Micromechanics of Particle-Modified Semicrystalline Polymers

Influence of Anisotropy due to Transcrystallinity and/or Flow

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1 Introduction

Semicrystalline polymeric materials are widely used in a range of engineering applications. Despite many advantages as low cost and weight, their application is limited by some unfavorable mechanical properties, such as brittle response in plain or notched applications. Toughening can be enhanced by rubber blending and a criterion proposed by Wu (1985) states that a sharp brittle-to-tough transition occurs for e.g. nylon/rubber blends when the average interparticle matrix ligament thickness $\Lambda_1$ is reduced below the critical value $\Lambda_{1c} = 0.3 \, \mu m$, as is schematically depicted in Figure 1. The critical value was shown to be independent of the rubber volume fraction and the particle size. Similar critical interparticle distances were reported in rubber-modified polyethylene (Bartczak et al., 1999a) and poly(ethylene terephthalate) (Sánchez-Solís et al., 2000; Loyens and Groeninckx, 2002, 2003). The explanation offered by Wu for this transition addressed the mutual interaction of particle-disturbed stress fields, enhancing matrix yielding. Ramsteiner and Heckmann (1985) concluded that the energy-dissipating deformation mode for rubber-modified nylon is shear yielding. Borggreve et al. (1987) confirmed the existence of a critical interparticle distance for the brittle-to-tough transition, however questioned the physical explanation by Wu. A modified theory was proposed, in which the critical ligament thickness corresponds to a local plane strain–to–plane stress transition in the matrix (Wu, 1988; Margolina and Wu, 1988). Based on numerical investigations, Fukui et al. (1991) and Dijkstra and Ten Bolscher (1994) attributed the toughening effect to extensive shear yielding due to the interaction of stress fields. However, since the stress field theory is only effective for changes in geometrical ratios, it can be concluded that stress field interaction is incapable of explaining an absolute length scale such as a critical interparticle distance. Clearly, a more sound explanation for the critical interparticle distance was needed.

Figure 1: Impact toughness of nylon/rubber blends vs. the average surface-to-surface interparticle ligament thickness $\Lambda$. Redrawn from Wu (1985).
1.1 Toughening mechanism

A physical explanation of the absolute length parameter was offered by Muratoglu et al. (1995a,c), who recognized the brittle-to-tough transition as a true material characteristic. It was attributed to thin layers of transcrysatisized material, with a reduced plastic resistance, appearing in the microstructural morphology of particle-modified semicrystalline materials. Effectively, the crystallization behavior of the matrix is influenced by the particle/matrix interface, leading to a layer of parallel crystalline lamellae (Chacko et al., 1982; Rybnikar, 1981, 1989; Muratoglu et al., 1995a,c; Bartczak et al., 1999a,b,c; Kim et al., 2001; Nam et al., 2001), with the crystalline planes having the lowest plastic resistance parallel to the interface. It was experimentally established that these transcrysatised layers have a well-defined thickness of approximately $\Lambda_c/2$. When the average matrix ligament thickness $\Lambda$ is below the critical value $\Lambda_c$, the preferentially oriented material percolates through the system, bridging between the dispersed particles, as is depicted in Figure 2(a). Situations with $\Lambda \gg \Lambda_c$ are represented in Figure 2(b) and (c) and interesting in this respect is Figure 2(c) that represents the same volume fraction as in Figure 2(a), only with larger particle size. The system represented in Figure 2 consists of (i) rubber particles with a low modulus, (ii) a preferentially oriented anisotropic matrix material, enveloping the particles and (iii) the bulk matrix material with a randomly oriented structure and consequently isotropic material properties. According to the toughening mechanism postulated by Muratoglu et al. (1995c), after cavitation of the rubber particles, the regions with a lowered yield resistance promote large plastic deformation and thereby improve the toughness. Toughness indeed can be defined as a delocalizing strain mechanism (Meijer and Govaert, 2003). Tzika et al. (2000) used a micromechanical numerical model, with a staggered array of particles, to study the influence of preferentially oriented anisotropic layers, modeled with anisotropic Hill plasticity, on the deformation mechanisms under high triaxiality conditions. They observed plastic deformation in the matrix to occur diagonally away from the particles (i.e. in the matrix material between particles, parallel to the interfaces) for $\Lambda \leq \Lambda_c$. The anisotropic matrix material was found to act as a nonstretching shell around the (cavitated) particles, leading to extensive shear yielding.

Bartczak et al. (1999a,b) generalized the Wu criterion to high density polyethylene (HDPE) and showed the critical interparticle distance ($\Lambda_c = 0.6 \mu m$ for HDPE) to be an intrinsic property of the matrix material, thereby opening the possibility of using mineral fillers for the toughening of semicrystalline polymers, the advantage of which would be an improved modulus of the blend, as schematically indicated in Figure 3. They argued that debonding of hard filler particles could be an alternative for the cavitation of the rubbery phase. However, the Bartczak et al. results showed a distinct effect of processing conditions on the toughness obtained. The importance of process conditions was demonstrated by Schrauwen et al. (2001a,b, 2002), who found toughness to be dominated by flow-induced effects. By using calcium carbonate filler particles in a nylon-6 matrix, Wilbrink et al. (2001) did not obtain the tough response of nylon/rubber blends, as was reported by Muratoglu et al. (1995c,b), and attributed this to the development of triaxial stresses. A four times increase of the Izod impact energy was obtained by Thio et al. (2002) by incorporation of calcium carbonate particles in polypropylene, reportedly resulting from combined mechanisms of crack deflection and local plastic deformation of interparticle ligaments. Similar results have been

![Figure 2: Transcrystallized layers around second-phase particles for (a) material with a decreased plastic resistance percolating through the blend, enhancing the toughness (adopted from Muratoglu et al. (1995c) and Bartczak et al. (1999a)), and for materials with a brittle response, with (b) a smaller volume fraction and (c) the same volume fraction as in (a), only with larger particles.](image)
obtained by Zuiderduin et al. (2003). Again, it can be concluded that more refined modeling is needed to explain the experimental findings and to suggest routes to design tough polymers.

1.2 Modeling strategy

Rigorous modeling of toughness enhancement of semicrystalline polymers should in the above context be based on describing the mechanisms schematically shown in Figure 4. It is based on the hypothesis that local anisotropy, induced by a specific microstructure, which results from preferred crystallization of polymeric material, leads to macroscopically tough behavior. The potential validity of this hypothesis is examined by methods of micromechanical modeling. Crystallization behavior itself is left out of consideration (because it is outside the scope of this study), and the starting-point is an assumed microstructure of a particle-modified system.

The deformation of polymeric materials, and thus also their either brittle or tough responses, are the result the interplay of various effects and mechanisms at different levels, such as for example (Michler, 1999) chain scission, microyielding, microcavitation, crazing, shear band formation, crack initiation and propagation, and fracture. For
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Semicrystalline materials, also phenomena as interlamellar slip and intralamellar deformation mechanisms as crystallographic slip, twinning, and stress-induced martensitic transformation play a role (e.g. Petermann and Ebener, 1999; G’Sell and Dahoun, 1994; Lin and Argon, 1994). A quantitative prediction of toughness would require a coupled and detailed modeling of the various deformation mechanisms and criteria for the different failure modes, which is at present still not feasible. Therefore, merely the influence of the microstructure on the qualitative individual occurrence of some of these phenomena, or the conditions that may induce them, is investigated.

