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Predictive modelling of the properties and toughness of polymeric materials

Part II *Effect of microstructural properties on the macroscopic response of rubber-modified polymers*

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The influence of microstructural properties on the macroscopic mechanical behaviour has been studied by finite element predictions of the response of different microstructures of polystyrene (PS) or polycarbonate (PC) containing voids or rubbery particles, subjected to unidirectional extension. The voids represent a low-modulus non-adhering dispersed phase. The rubbery inclusions, which are assumed to be pre-cavitated and perfectly adhering, idealise core-shell particles with a hard rubber shell and a soft non-adhering or pre-cavitated core. The predictions show that the inclusion properties strongly affect the averaged post-yield response of the heterogeneous systems. Especially the post-yield strain softening can be eliminated by the introduction of voids in PC or rubbery particles in PS. Since macroscopic strain softening is believed to be the main cause of catastrophical stress or strain localisations, the softening elimination is believed to be primarily responsible for toughness enhancement of the polystyrene or polycarbonate systems. The results and experiences are extrapolated in order to explain the influence of the absolute length scale of a sub-micron sized morphology on the macroscopic behaviour, especially toughness. Two potential sources of particle-size effects are presented that may result in a stabilised, and thus tougher, macroscopic mechanical response, i.e. the yield stress reduction near a surface or interface because of a locally enhanced mobility of the polymer segments, and the temporary excessive hardening because of a sufficiently small size of the yield zones which results in a reduced effective entanglement distance. The paper concludes with a discussion on the extension of this knowledge to all other, for the moment amorphous, polymers.

1. Introduction

The addition of a fine dispersion of easily cavitating rubbery particles is a common route to improve the toughness of a polymeric material. The fundamental basis of the toughness enhancement is not really understood yet. Since this knowledge could provide new routes to improved materials, it is the objective of this research to understand and predict the relationship between microscopic and macroscopic deformation behaviour.

An enormous amount of experimental and modelling work has been reported, elucidating the relationships between macroscopic and morphological properties [1–6]. Some important results, which are relevant for the present approach, can be summarised as follows:

- The most important and widely accepted micromechanical deformation mechanisms responsible for the increase in fracture toughness of rubber modified systems are internal cavitation of the rubber particles and the formation of shear bands [7]: easily cavitating rubber particles promote shear banding, and the majority of toughness is achieved by the dissipation of energy through shear band formation. This has been demonstrated, for example, by Pearson and Yee [7, 8] for rubber-modified epoxies, Magalhães and Borggreve [9] for polystyrene-rubber blends and van der Sanden *et al.* [10] for polycarbonate/core-shell rubber systems.
- Shearing involves a (local) change of the state of deformation in the sample. This implies that shearing does not prevail for volumetric loads, for instance behind a notch tip. However, if the material contains voids, a macroscopic volume change can be achieved by the combination of void growth and shear band formation, suggesting that voids

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must either exist or be generated before the material is subjected to critical dilative stress states. This was convincingly proved by Jansen *et al.* [11, 12] using poly(methyl methacrylate) with 20 vol.% aliphatic, thus rubber, epoxy particles, which was brittle under impact conditions because of the absence of cavitation, and tough in case that the particles were pre-cavitated (see also [13]).

- Voids are usually generated in a controlled manner by the introduction of easily cavitating or non-adhering rubber particles. Internal cavitation of rubber particles, however, will hardly occur if the particles are too small [5, 7] or if the shear modulus of the rubber is too high. An acceptable explanation for the size dependence was given by Bucknall *et al.* [14], who introduced an energy-balance model (essentially an extension of Griffith's fracture model: the energy gained by releasing triaxial stresses through cavitation must exceed the energy needed to create new void surface) to show that the critical cavitation stress and thus cavitation resistance increases with a decreasing particle diameter. A widely accepted description of the shear modulus influence was given by Gent and Lindley [15] who deduced that a dilative stress of approximately 2.5 times the rubber shear modulus could result in an unbounded growth of an infinitesimally small pre-existing void, driven by the elastic energy stored in the rubber.
- The properties of rubber particles that are (pre-) cavitated have been shown to be important also for rubber toughening [16, 17]. Particles with a higher modulus, that cavitated before the matrix yielded, were observed to result in more shear band formation and thus in a larger plastic deformation zone. Pearson and Bagheri [17] suggested that this could be caused by the larger cavitational resistance of the particles, which allows an increased build-up of strain energy prior to cavitation of the particles; the released energy after cavitation enables the formation of shear bands to proceed in a higher rate and more shear bands can develop before the material crazes or fractures, resulting in a larger plastic zone.
- The size of the rubber particles also affects the macroscopic mechanical response of heterogeneous polymeric systems. Van der Sanden [18] showed for polycarbonate-rubber systems that a high toughness could be obtained by the dispersion of low volume fractions of small non-adhering core-shell particles rather than high volume fractions large, weak rubbery particles. Notice that the absence of adhesion for the core-shell particles or the inferior properties of the rubbery particles imply that the properties of the dispersed phase can not affect the macroscopic mechanical response under positive hydrostatic stress states (e.g. in uniaxial extension or behind the notch tip in an impact test).

The aim of this paper is to elucidate these mainly experimental results by detailed finite element predictions of the microstructural deformations and macroscopic mechanical responses of heterogeneous polymeric materials, subjected to unidirectional extension. In order to avoid the difficult modelling and numerical problems concerning cavitation processes, the heterogeneities used in the present study are assumed to be either voids or perfectly adhering voided rubber inclusions. The voids idealise low-modulus pre-cavitated rubbery particles subjected to positive dilative stress states. The perfectly adhering voided inclusions represent rather special core-shell particles with a relatively hard rubbery shell and a soft pre-cavitated core.

