Results and discussion

The compressive behaviour of brittle PS and tough PC are presented in Fig. 1 showing the true stress as a function of the true (logarithmic) strain. Compared to polycarbonate, PS displays a more pronounced strain softening and, related to its lower entanglement network density, a weaker strain hardening. When loaded in uniaxial extension, strain softening will always lead to strain localisation. The development of the deformation zone is determined by a delicate balance between the amount of strain softening and strain hardening. In the case of PC the moderate strain softening allows the network to stabilise the deformation zones and let them develop throughout the bulk of the material. In the case of PS the strong strain softening cannot adequately be compensated for by the low strain hardening, leading to much stronger localisation phenomena. This was visualised in a numerical study on the influence of the intrinsic

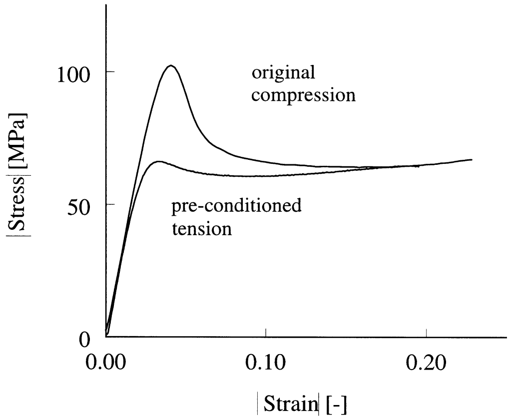

Fig. 3. Uniaxial tensile curve of mechanically pre-conditioned PS compared to the uniaxial compression curve of the untreated material.

post-yield behaviour on the evolution of the microstructure of a glassy polymer with voids by Smit et al. [18,19] showing the extreme differences between PC and PS.

The question rises whether, similar to PVC [9,10] and PC [11–14], the extreme localisation behaviour of PS can also be suppressed by removal or strong reduction of the intrinsic strain softening. The answer is shown in Fig. 2 where the results of a uniaxial tensile test on an untreated and on a mechanically pre-conditioned sample of PS are shown. As a result of the rolling treatment the material deforms homogeneously up to a strain to break of approximately 20%, compared to 2% for the untreated sample.

The influence of the mechanical pre-conditioning on the intrinsic deformation behaviour is shown in Fig. 3 where the uniaxial compression curve of the untreated material is compared to the tensile curve of the mechanically conditioned sample. The intrinsic softening has been strongly reduced as a result of the rolling treatment. With this strong reduction of strain softening, even the weak strain hardening of PS apparently is sufficient to stabilise the deformation in the vicinity of local stress concentrations and allow the plastic deformation to homogeneously spread over the bulk of the material.

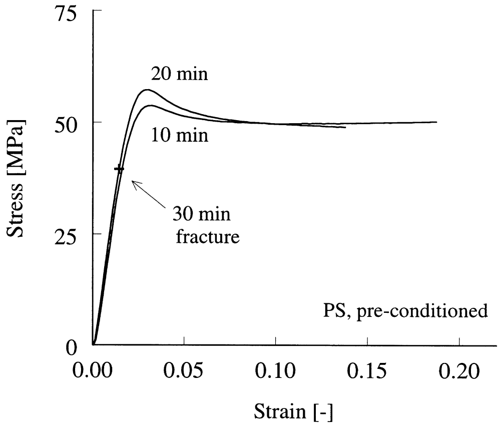

Fig. 4. Uniaxial tensile curves of PS at 10, 20 and 30 min after mechanical pre-conditioning.

It should be noted here that, as a result of the rolling treatment, the length of the tensile specimen has increased by 36%, implying that the treatment has also induced molecular orientation. This molecular pre-orientation will lead to enhanced strain hardening, which has been shown to induce macroscopic tough deformation (necking) in PS in the past by Ender and Andrews, who oriented PS samples above the glass-transition temperature [20]. In the present case, however, the toughening effect is predominantly related to the removal of intrinsic strain softening. This is supported by the results of tensile test on mechanically pre-conditioned PS samples at different time intervals after the treatment. The curves for 10, 20 and 30 min after rolling are shown in Fig. 4. After only 20 min a clear recovery of strain softening is observed, while after 30 min the material is brittle again. As the molecular orientation cannot be expected to change on this time scale (at room temperature), it is clear that the toughening observed must be solely attributed to the reduction of strain softening.

The recovery of strain softening, as depicted in Fig. 4, is in accordance with observations of Aboulfaraj et al. [21] on mechanically pre-conditioned epoxy. They employed the same technique as G'Sell [11], where the material is plastically cycled in simple shear. They showed that both quenched and mechanically pre-conditioned samples displayed an increase of the yield stress as a function of time. Typically, the kinetics and characteristic time scale was the same for both, whereas, compared to the quenched samples, the absolute level of the yield stress is always considerably lower after mechanical pre-conditioning. Although the origin of intrinsic softening is not yet completely clear, the observed increase of the yield stress, and simultaneous increase of strain softening, seems to indicate a relation to physical ageing processes (volume relaxation) that occur in the glassy state. With progressive physical ageing the specific volume decreases, leading to an increase of the elastic modulus, a decrease of the time dependence (age-shift) and an increase of the yield stress [22]. As the yield stress increases with ageing, intrinsic softening appears [23,24]. It is known that the effect of physical ageing can be 'erased' by heating the sample above the glass transition temperature (and allowing it there to reach the equilibrium state), followed by rapid cooling to the glassy state (quenching). In some glassy polymers, like for instance PVC, intrinsic softening completely disappears after this quenching from the rubbery into the glassy state [9]. On the other hand, there appears to be strong evidence that indicates that intrinsic softening cannot be completely explained in terms of free volume relaxation. The inability to explain intrinsic softening in experiments with a negative dilative strain (compression) is probably one of the strongest arguments. Xie et al. [25] measured a decrease of the actual free volume in PC under compression by means of Positron

Annihilation Lifetime Spectroscopy (PALS), whereas PC is known to display intrinsic softening in compression (Fig. 1). Also the observations of Aboulfaraj et al. [21] indicate the involvement of other factors. As mentioned, they found that the yield stress obtained during ageing of mechanically pre-conditioned epoxy samples was always considerably lower than that obtained in quenched samples, implying that erasure of physical ageing by heat treatment cannot be fully compared to that of mechanical pre-conditioning. The topic remains interesting and challenging for future research, including the possible relation between molecular structure and mobility of the entanglement network and the kinetics of strain softening recovery after mechanical pre-conditioning.

4. Conclusions

Mechanical pre-conditioning of PS by rolling results in a drastic reduction of strain softening leading to macroscopic ductile behaviour in uniaxial extension. Due to progressive physical ageing, the effect of the mechanical pre-conditioning is only temporary. Approximately 30 min after rolling, a pre-conditioned tensile bar of PS displays brittle behaviour again. Although mechanical pre-conditioning does not appear to be an industrially interesting route to toughen PS, it emphasises the key role of intrinsic strain softening in the localisation phenomena in amorphous polymers.

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