First a micromechanical investigation of the potential of local anisotropy around dispersed particles for enhancing the material properties is presented. Calculations are performed on an idealized semicrystalline material, blended with rubber particles, which are assumed to be cavitated and are thus, for simplicity, represented as voids. The system contains a scale parameter, which is the ratio of the average distance between particles and a critical distance. This length parameter is represented in the calculations by the relative thickness of the transcrystalline layer that results from the surface-nucleated crystallization process. The simulations on this idealized polymeric material are used to investigate the applicability of various types of representative volume elements (RVE) for soft and hard particle-modified semicrystalline materials. Furthermore, with these calculations, it is investigated in detail (i) whether local anisotropy can potentially improve the toughness of rubber-modified systems; (ii) what is the occurring effect of anisotropy that may improve the toughness; and (iii) what type of anisotropy (i.e. mesoscopic morphology) would be required.

To anticipate on the conclusions of our calculations, it is pointed out that the simulations, with both axisymmetric and multiparticle RVEs, show that local anisotropy of the matrix material around the particles can effectively replace localization by dispersed shear yielding and change the occurring hydrostatic stresses, potentially leading to toughened material behavior. However, to achieve these improvements, a morphology must be pursued with a radially oriented structure around the dispersed particles and it should, moreover, provide a sufficiently large amount of anisotropy. Furthermore, the possibility of using mineral fillers, rather than low-modulus rubber, for the toughening of semicrystalline polymers is evaluated. The presence of hard, easily debonding, particles is found to negatively affect the anisotropy-induced toughening mechanism, although some improvements remain, in accordance with the existing experimental evidence.

Figure 5: Different scales which can be identified in particle-toughened semicrystalline polymeric systems.

Now in more detail: to investigate whether the above-mentioned requirements can be achieved by a transcrystallized microstructure, a micromechanically-based numerical model for the elasto-viscoplastic deformation and texture evolution of semicrystalline polymers has been developed. For actual particle-modified polymeric systems, a distinction between three different scales is made, as is schematically depicted in Figure 5. The constitutive prop-

properties of the material are identified at the microscopic scale. At this scale, the individual crystallographic lamellae and amorphous layers determine the local material response. At the mesoscopic scale, an aggregate of individual phases is formed, which can be a spherulite or a sheaflike aggregate of preferentially oriented material. The local
inclusion-averaged deformation and stress fields are related to the mesoscopic fields by a polycrystalline aggregate model. The effect of a transcrystalline structure of matrix material versus randomly oriented material on both mesoscopic and microscopic results is examined. A limited effect of the preferential orientations is observed. Further improved properties are obtained for a partly flow-induced microstructure, if loaded in the appropriate direction.

2 Soft fillers: can local anisotropy induce toughness? 1

The potential of plastic anisotropy for enhancing the toughness of semicrystalline polymeric materials is investigated. Calculations are performed on idealized semicrystalline materials, blended with rubber particles, which are assumed to be cavitated and are represented by spherical voids. The system contains a length scale parameter, which is the ratio of the average distance between voids and a critical distance, and is represented by the absolute thickness of the transcrystalline anisotropic layer around the voids. We will start the analysis using a simple Hill anisotropic plasticity constitutive model, that is, subsequently, applied to a micromechanical RVE.

2.1 Constitutive model of the anisotropic bulk polymer

Our idealized polymeric material is modeled by isotropic elasticity (characterized by a Young’s modulus $E^0$ and a Poisson’s ratio $\nu^0$) combined with classical (Hill, 1950) anisotropic plasticity. During yield, the anisotropic Hill yield criterion is applied:

$$F(\sigma_{22} - \sigma_{33})^2 + G(\sigma_{33} - \sigma_{11})^2 + H(\sigma_{11} - \sigma_{22})^2 + 2L\sigma_{23}^2 + 2M\sigma_{13}^2 + 2N\sigma_{12}^2 = \sigma_y^2,$$

where $\sigma_{ij}$ are the stress components with respect to a local material vector basis, and the anisotropic constants $F$, $G$, $H$, $L$, $M$ and $N$ are given by:

$$F = \frac{1}{2} \left( \frac{1}{R_{22}^2} + \frac{1}{R_{33}^2} - \frac{3}{R_{11}^2} \right); \quad G = \frac{1}{2} \left( \frac{1}{R_{11}^2} + \frac{1}{R_{33}^2} - \frac{1}{R_{22}^2} \right); \quad (2)$$

$$H = \frac{1}{2} \left( \frac{1}{R_{11}^2} + \frac{1}{R_{22}^2} - \frac{1}{R_{33}^2} \right); \quad L = \frac{3}{2R_{23}^2}; \quad M = \frac{3}{2R_{13}^2}; \quad N = \frac{3}{2R_{12}^2}. \quad (3)$$

The constants $R_{11}$, $R_{22}$ and $R_{33}$ are the ratios of the actual tensile yield strength values of the anisotropic material, relative to the actual virtual bulk tensile yield strength, $\sigma_y$. The constants $R_{12}$, $R_{13}$ and $R_{23}$ are the ratios of the yield strength values in shear to the shear yield strength $\tau_y$ of the virtual bulk material, with $\tau_y = \sigma_y/\sqrt{3}$. The Hill yield criterion was previously used for anisotropic polymeric material by Kobayashi and Nagasawa (1966) and Tzika et al. (2000). Here, a linear dependency of the yield strength $\sigma_y$ on the effective plastic deformation measure $\dot{\varepsilon}_p$ and a power law dependency of $\sigma_y$ on the corresponding rate $\dot{\varepsilon}_p$ are assumed for the polymeric material:

$$\sigma_y = \sigma_{y0} \left\{ \dot{\varepsilon}_p + q \left[ 1 + \left( \frac{\dot{\varepsilon}_p}{q\dot{\varepsilon}_0} \right)^{\frac{1}{n}} \right] \right\}^{\frac{1}{n}}, \quad (4)$$

where $\sigma_{y0}$ is the reference yield strength, $h$ is the linear hardening parameter and $n$ is the stress exponent of the strain rate. A rate-independent contribution is introduced for strain rate values which are considerably smaller than the reference strain rate $\dot{\varepsilon}_0$, controlled by the parameter $q$. The plastic strain measure $\dot{\varepsilon}_p$ and the corresponding rate are, for anisotropic plasticity, assumed to be given by:

$$\dot{\varepsilon}_p = \int_0^t \dot{\varepsilon}_p \, dt; \quad \dot{\varepsilon}_p = \frac{\sigma}{\sigma_y}, \quad (5)$$

where $\sigma$ is the Cauchy stress tensor and $\dot{\varepsilon}_p$ is the plastic rate of deformation tensor. The material parameters that are used here are summarized in Table 1. As mentioned earlier, Equations (1)–(3), with the anisotropic strength

1Partly reprinted from Van Dommelen et al. (2003b), with permission from Elsevier.
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| $E^\text{m}$ [GPa] | $\nu^\text{m}$ | $\sigma^\text{m}$ [MPa] | $h$ | $\gamma_0$ [s$^{-1}$] | $q$ | $n$ | $R_{11}$ | $R_{22}$ | $R_{33}$ | $R_{12}$ | $R_{13}$ | $R_{23}$ |
|-------------------|----------|-------------------------|-----|---------------------|----|-----|--------|--------|--------|--------|--------|--------|--------|
| 1                 | 0.45     | 25                      | 0.6 | 10$^{-3}$           | 9  | 10$^{-2}$ | 1      | 1      | 1      | 1/\zeta | 1/\zeta | 1      |

Table 1: Material parameters for a fictitious polymer matrix.

ratios $R_{ij}$ are applied in a local coordinate system. The transcrystallized material around the voids is assumed to have a reduced plastic resistance with respect to the local 12 and 13 shear components (at the void/matrix interface, the 1-direction is defined to be perpendicular to the interface), and the reduction is controlled by only one adjustable parameter $\zeta$.