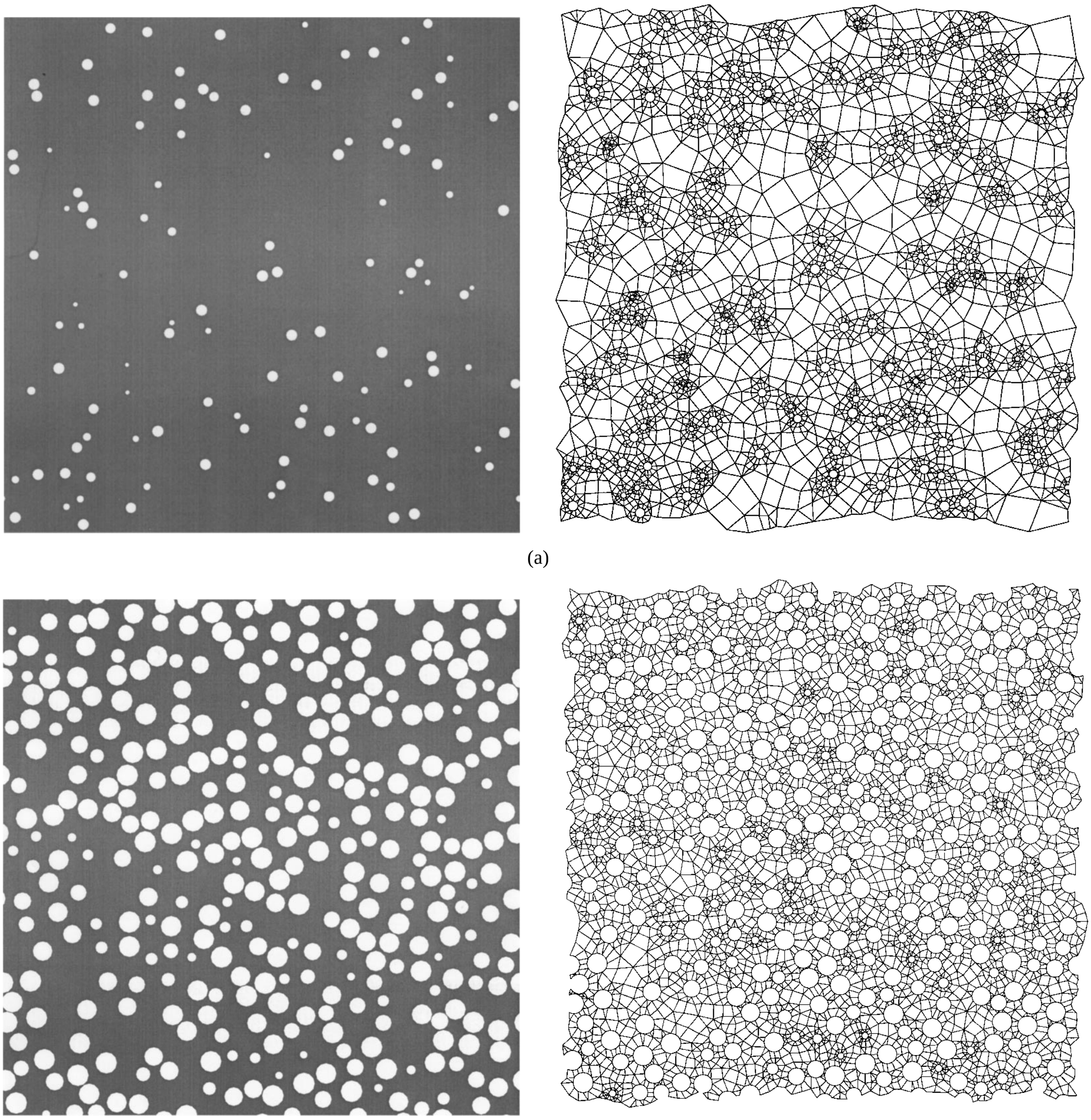
In Part I of this series [19] it has been shown that the differences in intrinsic mechanical properties of polycarbonate and polystyrene are the craze-initiation resistance and the stability of post-yield mechanical response. It has been demonstrated that the brittleness of polystyrene and toughness of polycarbonate can be explained from their distinct intrinsic mechanical behaviour. An earlier publication [20] demonstrated that the stability of the post-yield mechanical response of voided polycarbonate is extremely sensitive for the microstructural geometry: the addition of only 2.5 vol.% voids resulted in an elimination of strain softening and thus in a stable post-yield mechanical response. An additional study [21] showed that such a softening elimination is accompanied by a strong enlargement of the inelastic shear zone in hour-glass-shaped tensile specimens. It was suggested that stabilisation of the post-yield strain softening behaviour might be of paramount importance for the toughening mechanism.

Inspired by the results of the previous studies, this paper focuses on the effect of microstructural properties on the macroscopic post-yield mechanical response. The paper is organised as follows: First, a brief introduction of the modelling strategy is presented. Then, the most important results of the previous study on voided polycarbonate systems are summarised. The effect of the mechanical properties of the matrix material is investigated by comparing micro deformations and macroscopic responses of voided polycarbonate with those of voided polystyrene. Subsequently, the influence of the inclusion properties on the microscopic and macroscopic deformation of a polystyrene-rubber system is investigated. The possible mechanisms that might explain the relationship between particle size and macroscopic mechanical response (e.g. toughness) are discussed. Eventually, the results obtained so far are generalised towards arbitrary glassy polymeric systems and guidelines for toughness enhancement are given. The paper ends with the conclusions.

2. Modelling strategy

Heterogeneous materials are usually characterised by a complex morphological geometry on a very small scale, e.g. a continuous matrix with randomly distributed isolated μm sized particles. The prediction of the overall mechanical behaviour of such materials has been approached by the introduction of a substitute (finite element) model of the microstructure, a so-called representative volume element (RVE; see [22–25]). The averaged response of the RVE can be obtained by stating that the (local) macroscopic stresses and strains equal the volume averaged RVE stresses and strains [25].

The RVE concept, combined with the finite element method, has frequently been used to investigate the behaviour of heterogeneous polymers subjected to a certain load history. Most of these studies involved the analysis of geometrically simple unit-cell models, representing regularly distributed particles in a continuous matrix. In a previous paper [20], however, it was demonstrated that the predictive nature of those models can be severely affected by the presumed regularity of the microstructure. Two dimensional (plane strain) RVEs, representing microstructures of polycarbonate with different volume fractions of voids were used as a pilot study to investigate the effect of the microstructural irregularity on the macroscopic mechanical response. The RVEs were constructed by cutting a 3D cube randomly filled with equally sized spheres by a 2D plane. Typical examples of the RVEs, containing 2.5 and 30 vol.% voids, and their meshed counterparts are displayed in Fig. 1. In order to avoid erroneous boundary effects, it was assumed that an RVE deforms in a repetitive way identical to its neighbouring RVEs. Notice that this assumption implies that the microstructure next to the RVE deforms in approximately the same way as that in the RVE considered, which is often the case for small particles (see, e.g. [16, 26], and Cheng *et al.* [27] who investigated the morphological deformation in polymer blends before and after impact tests). The spatially repetitive deformation of the RVE could easily be enforced by applying appropriate periodic boundary conditions, see for more details [20, 25]. An intriguing and important consequence of the spatial periodicity assumption is that the whole RVE can be considered as a substitute material model for the heterogeneous system: it provides an unambiguous relationship between RVE averaged strains and RVE averaged stresses, and thus a non-closed form of the ‘constitutive’ relationship between macroscopic strains and macroscopic stresses,


(a)

(b)

Figure 1 RVE geometries and finite element models of two-dimensional spatial periodic RVEs, representing the morphologies of blends with (a) 2.5 vol.% and (b) 30 vol.% voids, where the voids idealise cavitating or non-adhering low-modulus rubber particles.

assuming that local macroscopic strains and stresses equal RVE averaged strains and stresses [25].

The local mechanical response of the glassy polymeric matrix is described with a so-called generalised compressible Leonov model, essentially a Maxwell model with an Eyring viscosity and a neo-Hookean spring in parallel. This model is, in fact, comparable to the well-known BPA model, proposed by Boyce *et al.* [28, 29]. Model and material parameters are discussed in Part I [19]. The generalised compressible Leonov model has shown to be able to describe and predict the yield and post-yield behaviour of glassy polymers accurately.

The microstructural models are loaded in unidirectional extension at low strain rates (0.01 s^{-1}). Because of the low strain rates prescribed, the deformation process can be assumed to be isothermal and thus any temperature rise through viscoplastic dissipation has been neglected. From the forces that were needed to prescribe the strains, the volume averaged true uniaxial stress is deduced (see References [20, 25] for more details).

3. Predicted response for voided polycarbonate

Upon loading the plane strain voided RVEs in uniaxial extension, the stresses and strains are distributed inhomogeneously inside the RVE, as illustrated in Fig. 2, where the equivalent strain ε_{eq} is defined as the scalar

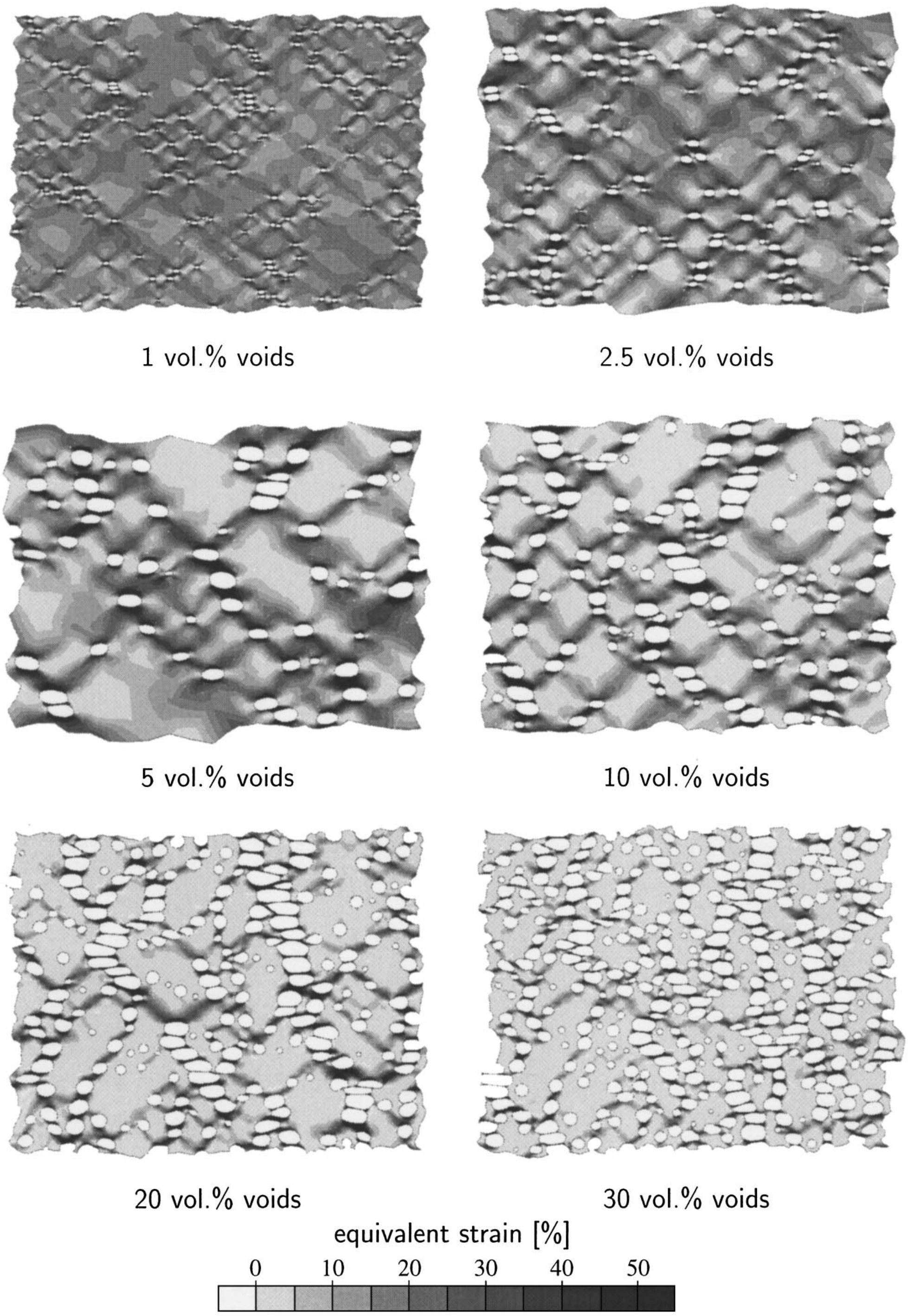


Figure 2 Contour plot of the equivalent strain in the uniaxially stretched polycarbonate RVEs at 20% global strain. The associated stress-strain curves are shown in Fig. 3.

norm of the logarithmic strain tensor $\boldsymbol{E}$ according to $\varepsilon_{\text{eq}} = \sqrt{\frac{2}{3}\boldsymbol{E}^d : \boldsymbol{E}^d}$. Yield preferably starts at places where two voids are accidentally close together. Once such a 'yield zone' strain hardens sufficiently, yield can be initiated at other locations. The total stress-strain response of the RVE can, however, be remarkably smooth, see Fig. 3. Note that already a few percent voids in polycarbonate causes a complete disappearance of strain softening in the averaged mechanical response. The vanishing softening originates from the irregular distribution of the voids, which induces that the global yielding takes place as a sequence of isolated 'yielding events' scattered over the whole sample, so-called sequential yielding. At each yield location the material subsequently strain softens and strain hardens. Since the overall response is the averaged behaviour over both stable and unstable deformation zones, the temporary unstable (strain softening) behaviour of the local deformation zones is, in this case, evened out in the global response [20].

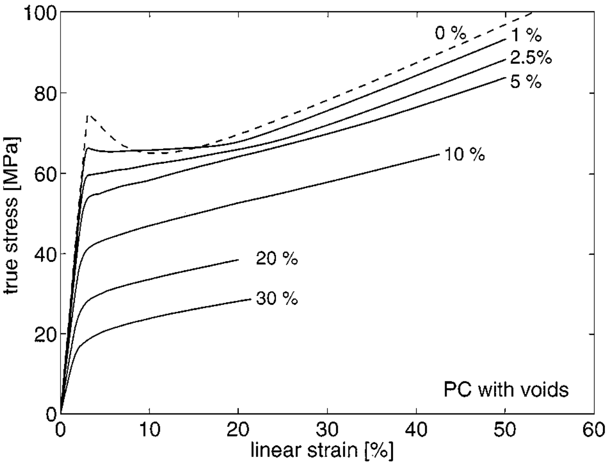


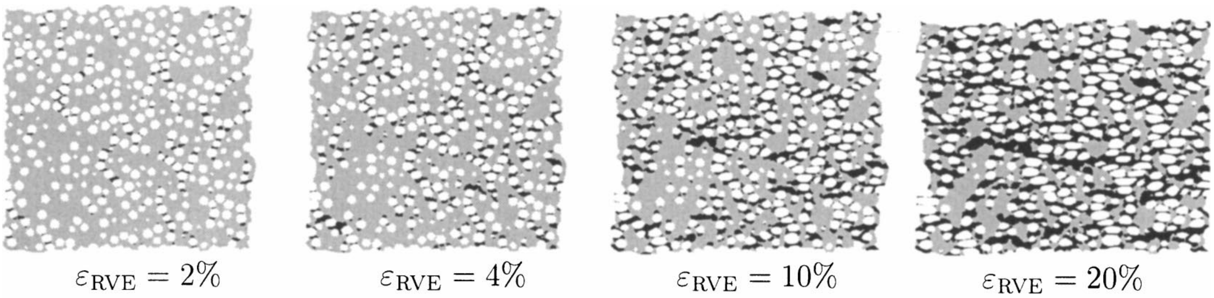
Figure 3 RVE averaged tensile stress versus linear strain for uniaxial tensile tests at $\lambda = 0.01\,\text{s}^{-1}$ on polycarbonate RVEs with different volume fractions voids.