2.2 Micromechanical models

The heterogeneous particle-filled system is described by a finite element model of a representative volume element that generally and intrinsically have a three-dimensional structure. Full three-dimensional numerical analyses, however, are computationally extremely demanding and, therefore, first two different simplified models are used.

For an adequate representation of the triaxial stress state around a void, an axisymmetric RVE is used, as suggested by Socrate and Boyce (2000) and Tzika et al. (2000). However, because of the regular void stacking associated to such RVEs, important effects as sequential yielding of the matrix material between the different voids (Smit et al., 1999) cannot be accounted for. In order to capture the essentially irregular nature of a system of dispersed voids, also a plane strain RVE is used, which is incapable of capturing the triaxial stress-effects. A comparison of the simplified two-dimensional models with three-dimensional calculations is presented in Van Dommelen et al. (2003b).

2.2.1 The first model: an axisymmetric RVE, the SA model

An axisymmetric RVE model of a staggered array of voids (referred to as the SA model) is considered which resembles a body centered tetragonal stacking of voids. A schematic representation of the unit cell, with $L_0 = R_0$, is shown in Figure 6. The axis of rotational symmetry, as well as the loading direction are horizontal. The RVE is subjected to anti-symmetry conditions (with respect to point M) along the outer radius, which were introduced by Tvergaard (1996, 1998). Axial compatibility along the radial boundary $\Gamma_{34}$ is written as

$$u_z(z_0|\text{M} - \eta) + u_z(z_0|\text{M} + \eta) = 2u_z|\text{M}. \quad (6)$$

The combined cross-sectional area of neighboring cells is assumed to remain constant along the axial coordinate:

$$[R_0 + u_r(z_0|\text{M} - \eta)]^2 + [R_0 + u_r(z_0|\text{M} + \eta)]^2 = 2[R_0 + u_r|\text{M}|]^2. \quad (7)$$

Figure 6: (a) Schematic visualization of an axisymmetric RVE model of a staggered array of voids (Socrate and Boyce, 2000; Tzika et al., 2000) and (b) its position with respect to three neighboring RVEs in a deformed state.
Symmetry conditions along the right and left boundaries are written as
\[ u_z\rvert_{\Gamma_{23}} = u_z\rvert_{C_2} \] (8)
and
\[ u_z\rvert_{\Gamma_{45}} = u_z\rvert_{C_5} \] (9)
respectively. Since the axis of rotational symmetry coincides with boundary \( \Gamma_{12} \), the following condition is imposed on this boundary:
\[ u_r\rvert_{\Gamma_{12}} = 0. \] (10)
The axisymmetric RVE is subjected to tension at a macroscopically constant strain rate:
\[ u_z[C_2] - u_z[C_3] = L_0[\exp(\dot{\varepsilon}t) - 1]. \] (11)
where the deformation rate \( \dot{\varepsilon} \) is set equal to the material reference shear rate \( \dot{\gamma}_0 \) in Equation (4).

The finite element mesh of the axisymmetric SA model, with void fraction \( f = 0.2 \), is visualized in Figure 7(a). In each integration point of the 196 four-noded bilinear elements, a local coordinate system is generated. The local

![Figure 7](image)

1-directions are taken perpendicular to the closest particle/matrix interface, taking into account the periodicity of the structure, and are shown in figure 7(b).

2.2.2 The second model: a multiparticle plane strain RVE, the ID model

To account for the irregular nature of particle-dispersed systems, a plane strain RVE with randomly dispersed voids (referred to as the ID model) is used. In Figure 8, a schematic illustration of this RVE is shown, as well as its arrangement with respect to the neighboring RVEs. The periodicity assumption requires full compatibility of each opposite boundary pair. The corresponding kinematic and natural boundary tyings (Smit et al., 1998) for related points on opposite boundaries are given by:

\[ u\rvert_{\Gamma_{34}} - u\rvert_{C_4} = u\rvert_{\Gamma_{12}} - u\rvert_{C_1}; \] (12)
\[ u\rvert_{\Gamma_{14}} - u\rvert_{C_1} = u\rvert_{\Gamma_{23}} - u\rvert_{C_2}; \] (13)
\[ \sigma \cdot n\rvert_{\Gamma_{12}} = -\sigma \cdot n\rvert_{\Gamma_{34}}; \] (14)
\[ \sigma \cdot n\rvert_{\Gamma_{14}} = -\sigma \cdot n\rvert_{\Gamma_{23}}; \] (15)

where \( n \) denotes the outward unit normal of the boundary. A tensile loading condition in \( x \)-direction is prescribed:
\[ u_x[C_2] - u_x[C_1] = L_0[\exp(\dot{\varepsilon}t) - 1]. \] (16)
where \( \dot{\varepsilon} \) is set equal to the reference strain rate \( \dot{\gamma}_0 \) of the material. Furthermore, rotations are prevented by the following condition for the vertices \( C_1 \) and \( C_2 \):
\[ u_y[C_1] = u_y[C_2]. \] (17)
Figure 8: (a) Schematic visualization of a multiparticle plane strain RVE (Smit et al., 1998) and (b) its position with respect to neighboring RVES in a deformed state.

The relative displacements of \( C_4 \) are unspecified and follow from the analysis, whereas the displacements of \( C_3 \) are tied to the other vertices.

A structure with 20 volume percent irregularly dispersed voids is generated using a procedure from Hall (1991) and Smit et al. (1999). In order to obtain initially straight boundaries, no void is allowed to cross a boundary. The mesh with 2,622 four-noded bilinear plane strain elements is shown in Figure 9(a). A local orientation field is generated by taking the local 1-direction perpendicular to the closest void/matrix interface, taking into account the periodicity of the structure, and is shown in Figure 9(b).

2.3 Results

The constitutive behavior and micromechanical models just discussed were implemented in the finite element package ABAQUS (HKS, 2001) to study the potential of local anisotropy enveloping dispersed voids for the toughening of semicrystalline polymers. The potential of toughening by local anisotropy is investigated by using different amounts of anisotropy in both the SA and the ID model.