It is emphasised that the results of the finite element analyses appeared to depend qualitatively on just the distribution of voids and not on the number of voids. Quantitatively, however, 300 or more voids were needed to obtain a reliable result for the 30 vol.% voided RVE.

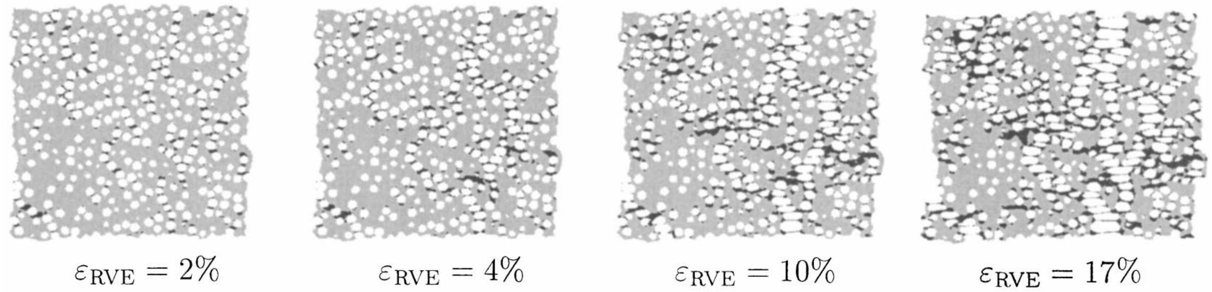
4. Voided polystyrene versus voided polycarbonate

Part I [19] reveals that the main differences between polystyrene and polycarbonate concern the post-yield behaviour and craze-initiation resistance: PS features more softening, less hardening and a lower craze-initiation stress than PC. If it is assumed that by optimisation of the volume fraction and size of the dispersed phase, the ligament thickness between the inclusions is such small (in the order of 30–50 nm) that crazes do not fit in between (see Kramer's analysis in the appendix of [18]), the problem of local matrix crazing can be circumvented. Encouraged by the results of the previous RVE study, the attention is focused on an RVE structure with 30 vol.% voids (see Fig. 1b), but now by mutually comparing polycarbonate and polystyrene behaviour, see also Fig. 5 in Part I of this series [19].

Fig. 4 shows the sequential yield processes in polycarbonate and polystyrene. Up to an overall strain of 4%, the plastic zones develop at approximately the same location and manner. Upon increasing the strain, however, distinct localisations develop in polystyrene, this in contrast to the situation for polycarbonate. The results suggest that for polystyrene the stabilisation of strain localisations is postponed too much by the


$\varepsilon_{\text{RVE}} = 2\%$ $\varepsilon_{\text{RVE}} = 4\%$ $\varepsilon_{\text{RVE}} = 10\%$ $\varepsilon_{\text{RVE}} = 20\%$

polycarbonate


$\varepsilon_{\text{RVE}} = 2\%$ $\varepsilon_{\text{RVE}} = 4\%$ $\varepsilon_{\text{RVE}} = 10\%$ $\varepsilon_{\text{RVE}} = 17\%$

polystyrene

Figure 4 Shear zones in uniaxially stretched polycarbonate and polystyrene RVEs with 30 vol.% voids at various deformation stages. The dark areas represent shear yielded zones. The corresponding stress-strain curves are depicted in Fig. 5.

unstable post-yield behaviour (strong softening and insufficient hardening). In fact, the stabilisation takes place at such high strains that the fibrils formed in the localisation zones are too thin to transfer any substantial force. This will inevitably lead to disentanglement or chain scission of the fibrils developed and eventually result into catastrophic failure for the overall response of the RVE. This is once more reflected in the post-yield mechanical responses of the RVEs as illustrated in Fig. 5: polystyrene still shows a distinct strain softening behaviour and remains unstable, while polycarbonate exhibits no softening at all. The conclusion from these results is that polystyrene is in fact too ductile, resulting in macroscopically brittle behaviour, caused by too strong, and thus catastrophic, localisations of the strains. So besides its apparent defect sensitivity and low craze resistance, polystyrene may also feature extreme localisations of deformation, leading to early failure at low macroscopic strains.

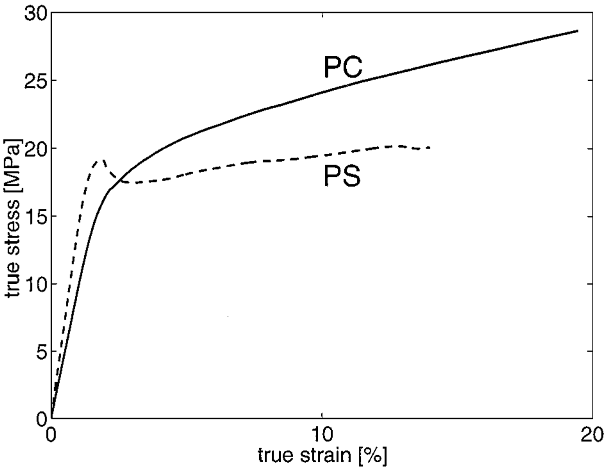
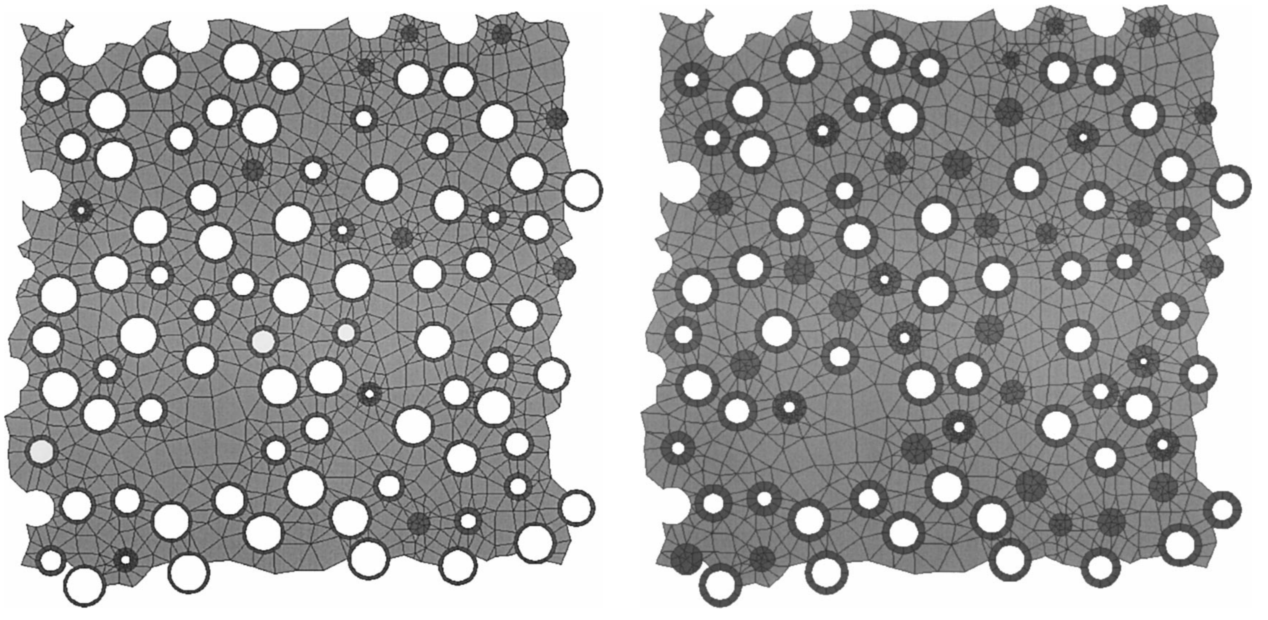


Figure 5 RVE averaged tensile stress for uniaxial tensile tests on RVEs with 30 vol.% voids, predicted for polystyrene and polycarbonate material behaviour.

5. Effect of the properties of pre-cavitated rubber particles

The influence of the properties of perfectly adhering rubber fillers on the overall mechanical behaviour of polystyrene blends is investigated by the analyses of RVEs with perfectly adhering voided rubber inclusions, representing rather special core-shell particles with a relatively hard rubber shell (30 MPa shear modulus) and a soft pre-cavitated core, see Fig. 6. As explained in the introduction, the particles are assumed to be pre-cavitated in order to reduce the averaged triaxial stresses and to avoid the modelling of cavitation processes inside the rubber. The rubber shell thickness is varied in order to examine the effect of inclusion properties on the macroscopic behaviour. The mechanical behaviour of the rubber is described by a simple neo-Hookean model $(\boldsymbol{\sigma} = G_{\mathrm{r}}(\tilde{\boldsymbol{F}} \cdot \tilde{\boldsymbol{F}}^{c})^{d} + \kappa_{\mathrm{r}}(\det(\boldsymbol{F}) - 1)\boldsymbol{I}$, where $\boldsymbol{\sigma}$ represents the Cauchy stress tensor, $\tilde{\boldsymbol{F}}$ the isochoric part of the deformation gradient tensor $\boldsymbol{F}$, $\boldsymbol{I}$ the identity tensor, det the determinant operator and superscripts d and c the deviatoric and conjugate form respectively). The material parameters used are a shear modulus $G_{\mathrm{r}} =$ 30 MPa and a bulk modulus $\kappa_{\mathrm{r}} = 1000$ MPa.

Figs 7 and 8 shows the deformed microstructures and the associated macroscopic stress-strain curves. The rubber inclusions have indeed an important effect on the local deformations and on the global response: local yield zones are stabilised sooner by the load-bearing capacity of the rubber particles, causing more yield zones to be formed during the deformation process. The yield process is taking place more or less sequentially, which is, in fact, comparable to that in voided polycarbonate. As a result, the unstable macroscopic strain softening behaviour has been eliminated completely. Moreover, the considerable shear modulus of the perfectly adhering rubber particles results in an improved macroscopic hardening behaviour. The predicted overall mechanical response for the polystyrene-rubber system is,



(a)

(b)

Figure 6 Geometries and finite element meshes of undeformed plane strain RVEs representing a continuous matrix blended with core-shell rubber particles with a voided core and a thin (a) or thick (b) rubber shell.

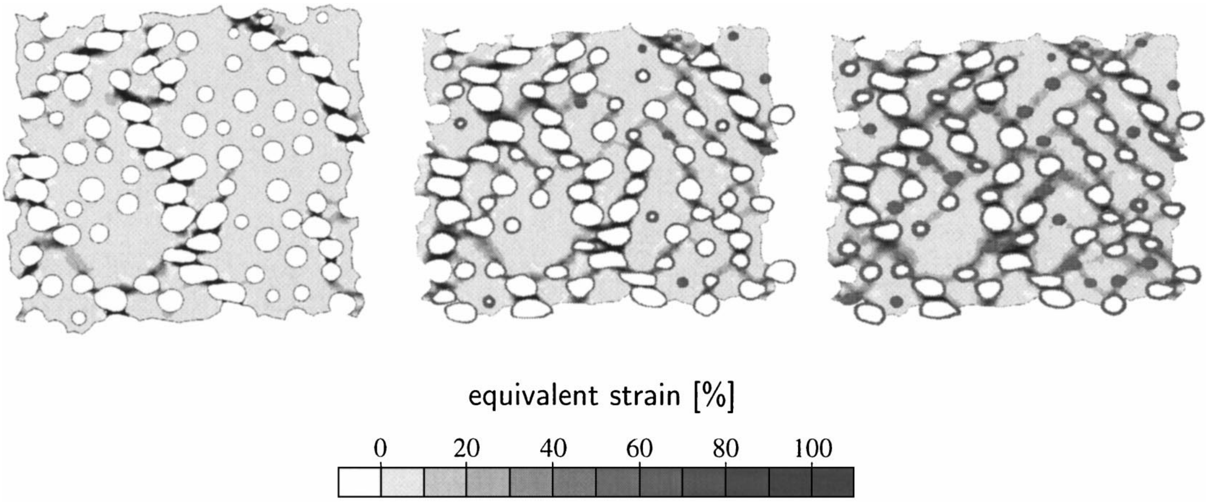


Figure 7 Contour plots of equivalent strain in uniaxially stretched RVEs at a global strain of 20%, predicted for polystyrene matrix behaviour with voids (left), and thin (middle) and thick (right) core-shell rubber particles.

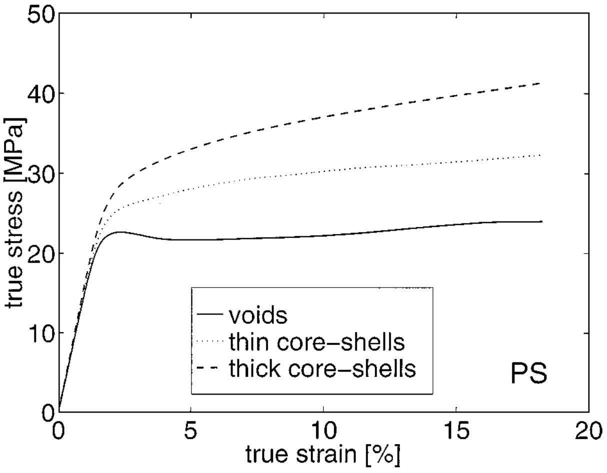


Figure 8 RVE averaged tensile stress, predicted for polystyrene matrix behaviour with different inclusions.

therefore, stable and it even resembles that of voided polycarbonate (compare Figs 5 and 8).

The results suggest that the key-role of cavitated load-bearing rubber particles is to accelerate the stabilisation of the local yield zones in order to promote massive shearing. Despite the fact that the analysis neglects the details of the rubber cavitation process, it is believed that the mechanism presented is indeed active in rubber-modified systems if (i) the rubber shear modulus is relatively high and (ii) the rubber cavitates or is precavitated. This is also a possible explanation for the toughness enhancement of epoxy-rubber blends with enhanced particle properties as reported by Pearson and Yee [7].