Isotropic material, with \( \zeta = 1 \), is used as a reference case for large scale, randomly crystallized material. For the small scale transcryrstallized material, several levels of anisotropy are considered, ranging from \( \zeta = 1.5 \) to \( \zeta = 5 \). In Figure 10, the magnitude of the plastic deformation is given for the irregular plane strain model. For fully isotropic material, the deformation is strongly localized in a specific path through the microstructure, determined...
by the irregular void arrangement. For increasing anisotropy, increasingly dispersed shear yielding is observed, which is highly favorable to enhance the toughness (equivalent to delocalisation of strain). Maximum $\varepsilon_p^{\text{mag}}$-values are reduced, and are located both in the matrix material, away from the void surface and at the void/matrix interface for the transcrystallized material. In the largely anisotropic material, double shear bands can be observed at each side of a void, positioned at the inclined 30°–50° off-polar regions, whereas in the isotropic material mostly single shear bands at the void equators are found. The shear yielding mechanism becomes truly effective for anisotropy ratios $\zeta = R_{11}/R_{12}$ above the value of 3.

Although not shown here, it is mentioned that for all levels of anisotropy, in the ID model, the highest tensile triaxial stresses are found at the void equator regions, which is not in agreement with three-dimensional simulations (Van Dommelen et al., 2003b). More realistic predictions of the triaxial stress state around dispersed voids are obtained with the axisymmetric SA model, as represented in Figure 11. In the isotropic material, the maximum tensile triaxial stresses are found to occur at the void equators. For small anisotropy levels, these negative hydrostatic pressures are reduced. At higher levels of anisotropy, however, the tensile pressures again increase with increasing $\zeta$, but the maximum values are now found in the matrix material near the void pole. The SA model is in much better agreement with the three-dimensional situation (Van Dommelen et al., 2003b) than the ID model. Despite, the peak values of the tensile hydrostatic stress are significantly lower for the axisymmetric SA model than for the full three-dimensional model.

The distinct effect of anisotropy on the triaxial stress field is also reflected in the maximum in-plane principal stress, $\sigma_{\text{max}}$, as is shown in Figure 12. For the isotropic matrix material, the locations of large equivalent stress and

\begin{align*}
(a) & \quad \zeta = 1 \\
(b) & \quad \zeta = 1.5 \\
(c) & \quad \zeta = 2 \\
(d) & \quad \zeta = 3 \\
(e) & \quad \zeta = 5
\end{align*}

Figure 10: The influence of radially oriented anisotropy on the magnitude of plastic deformation, $\varepsilon_p^{\text{mag}}$, for the irregular plane strain model, at $\dot{\varepsilon} = 0.05$.

\begin{align*}
(a) & \quad \zeta = 1 \\
(b) & \quad \zeta = 1.5 \\
(c) & \quad \zeta = 2 \\
(d) & \quad \zeta = 3 \\
(e) & \quad \zeta = 5
\end{align*}

Figure 11: The influence of radially oriented anisotropy on the normalized hydrostatic pressure, $p/\sigma_{y0}$, for the axisymmetric SA model, at $\dot{\varepsilon} = 0.05$. 
negative hydrostatic stress coincide, leading to a relatively high maximum in-plane principal stress, concentrated at the void equators, and the void-bridging ligaments. As the anisotropy parameter \( \zeta \) is increased, the values of \( \sigma_{\text{max}} \) are considerably reduced and the location of the largest \( \sigma_{\text{max}} \) changes to the void poles for \( \zeta = 5 \).

### 2.4 Failure mechanisms

Based on the investigations with both the ID and the SA model, two distinct effects of local, radially oriented, anisotropy can be observed. The influence on the triaxial stress field is a change of the position of maximum tensile values. Under high tensile triaxial stress, crazelike features, as interlamellar separation and voiding of amorphous regions (Friedrich, 1983; Narisawa and Ishikawa, 1990; Kausch et al., 1999; Michler and Godehardt, 2000), may be initiated in the matrix material, and upon extension and coalescence of cavities, crazes are formed. Although crazing leads to brittle behavior, the crazing process itself may under certain conditions also lead to some plasticity via a multiple crazing process (Argon et al., 1983, 1994).

In the simulations, the highest negative hydrostatic pressures are found at the void equators for the large scale, isotropic material. For the small scale anisotropic material however, the large tensile pressures are shifted towards the void poles. Therefore, the initiation of crazing may, for the voided system with radially oriented anisotropy, be expected to occur at the particle poles, rather than in the equator region. The growth of initiated crazes is likely to occur along planes which are perpendicular to the direction of maximum principal stress (Kramer, 1983; Narisawa and Ishikawa, 1990; Kausch et al., 1999). In Figure 13, the direction of the maximum in-plane principal stress is given for the SA model, for both isotropic (\( \zeta = 1 \)) and largely anisotropic (\( \zeta = 5 \)) material. For both situations, in the region of large tensile triaxial stress, the maximum in-plane principal stresses are relatively large, and directed parallel with the void interface. Therefore, craze growth is expected to occur perpendicular to the interface. Moreover, the large principal stresses at the particle equators of the isotropic material will lead to brittle fracture of the matrix material given the direction of the craze growth, perpendicular to the loading direction. The decrease of maximum in-plane principal stresses in the anisotropic material and the shift of the directions of an eventual craze growth, makes this system less susceptible to brittle fracture. It is noted that in the current simulations, no failure and crazing initiation/growth criteria have been used (as for example in Tijssens et al., 2000; Estevez et al., 2000; Socrate et al., 2001). But still the conclusions based upon the analysis this far can be schematically summarized, see Figure 14. The actual mechanism that will occur for a specific matrix material will depend on the
values of the brittle fracture strength, the resistance against craze initiation and growth and the yield strength of the material (Bicerano and Seitz, 1996). In isotropic materials, possible crazes are initiated at the particle equators, and grow transversely to the macroscopic tensile direction. The plastic deformation is localized in a few bands, located in crazing regions. For this large scale system, the crazes may act as precursors to cracks, and ultimately failure. For the small scale situation, with radially oriented anisotropic material around the cavitated particles, maximum tensile triaxial stresses are predominantly found in zones of limited plastic deformation. Possible crazes are initiated at the particle poles, and grow in the direction of macroscopic loading. In this situation, crazing may become a mechanism of energy-absorbing inelastic deformation. Additionally, extensive matrix yielding, which is another beneficial energy-absorbing mechanism, occurs in noncrazing regions. Therefore, by changing the nature of matrix crazing, reducing principal stresses and inducing extensive matrix shearing, a local, radially oriented, anisotropy, with sufficiently reduced shear strengths, may be a highly efficient method for the toughening of semicrystalline materials.

2.5 Conclusions

The effect of matrix materials with a reduced yield strength in the local shear directions around well-dispersed voids has been investigated by numerical simulations of idealized systems. The local principal anisotropy directions were assumed to be radially oriented around second-phase soft particles. The fictitious polymeric material was modeled in the context of anisotropic Hill plasticity, where the yield strength has been taken to depend on an effective plastic deformation measure, and its time derivative. Two extreme size scales were investigated; the largest scale with completely isotropic material properties and the smallest scale having a fully percolated anisotropic structure.