6. Possible consequences of a decreasing particle size

The analyses so far were based on continuum mechanics theory, where the influence of the absolute length scale was completely left out of consideration. This approach can, therefore, not explain the striking experimental findings proving the existence of a material specific critical thickness which causes a sudden transition in the material behaviour (e.g. brittle-to-ductile). In the past, different theories were proposed to explain this material dependent (read: entanglement or cross-link density dependent) critical interparticle distance (see, e.g. [30]), but no satisfactory explanation was found. In retrospective, it is realised now that material behaviour can only be understood and predicted if a large enough, inhomogeneous microstructure is analysed. Without intending to provide a full explanation it is attempted to extrapolate the presented results to indicate what the reason could be for a size-dependent mechanical behaviour.

One of the most important results of the study performed is that the post-yield behaviour of a homogeneous or heterogeneous material is a crucial feature. Stabilisation is possible by softening reduction or hardening improvement. It is proposed, therefore, to reformulate the size-effect problem as: what mechanism(s) could possibly establish a relationship between the absolute size of the deformation zone (e.g. the thickness of a shear band between two heterogeneities) and the local softening or hardening behaviour? Apart from the absolute size effects mentioned in Section 4 that prevent the formation of crazes in the ligaments of the heterogeneous material, it is stated now that there are at least two (intriguing) possibilities:

I. An enhanced mobility of the polymer segments near a surface or interface causing a yield stress and strain softening reduction. Keddie *et al.* [31] measured a considerable absolute size-dependent depression of the glass transition temperature T_g in thin polystyrene films, down to a T_g of 345 K for a 10 nm thin film (instead of 375 K for thick specimens). Given the interpretation of the yield stress as a stress activated passage of the glass transition temperature [32], such a T_g reduction of 30 K could also result in a considerable yield stress reduction and an elimination of strain softening. Fig. 9 shows the possible effects of yield stress reductions near (void) surfaces on the response of the 30 vol.% voided polystyrene RVE. The different intrinsic mechanical responses of the hypothetical matrix material are displayed in Fig. 10. Apparently, a total elimination of the softening behaviour indeed results in the desired stable macroscopic response. Notice that the global yield stress of the material has also decreased as a result of the yield stress modification. Fig. 11 displays

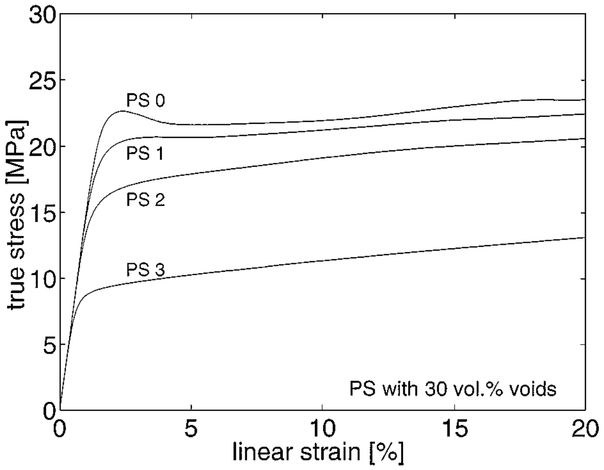


Figure 9 Effect of yield stress reduction on the RVE averaged stress-strain response of 30 vol.% voided polystyrene. The intrinsic mechanical behaviour of the modified matrix material is depicted in Fig. 10.

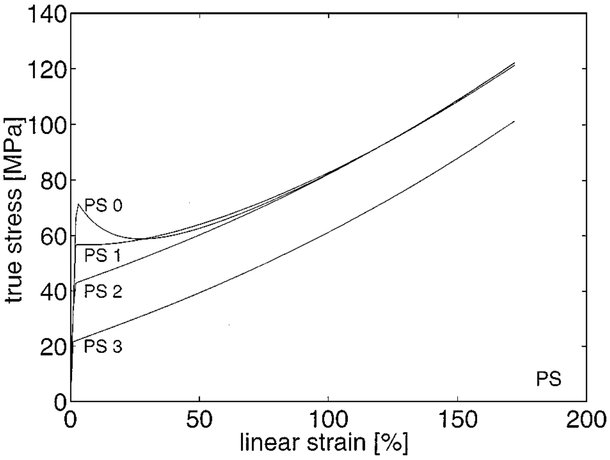


Figure 10 The intrinsic uniaxial stress-strain response of unmodified (0) and modified (1–3) polystyrene (strain rate 0.01 s^{-1}).

contours of the equivalent strains in the RVEs with modified yield stress. Clearly, the reduction of the post-yield strain softening results in a much more homogeneous deformation of the microstructure, where almost all the voids are involved in the deformation process.

II. A (temporarily) excessive hardening behaviour because the yield zone is (temporary) smaller than the entanglement distance d. In Part I of this series [19] it was already stated that the hardening modulus H scales with the entanglement distance d as $H \sim d^{-2}$, so a reduced entanglement distance results in an enhanced hardening. Assuming that a molecular strand between two entanglements can be partially immobile by active secondary bonds (an elastic, 'glassy' state), and partially mobile because of stress-activated segmental motion (yielding), then the immobile parts will naturally act as physical cross-links for the mobile, deforming part of the strand. As a result, the deforming, mobile part of the strand will experience a reduced entanglement distance. So if a yield zone (e.g. a shear band) is smaller than the distance between two entanglements, then the effective entanglement distance is reduced, resulting in an improved strain hardening behaviour.

For polystyrene, the average entanglement distance d is ca. 9.6 nm [33]. Finite element calculations, based on continuum mechanics, show that the thickness of the shear bands formed in a heterogeneous microstructure are typically one order of magnitude smaller than the size of the dispersed phase. Hence, if the assumption is valid that shear processes still take place on a -more or less- molecular scale, then particles with a size of 30 nm would result in shear bands of the order of 3 nm, which is considerably smaller than the real entanglement distance of polystyrene. A local, but substantial increase of the hardening behaviour of polystyrene inside these shear bands results. It is important to realise that such a hardening enhancement is only temporary, since the original entanglement distance returns when the total matrix yields (all the secondary bonds are broken, no immobile parts survive, and thus the effective entanglement distance equals the original value). However, this temporary behaviour might be sufficient to overcome the first, critical stages of the local deformation process. Massive matrix yielding implies, of course, that the microstructure deforms relatively ductile and that the majority of energy is dissipated by shear band formation. So the deformation has been stabilised and, consequently, this peculiar stabilisation mechanism is no longer needed.

A first order estimation of the effects of such a non-local behaviour of the matrix material on the overall mechanical response of a heterogeneous system of voided polystyrene can be obtained by some simple (two-dimensional) considerations. For each (integration) point inside a shear band it is assumed that the quadratic effective entanglement distance d_{eff}^2 is proportional to the fraction of area A_{y} enclosed by a circle with radius d where yielding takes place. Furthermore it is assumed that the actual hardening modulus H inside the shear bands scales as $H \sim 1/d_{\text{eff}}^2 \sim 1/A_{\text{y}}$. The result for a unidirectional extension test on a 30 vol.% voided polystyrene RVE, with an average void diameter of 30 nm and a distance between entanglements of 10 nm, is shown in Fig. 12. It is clear that the temporarily enhanced hardening indeed eliminates the softening behaviour. A detailed examination of the local matrix deformations revealed that the enhanced hardening is accompanied by a subtle increase of the size of the yield zones. Realising that those considerations are based on coarse first order approximations of the local molecular deformation processes, it is believed that the simulations presented give a strong indication that the proposed mechanism of temporarily enhanced hardening may indeed result in a stable macroscopic behaviour. Therefore, this could be a possible explanation for the experimental observations [30] that polystyrene can be toughened by microstructural modifications on a 30 nm scale.

7. Key routes to improved toughness, a discussion

The results presented in this paper and the previous findings [19, 21] suggest that only two effects are extremely important for toughening of (heterogeneous) material, i.e. the stability of the post-yield behaviour and the maximum dilative stress. The stability of the post-yield behaviour determines, essentially, whether

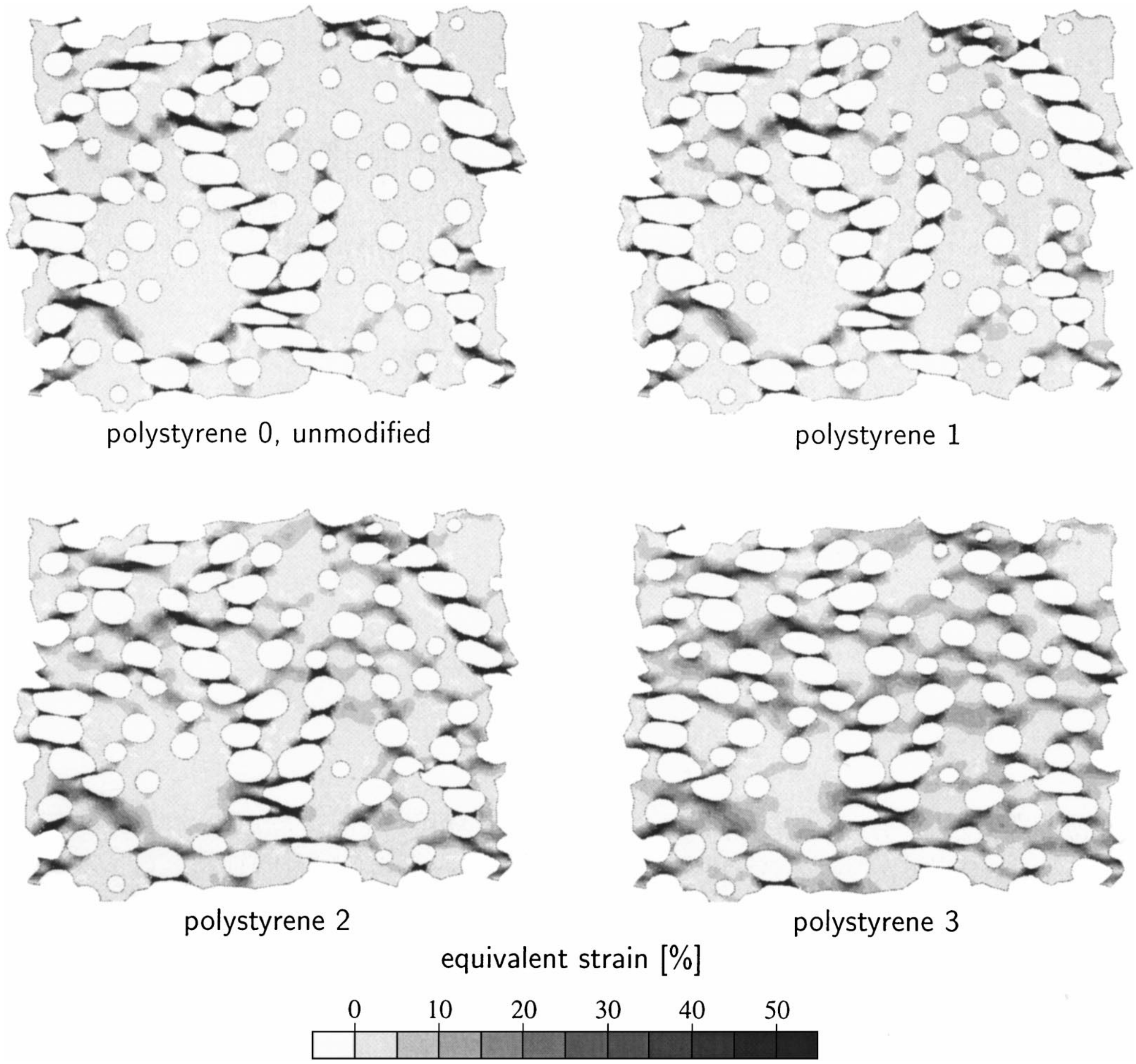


Figure 11 Contour plots of the equivalent strain in unidirectionally stretched RVEs at a total strain of 20%, predicted for polystyrene material behaviour with modified yield and post-yield responses. The associated stress-strain responses for the modified homogeneous polystyrene are displayed in Fig. 10.

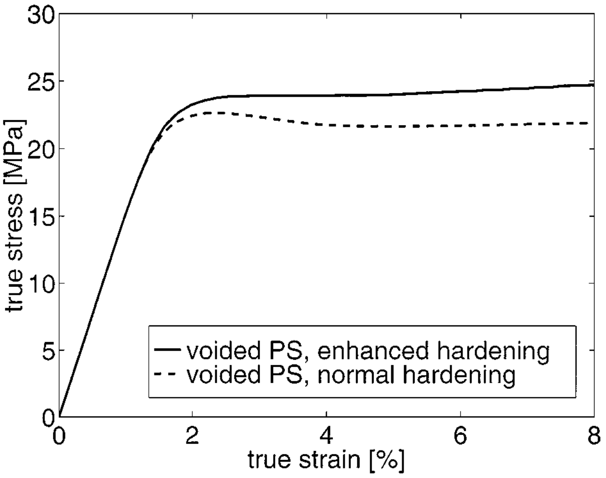


Figure 12 RVE averaged tensile stress versus strain in uniaxially stretched polystyrene RVEs with 30 vol.% 30 nm sized voids, predicted for (ordinary) constant and locally enhanced hardening behaviour. The distance between entanglements is assumed to be 10 nm.

the plastic strains are spread out over a larger volume of the sample or remain concentrated in the vicinity of a small but critical stress concentrating defect. An enlargement of the plastic deformation zone is obviously effective in energy dissipation and is thus the preferred toughening mechanism. The opposite phenomenon, a strong strain localisation, usually involves high strains and critical (dilative) stresses and, consequently, early craze or crack nucleation followed by fast crack propagation. The maximum dilative stress is, consequently, also important, especially since many (dilative) stress concentrations are governed by the shape of the macrostructure (e.g. a sharp radius acting as a notch, or sometimes even a defect, see Part I [19]). The critical correlations between global shape and dilative stress can, however, effectively be diminished by the introduction of voids or easily cavitating rubber particles. This enables a microstructure to respond on imposed dilative strains or stresses through the combination of shearing and void growth.