The three-dimensional structure of the voided material was simplified to two different micromechanical models. The irregular distribution of voids is captured by a multiparticle plane strain RVE. The irregular nature of this RVE is essential in capturing the effects of local anisotropy on the mechanics of plastic deformation. For the large scale, plastic deformation localizes in a specific path through the matrix material, inducing macroscopically brittle behavior, whereas for the small scale configuration, a heterogeneous field of void-bridging shear bands was found throughout the entire domain, which could lead to a macroscopically toughened behavior. The extent of shear yielding increases with increasing anisotropy. The localization of deformation vanishes due to a large reduction of local shear yield strengths. However, the ID model is incapable of capturing the distinct effects of local anisotropy on the triaxial stress state. A better representation thereof is obtained with the axisymmetric SA model, where a regular distribution of voids is assumed. The most striking effect of local anisotropy on the hydrostatic stress field is a shift of the highest tensile triaxial stresses from the void equator region (where the surface normals are perpendicular to the loading direction) to the void polar region (the surface area where the normals are aligned with the loading direction). Consequently, the maximum principal stresses at the void equator are considerably reduced.

The calculations confirm that the mechanism as proposed by Muratoğlu et al. (1995c) could indeed lead to toughened material behavior. The presence of an absolute length scale is related to the thickness of a layer of anisotropic matrix material enveloping the dispersed voids. Required for toughening by this mechanism is then (i) a structure of well-dispersed voided particles with an average surface–to–surface interparticle distance which is smaller than the critical length parameter of the matrix material; (ii) locally anisotropic material with the principal
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1-direction radially oriented with respect to the nearest void surface; and (iii) a sufficiently reduced shear yield strength in the local 12- and 13-directions (with $\zeta = R_{11}/R_{12}$ at least of the order of 3).

It is noted that although the large potential of local anisotropy for toughening of semicrystalline polymers was shown, the origin of this anisotropy has not been addressed here. The material was merely assumed to be oriented with the principal 1-direction of anisotropy towards the nearest void and having a finite anisotropic layer thickness. The origin of these layers is attributed to a preferred crystallization at the particle/matrix interface by Muratoğlu et al. (1995c) and Bartczak et al. (1999a,b). The consequences of such a morphology for local anisotropy will be addressed in Section 4.

3 Hard particles: can they also act as toughness modifiers? ²

A physically-based mechanism for the toughening of semicrystalline polymeric materials due to the dispersion of particles originates from the presence of a layer of anisotropic transcrysallized material enveloping the particles, and was proposed for nylon by Muratoğlu et al. (1995c). Bartczak et al. (1999a,b) generalized this mechanism to other semicrystalline materials (like high density polyethylene) and showed the critical interparticle distance to be an intrinsic property of the matrix material, thereby opening the possibility of using mineral fillers instead of rubber particles for the toughening of semicrystalline polymers, the advantage of which would be an improved modulus of the blend. They argued that debonding of hard filler particles could be an alternative for the cavitation of the rubbery phase.

In Section 2, an idealized, polymeric matrix material was modeled by anisotropic Hill plasticity, and various representative volume elements were used to describe the system containing dispersed voids. It was shown that a local plastic anisotropy of matrix material around the voids can effectively replace localization by dispersed shear yielding and change the occurring hydrostatic stresses, potentially leading to toughened material behavior. However, to achieve these improvements, a morphology should be pursued that has a radially oriented structure around the dispersed voids and provides a sufficiently large amount of anisotropy.

In this section, the consequence of using hard mineral particles for the toughening of semicrystalline polymers is investigated. For this purpose, again the anisotropic Hill model is used. The system contains a scale parameter, which is the ratio of the average distance between particles and a critical distance. The value of this parameter is represented in the calculations by the relative thickness of an anisotropic layer around the particles. Large and small scale configurations are modeled again by entirely isotropic or anisotropic matrix material, respectively.

3.1 Model description

The influence of mineral (i.e. hard) filler particles in semicrystalline polymeric material is investigated, and particularly the effect of these fillers on the mechanism of toughening by locally induced anisotropy. As a reference situation, voided matrix material will be used. A distinction is made between fully bonded particles, for which a tied particle/matrix interface is used, and debonding particles. For the latter, a contact algorithm (HKS, 2001) with a relatively low maximum tensile strength $\sigma_i/\sigma_y = 0.4$ is used to describe the particle/matrix interaction. The effect of relatively stiff rubber particles is presented in Van Dommelen et al. (2003e).

For the yield behavior, again the anisotropic Hill yield criterion (Hill, 1950) is used, with a rate-dependent and hardening yield stress, as discussed in Section 2. The mineral filler particles are modeled as linearly elastic, with Young’s modulus $E_p = 80$ GPa and Poisson’s ratio $\nu_p = 0.3$. Particle-modified material is again described by a finite element model of a representative volume element (RVE). The particle-modified system, having a three-dimensional nature, is simplified to a two-dimensional RVE, for which two different approaches are used, as discussed in Section 2.

3.2 Results

In Figure 15, the magnitudes of plastic deformation as obtained by the ID model are shown for systems containing both debonded and fully bonded hard filler particles, for both isotropic ($\zeta = 1$, i.e. large scale) and anisotropic ($\zeta = 3$, i.e. small scale) matrix material, respectively. For the voided isotropic matrix material (Figure 15(a)), the

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macromechanics of Particle-Modified Semicrystalline Polymers  

(a) $\zeta = 1$  
(b) $\zeta = 1$  
(c) $\zeta = 1$  

(d) $\zeta = 3$  
(e) $\zeta = 3$  
(f) $\zeta = 3$  

Figure 15: The magnitude of plastic deformation, $\varepsilon_{\text{pl}}^{{\text{mag}}}$, for the ID model with (a), (d) voids, (b), (e) easily debonding hard particles, and (c), (f) fully bonded hard particles, at $\dot{\varepsilon} t = 0.1$.

macroscopic contraction in the free direction is small, corresponding to the growth of voids, due to stretching of relatively thin ligaments. Therefore, for this matrix material, the inclusion of easily debonding hard particle fillers has no significant effect on the deformation observed, as can be seen by comparison with Figure 15(b), where the interface strength $\sigma^I$ is negligibly small. For radially oriented anisotropic voided material, a dispersed mode of massive shear yielding is observed, with double shear bands at each side of a particle. As a result of matrix shearing, for the voided anisotropic system, however, the voids become smaller in the macroscopically free direction, see Figure 15(d). Consequently, the presence of hard mineral fillers interferes with the mechanism of matrix shearing, as can be observed in Figure 15(e). Therefore, although there is some effect of anisotropy, the mechanism of toughening by locally induced anisotropy is expected to be considerably less efficient for nonadhering hard fillers than for low modulus rubber particles.