Possible routes to improved toughness are, therefore, stabilisation of the post-yield behaviour and reduction of dilative stresses. Local dilative stresses can simply be reduced, as mentioned before, by the introduction of voids or easily cavitating or pre-cavitated rubber particles. Stabilisation of the post-yield behaviour is, however, more difficult. This subject is considered in the following subsection.

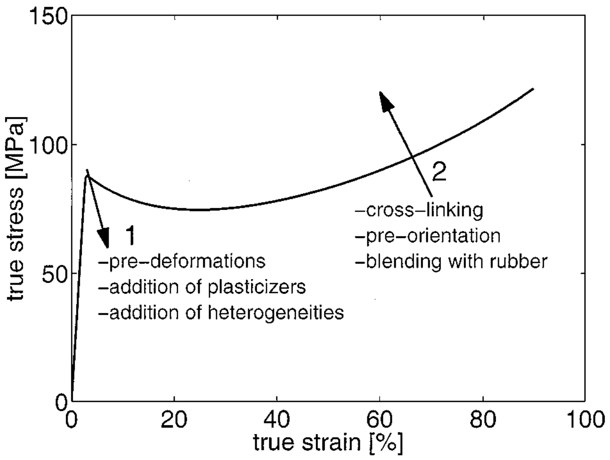


Figure 13 Two possibilities to obtain a stable post-yield behaviour.

7.1. Stabilisation of the post-yield behaviour

The stability of the post-yield behaviour of a glassy polymer is determined by two characteristics, i.e. the intrinsic (de-stabilising) strain softening and subsequent (stabilising) strain hardening. This suggests that materials can be toughened by either reducing the intrinsic strain softening and/or improving the strain hardening, see Fig. 13. It is, however, generally known that strain softening is closely related to viscoelasticity and yield because of a shared origin (secondary interactions), and that softening can be manipulated by modifying the yield stress. The underlying relationships between yield stress, viscoelasticity and strain softening are, unfortunately, not fully understood yet, but many experiments seem to indicate that a softening reduction inevitably combines with a yield stress reduction (see, e.g. the yield and post-yield behaviour of the thermally pre-treated polystyrene in the work of Hasan *et al.* [34]). It is noteworthy that a yield stress reduction is not preferable from an engineering point of view (a lower material strength!). However, with respect to the (critical) dilative stress a yield stress reduction can be necessary since it can result in lower dilative stresses inside the microstructure. The results presented in this study (see also the results of Part III of this series [35]) do, in fact, confirm the major importance of a yield stress reduction and suggest that the softening can be reduced or eliminated by:

- Lowering the yield stress by mechanical, thermal or chemical pre-treatments. Mechanical or thermal pre-treatments are known to be effective, but the fast recovery of yield stress, strain softening and brittleness by enhanced aging is generally unacceptable for commercially interesting applications (see also Part I [19]). A well-known example of a chemical pre-treatment is the addition of a solvent (plasticiser) [36]. An example is plasticised polystyrene, where the solvent induces a drastic yield stress reduction down to a value of approximately 20 MPa, which is low compared with the 70–110 MPa yield stress of the untreated material. As a result, plasticised polystyrene behaves tough. Plasticisers are, however, not generally applicable and for some cases it is known that the addition of a plasticiser may even lead to an increased craze sensitivity.
- The introduction of randomly distributed low-modulus heterogeneities. The heterogeneities cause sequential yielding and can result in a complete elimination of the post-yield strain softening behaviour of the polymeric system, e.g. see Fig. 3. This mechanism fails, however, when the local yield zones are not stabilised by sufficient strain hardening.

The possible routes to improved strain hardening behaviour are:

- Modification of the molecular network by either cross-linking or excessive pre-orientations. Both methods are rather academic and not convenient for most practical applications. Henkee and Kramer [37] demonstrated that cross-linked polystyrene can have a similar mechanical behaviour as polycarbonate. Note that cross-linking results in a lower molecular weight between cross-links (M_c) and/or entanglement points (M_e) and thus in an increased hardening modulus H ($H \sim 1/M_{c,e}$ according to rubber elasticity theory). Cross-links do normally not affect the yield behaviour but reduce, of course, the maximum drawability and, therefore, the intrinsic ductility of the material.
- Incorporation of relatively stiff pre-cavitated rubber particles with a good matrix adhesion. It must be emphasised that the particles must either be cavitated or must have easily cavitating inclusions (e.g. core-shell, soft rubber core, relatively hard rubber shell) in order to reduce the triaxial stress. Then, the properties of the cavitated rubber will have a significant contribution to the post-yield behaviour of the heterogeneous material, as was shown in Figs. 7 and 8.

8. Discussion and conclusions

A traditional route to enhanced toughness is the introduction of a fine dispersion of easily cavitating or non-adhering rubber particles. Cavitated rubber particles should release volumetric strains, prevent critical dilative stresses, promote massive shearing and, as a result, improve the toughness. The results of this research confirm these statements. Simple, two-dimensional finite element models for heterogeneous microstructures, the so-called representative volume elements (RVEs), were used to investigate the influence of a fine dispersion of randomly distributed voids on the macroscopic mechanical response of polystyrene and polycarbonate. The voids idealise easily cavitating or non-adhering rubber particles subjected to positive hydrostatic stress states. It has been shown that voids indeed enable volumetric deformations and reduce macroscopic dilative stresses. Moreover, an irregular distribution of voids promotes the spread out of plastic strains over the whole microstructure. For voided polycarbonate, the surprising result was a total elimination of the softening and hence a stable 'intrinsic' macroscopic mechanical response. This remarkable and important effect is almost independent of the void volume fraction (only 2.5 vol.% voids suffices). Apparently, the post-yield mechanical response of a heterogeneous polymeric system is extremely sensitive to microstructural modifications. Especially the irregularity of the microstructural geometry seems to promote massive sequential shearing. The sequential shearing severely affects the yield and post-yield response of the heterogeneous system by a complete elimination of the strain softening at the microscopic (RVE) level, provided that enough strain hardening is present.

Voids in polystyrene do, in contrast, not result in an overall softening elimination. PS simply shows too much (unstable) strain softening and insufficient (stabilising) strain hardening. Consequently, the strains localise in ligaments between the voids and narrow deformation zones are formed more or less perpendicular to the draw direction. The resulting macroscopic mechanical response is unstable because it is dominated by the behaviour of the (unstable) localisation zone. In the end, the thin fibrils can not transfer any noticeable force to the unyielded regions and will break. The excessive stretching of the ligaments between the voids can be prevented by the introduction of perfectly adhering pre-cavitated rubber particles with a considerable modulus (≈30 MPa). The load-bearing rubber, attached to the sides of the ligaments, stabilises the local ligament deformation and, thereby, results in a distribution of plastic strains over the whole microstructure. This is accompanied by a stable overall 'intrinsic' mechanical response of the rubber-modified polystyrene system. Appropriate microstructural modifications may result in a total elimination of the unstable post-yield strain softening, in an improved strain hardening and thus in a stabilised macroscopic mechanical response.

Part III of this series [35] investigates the effects of the microstructural modifications (on RVE level), on the macroscopic deformation behaviour of hour-glass shaped or notched tensile bars. The results of these analyses confirm the conclusions of this Part II, that only dealt with the intermediate RVE level.

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