For materials filled with well-bonded stiff particles, which is shown in Figures 15(c) and (f), massive shear yielding is found for both isotropic and anisotropic matrix behavior. However, bonding has negative effects concerning craze initiation and growth direction. In Figure 16, the effect of hard filler particles on the normalized hydrostatic pressure, $p/\sigma_{0y}$, as predicted by the SA model, is displayed for (large scale) isotropic and (small scale) anisotropic matrix material. For voided systems, the effect of anisotropy on the triaxial stress field is a change of the position of maximum tensile values. The highest negative (tensile) hydrostatic pressures are found at the particle poles, rather than in the equator region. For easily debonding hard particles, a similar effect of local anisotropy on the tensile triaxial stresses is observed, with an increase of the peak value for the anisotropic situation. The well-bonded configurations both show peak tensile triaxial stresses at the poles. The growth of initiated crazes is likely to occur along planes which are perpendicular to the direction of the maximum principal stress. In Figure 17, the normalized maximum in-plane principal stress, $\sigma_{\text{max}}/\sigma_{0y}$, is depicted for the SA model, for both isotropic ($\zeta = 1$) and anisotropic ($\zeta = 3$) material, with either a void, or easily debonding or adhering hard particles. Moreover, in Figure 18, the direction of the maximum in-plane principal stress is given for the systems containing a hard particle. For both nonadhering situations, the maximum in-plane principal stresses in the region of large tensile triaxial stress, are parallel with the particle/matrix interface. Therefore, craze growth is expected to occur perpendicular to the interface, i.e. perpendicular to the loading direction for the isotropic material and parallel to the loading direction for the anisotropic system. However, for the well-bonded systems, which did show advantageous shear yielding for both the isotropic and the anisotropic configuration, the maximum principal stresses in the polar region (where the largest tensile triaxial...
stresses are observed) are directed approximately in the loading direction. Consequently, for these systems craze growth or microcracking may be expected to occur perpendicular to the loading direction, thereby possibly leading to macroscopic failure. Anyhow, for the systems containing well-bonded hard particles, an isotropic matrix seems
to be favorable over locally anisotropic material.

### 3.3 Conclusions

Fictitious, idealized, polymeric matrix materials were modeled by anisotropic Hill plasticity in Section 2, where the distinct effect of local plastic anisotropy of matrix material around the voids was shown, viz. an effective replacement of localization by dispersed shear yielding and a change of the occurring hydrostatic stresses, potentially leading to toughened material behavior. In this section, a similar modeling approach was used to investigate the influence of mineral filler particles on this toughening mechanism.

The use of mineral filler particles for toughening of polymeric materials requires debonding in order to prevent excessive tensile hydrostatic stresses. These debonded hard particles show a relocation of tensile triaxial stresses to the particle polar areas by local anisotropy, similarly to anisotropic voided systems, with the maximum principal stresses directed such that crazes or microcracks are expected parallel to the loading direction. However, the anisotropy-induced shear yielding mechanism is affected by the presence of stiff inclusions.

### 4 Full multiscale modeling: what did we learn? 3

To investigate the possibility that a particular microstructure satisfies the requirements for sufficient anisotropy, a full multiscale micromechanically-based numerical model for the elasto-viscoplastic deformation and texture evolution of semicrystalline polymers was developed (Van Dommelen et al., 2003c) and is used to simulate the behavior of particle-modified high density polyethylene (HDPE). For the analysis of these systems, a distinction between three different scales is made, as schematically depicted in Figure 19. The constitutive properties of the material components are characterized at the microscopic scale. At this level, the individual crystallographic lamellae and amorphous layers are identified. At the mesoscopic scale, an aggregate of individual phases is considered, which can be a spherulite or a sheaflike aggregate of preferentially oriented material. To bridge between those scales, the polycrystalline composite inclusion model is used. At the macroscopic scale, for particle-modified...
materials, a structure of dispersed particles and matrix material can be identified. At this level, the system is represented by a finite element model using various representative volume elements, as suggested by the Hill-type simulations of Section 2. A bridge to the mesoscopic level is obtained by using an aggregate of composite inclusions as a representative microstructural unit in each integration point. The effect of transcry stallized orientations of matrix material versus randomly oriented material on both mesoscopic and microscopic results is investigated, as well as a hypothesized microstructure, which may be the result of process conditions.

4.1 Microscopic scale: material models

The anisotropic constitutive behavior of intraspherulitic material is modeled by an aggregate of elasto-viscoplastic two-phase composite inclusions Lee et al. (1993a,b). Each inclusion consists of a crystalline and an amorphous phase. In this section, the constitutive models of the constituent phases are shortly discussed. For a more elaborate presentation of these models, see Van Dommelen et al. (2003c).

4.1.1 Crystalline phase

The crystalline domain of polymeric material consists of regularly ordered molecular chains. The crystal structure results in (i) anisotropic elastic behavior where the elastic properties are given with respect to the crystallographic directions, and (ii) plastic deformation governed primarily by crystallographic slip on a limited number of slip planes (G’Sell and Dahoun, 1994; Argon, 1997). Moreover, plastic deformation may result from mechanical twinning or stress-induced martensitic phase transformations (Lin and Argon, 1994; G’Sell and Dahoun, 1994; Frank et al., 1970; Young and Bowden, 1974). Since crystallographic slip is assumed to be of most importance for polymeric materials, in the modeling process the latter two mechanisms are left out of consideration.

The elastic component of the deformation in the crystalline phase is characterized by an anisotropic fourth-order elastic modulus tensor. The anisotropic elastic properties are coupled to the crystallographic directions. For the viscoplastic behavior of the crystalline phase, a rate-dependent crystal plasticity model is used. In this model, the plastic velocity gradient of the crystalline lamella, consisting of a single crystal, is composed of the contributions of all physically distinct slip systems, being 8 for high density polyethylene (HDPE), with a lowest slip resistance of 8 MPa. The shear rate of each slip system is assumed to be related to the resolved shear stress according to a viscoplastic power law.

4.1.2 Amorphous phase

The amorphous phase of semicrystalline polymeric material consists of an assembly of disordered macromolecules, which are morphologically constrained by the neighboring crystalline lamellae. Plastic deformation in these domains occurs by a thermally activated rotation of segments. At room temperature, the amorphous phase of HDPE, which is the material of interest in this work, is in the rubbery regime, with the glass transition temperature near −70 °C. The deformation in this regime is characterized by a limited strain rate-sensitivity and a strong entropic hardening at large deformations.

The initial elastic resistance of the rubbery amorphous phase is well below the elastic resistance of the crystalline domain. Consequently, elastic deformations can be considerably large and are modeled by a generalized neo-Hookean relationship. A relatively strain rate-insensitive viscoplastic power law relation between an effective shear strain rate and the effective shear stress (Lee et al., 1993a) is used in conjunction with a back stress tensor for which the Arruda–Boyce eight-chain network model of rubber elasticity (Arruda and Boyce, 1993) is used.

4.2 Mesoscopic scale: composite inclusion model

The mechanical behavior at the mesoscopic level is modeled by an aggregate of layered two-phase composite inclusions as was first proposed by Lee et al. (1993a,b) for rigid-viscoplastic material behavior. Each separate composite consists of a crystalline lamella which is mechanically coupled to its corresponding amorphous layer, as is shown in the upper right part of Figure 19. The stress and deformation fields within each phase are assumed to be piecewise homogeneous; however, they may differ between the two coupled phases. It is assumed that the crystalline and amorphous components remain fully mechanically coupled. Interface compatibility within the composite inclusion and traction equilibrium, across the interface, are enforced. To relate the volume-averaged
mechanical behavior of each composite inclusion to the imposed boundary conditions for an aggregate of inclusions, a hybrid local–global interaction law is used. This class of hybrid-inclusion models was introduced by Lee et al. (1993a, b) for rigid/viscoplastic composite inclusions. A more detailed description of the composite inclusion model is presented elsewhere (Van Dommelen et al., 2003c). Moreover, an application of this model to study the intraspherulitic deformation of polyethylene is presented in Van Dommelen et al. (2003a). Some aspects of the finite element implementation in HKS (2001) are given in Van Dommelen et al. (2001).

The anisotropy of preferentially oriented intraspherulitic material, as predicted by the composite inclusion model, is investigated. A mesoscopic aggregate of composite inclusions, represented by a set of crystallographic orientations and corresponding lamellar orientations, is subjected to constant strain rate uniaxial tension in the three principal directions $e_i$ of the material coordinate system. Consider the right polar decomposition $\bar{F} = \bar{R} \cdot \bar{U}$ of the volume-averaged deformation gradient, where $\bar{R}$ is the mesoscopic rotation tensor, and $\bar{U}$ is the corresponding right stretch tensor. Then, the following conditions are imposed:

\[
\bar{R} = I; \quad \bar{U}_{ii} = \lambda(t); \quad i = 1 \lor i = 2 \lor i = 3,
\]

with \(\lambda(t) = \exp(\dot{\varepsilon}t),\)

where $\dot{\varepsilon}$ is set equal to the material reference shear rate $\dot{\gamma}_0$. Furthermore, the components of the Cauchy stress tensor should satisfy:

\[
\bar{\sigma}_{jj} = \bar{\sigma}_{12} = \bar{\sigma}_{13} = \bar{\sigma}_{23} = 0; \quad j \in \{1, 2, 3|j \neq i\}.
\]

In another test case, pure shear deformation is applied by prescribing one of the basic shear components $ij$ of the (symmetric) right stretch tensor:

\[
\bar{R} = I; \quad \bar{U}_{ij} = \gamma(t); \quad ij = 12 \lor ij = 13 \lor ij = 23,
\]

with \(\gamma(t) = \frac{1}{2} \sqrt{3} \dot{\gamma}_0 t,\)

and \(\bar{\sigma}_{11} = \bar{\sigma}_{22} = \bar{\sigma}_{33} = \bar{\sigma}_{kl} = 0; \quad kl \in \{12, 13, 23|kl \neq ij\}.
\]

### 4.2.1 Anisotropy of preferentially oriented material

The full multiscale model is used to examine the effect of the microstructural morphology on the mechanics of particle-modified systems (Van Dommelen et al., 2003d). First, the anisotropy, at the mesoscopic level, of (microscopically) preferentially oriented material, as predicted by the composite inclusion model, is investigated.

**Randomly oriented material** The local spherulitic structure of melt-crystallized HDPE is represented by an aggregate of 125 composite inclusions with randomly generated initial orientations of the crystallographic phases, having an orthorhombic lattice. Experimental studies of melt-crystallized polyethylene show that lamellar surfaces are of the \{h0l\}-type, where the angle between the chain direction $c$ and the lamellar normal $n$ varies between 20° and 40° (Keller and Sawada, 1964; Bassett and Hodge, 1981). Gautam et al. (2000) found by molecular simulations the [201] planes to provide the lowest amorphous/crystalline interface energy. For randomly oriented material, the initial angle between $e_0$ and $n_0^i$ is set at 35°, corresponding to the [201] planes. Since the distribution of the crystallographic orientations is random, the mechanical behavior of this aggregate will be quasi isotropic.
Transcrystallized material For thin HDPE films, crystallized on rubber and calcium carbonate substrates, Bartczak et al. (1999c) found a sheaflike morphology of the lamellae, which were oriented preferentially edge-on against the substrate, resulting from a surface-induced crystallization. The (100) planes, containing the two crystallographic slip systems with the lowest slip resistance, (100)[001] and (100)[010], were found to be directed preferentially parallel to the plane of the film with a random orientation of the molecular chains within this plane. The lamellar normals were either parallel to the plane of the substrate or somewhat tilted with respect to the plane. However, twisting of lamellae was found to be substantially reduced. The preferred crystallographic planes for the crystalline/amorphous interface remain unclear for this morphology. It can be assumed that these planes are still of the {h0l}-type. The observation by Bartczak et al. (1999c) that crystal growth is unidirectional with little divergence sideways, and the reduction of lamellar twisting, suggest a smaller angle between the crystallographic chain direction $c$ and the lamellar normal $n$ than observed in randomly crystallized material. Here, the plane of the crystalline/amorphous interface is assumed to be of the {102}-type, corresponding to an initial chain tilt angle of 9.7°. Besides the crystallographic and lamellar orientations, all microscopic material properties are assumed to be identical to the properties of the randomly crystallized material. A set of crystallographic orientations is generated with the (100) poles preferentially aligned in the direction of the normal of the substrate, with a certain random deviation from the substrate normal direction. Furthermore, a random rotation around this normal direction is applied. Therefore, the mechanical properties at the mesoscopic scale can be expected to be transversely isotropic with the (fiber) symmetry direction corresponding to the substrate normal direction. All differences in mechanical response in the 22 and 33 tensile directions and the 12 and 13 shear directions will be of statistical origin. After a set of crystallographic orientations has been generated, the lamellar normals are obtained as described above. In Figure 20(a)–(d), the orientations of a set of 125 composite inclusions are displayed. The view direction of the

![Equal area projection pole figures representing (a)–(c) the principal crystallographic lattice directions, and (d) the lamellar normals of a set of transcrystallized orientations and (e), (f) the normalized equivalent mesoscopic stress $\bar{\sigma}/\ell_0$, vs. the imposed deformation for tension and shear, respectively, in the basic material directions as predicted by the composite inclusion model.](image)

Figure 20: Equal area projection pole figures representing (a)–(c) the principal crystallographic lattice directions, and (d) the lamellar normals of a set of transcrystallized orientations and (e), (f) the normalized equivalent mesoscopic stress $\bar{\sigma}/\ell_0$, vs. the imposed deformation for tension and shear, respectively, in the basic material directions as predicted by the composite inclusion model. Equal area pole figures is the substrate normal direction. This direction is the preferred direction for the (100) poles. In Figure 20(e) and (f), the corresponding mesoscopic stress–strain response of the composite inclusion model is shown in the basic tensile and shear directions. The equivalent stresses are normalized by the lowest slip resistance $\ell_0 = 8$ MPa. Additionally, also the response of a randomly oriented aggregate is shown. With respect
to the randomly oriented aggregate, the equivalent stresses in the transverse tensile directions are increased. The reduction of the 12 and 13 shear resistances is related to these tensile 22 and 33 resistances. The ratio of transverse tensile and 12/13 shear resistances at the onset of yielding is of the order of 2. At higher strains, this ratio decreases to approximately 1.5. Simulations with an anisotropic Hill plasticity model (Section 2) showed that for the effectiveness of the toughening mechanism under investigation, a larger amount of anisotropy would be necessary (ζ ≥ 3). A sharper texture, however, does not increase the $R_{22}/R_{12}$ anisotropy ratio.

4.3 Macroscopic models

For particle-modified materials, a structure of dispersed particles and matrix material can be identified. The system is described by a finite element model of a representative volume element (RVE). The blended system, having a three-dimensional nature, is simplified to a two-dimensional RVE, for which two different approaches are used (see Section 2). In order to capture the important effects of the essentially irregular nature of particle-dispersed systems, a plane strain RVE with randomly dispersed particles is used, where the cavitated particles are represented by voids.

A similar structure as was used in the Hill-type simulations in Section 2 is adopted, containing 20 volume percent irregularly dispersed voids. The mesh with 565 four-noded bilinear reduced integration plane strain elements is shown in Figure 21(a). An orientation field is generated by taking the local 1-directions perpendicular to the closest void/matrix interface, respecting the periodicity of the structure, as shown in Figure 21(b).

For the representation of the triaxial stress state around a particle, an axisymmetric RVE model of a staggered array of particles is considered. The finite element mesh of the SA model, with 20 volume percent voids, was visualized in Figure 7(a). In each integration point of the 196 reduced integration four-noded bilinear elements, a local coordinate system is generated, such that the local 1-directions are again perpendicular to the closest void surface.

4.4 Effect of transcrystallized anisotropy on toughness

Now, the full multiscale model will be used to investigate the effect of a transcrystallized orientation on the deformation of particle-modified systems. Both RVE models, as described in the previous section, are applied, with in each integration point either an aggregate of randomly generated orientations or a (unique) set of orientations with a similar distribution as in Figure 20. For the latter situation, the local (fiber) symmetry directions correspond to the 1-directions as described in Section 4.3. In each integration point, 64 composite inclusions per aggregate are used.

In Figure 22, for the plane strain ID model, the obtained fields of the magnitude of plastic deformation, $\varepsilon_p^{\text{mag}} = \sqrt{\frac{2}{3} \bar{\varepsilon}_p : \bar{\varepsilon}_p}$, are shown for $\dot{\epsilon} t = 0.025$. For the large scale RVE, containing randomly oriented, and thus quasi isotropic, matrix material, the plastic deformation is localized in particle-bridging paths, percolating through
the matrix, approximately perpendicular to the loading direction (Figure 22(a)). The small scale RVE, having trans-
crystallized orientations, shows more widespread localized plastic deformation, with also shear bands in relatively
thick interparticle ligaments, in the 30° to 50° direction with respect to the particle poles (the term pole refers to
the location where the particle/matrix interface normals are aligned with the loading direction, Figure 22(b)). In
the relatively thin ligaments, still localized deformation is observed. In Figures 23 and 24, the magnitude of the
plastic deformation is shown for $\dot{\epsilon}_t = 0.05$, as well as some selected microscopic texture evolutions and defor-
mation quantities in two integration points, for random and transcrystallized initial orientations, respectively. For
both situations, most plastic deformation is concentrated in relatively thin interparticle ligaments. The presence of
a layer of preferentially crystallized material with significant thickness around cavitated rubber particles does have
some effect on the mechanism of matrix shear yielding. This effect is, however, limited due to the relatively small
level of anisotropy in the material.

In the pole figures showing the evolution of crystallographic and morphological texture, the initial orientation
of each composite inclusion is represented by a dot. The arrow connects it with the corresponding final orientation,
which is located at the arrow-head. In the pole figures showing microscopic deformation quantities, the location of
each dot denotes the initial orientation of the lamellar normal of an inclusion and its gray intensity represents
the value of the indicated quantity for the inclusion. To enrich the information shown in the latter pole figures,
the mirror location of each pole with respect to the central point of the plot is also given. The view direction is
the macroscopic out-of-plane direction. The term intralamellar deformation is employed for the magnitude of the
def ormation of the crystalline phase. For the amorphous deformation, a distinction is made between so-called
interlamellar shear and interlamellar separation. Let $y^i$ be a material vector in the amorphous phase of inclusion
$i$, with $y^i = n^i_0$. Then, interlamellar shear is assumed to be represented by the angle (in radians) between the
cov ected material vector, $y^i = F^i \cdot n^i_0$, and the current lamellar normal, $n^i$. Lamellar separation is represented
by $\ln(y^i_0)$, with $\lambda_0 = n^i \cdot y^i$.

The integration point indicated by A in Figures 23 and 24, represents, for the initially randomly oriented mate-
rial, a material point in the highly localized zone. Since this integration point is located in the equatorial area (the
equator is defined as the area where the particle/matrix interface normal is perpendicular to the loading direction),
the local 1-direction is almost perpendicular to the global loading direction. The microscopic results for this point
show moderate crystallographic deformation, mainly for inclusions with their lamellar normals close to the local
1-direction. The (100) poles, which represent the planes containing the two most easily activated slip systems,
migrate towards a direction which is approximately 40° away from the local 1-direction. The lamellar normals are
moving towards the same direction, with the largest activity for lamellar poles initially far from the target di-
tection. Amorphous deformations are relatively large, with interlamellar shear predominantly in inclusions with
their crystalline/amorphous interface approximately 45° inclined with the loading direction. Interlamellar separa-
tion is found predominantly in inclusions with their interface normals perpendicular to the local 1-direction. For
the RVE with transcrystallized orientations (Figure 24), deformation is still localized in the ligament containing
integration point A. In this point, the maximum intralamellar (crystallographic) deformation has increased with
respect to the quasi isotropic material, whereas both maximum interlamellar shear and separation have decreased.
Crystallographic deformation is concentrated in inclusions with their lamellar normals perpendicular to the load-

Figure 22: The influence of radially oriented anisotropy on the magnitude of the plastic deformation, $\bar{\varepsilon}_p^\text{mag}$, for
the ID model, at $\dot{\epsilon}_t = 0.025$, with (a) randomly generated initial orientations, and (b) transcrystallized preferential
orientations.
In Figures 25 and 26, the normalized hydrostatic pressure $\bar{p}/\tau_0$, as well as some selected microscopic texture evolutions and deformation quantities in two integration points, are shown for the SA model, with random and transcrysallized initial orientations, respectively. The region of peak tensile triaxial stresses is located in the matrix material near the polar region for the preferentially oriented material, rather than in the equator area, as is observed for the randomly oriented material. In the equator region, the hydrostatic pressures remain negative; however, the absolute values are reduced with respect to the quasi isotropic material. In Figure 27, the direction and the magnitude of the normalized maximum in-plane principal stress, $\bar{\sigma}_{\text{max}}/\tau_0$, are shown for the SA model. For the large scale, quasi isotropic material, the maximum principal stresses are found to be negligible in the polar region, whereas for the small scale configuration, with transcrysallized orientations, also in this region, maximum principal stresses are significant. In the equator region, maximum values are slightly increased with respect to the principal stresses in the isotropic material.

For the initially randomly oriented configuration, in integration point C, which is located in the equatorial region, the intralamellar deformations are relatively small, and are found predominantly for inclusions with their lamellar normals either perpendicular or parallel to the loading direction. In the remaining inclusions, interlamellar shear is considerably large and a significant amount of interlamellar separation is found for inclusions with their lamellar normals aligned with the loading direction. For these inclusions, the preferred direction of possible craze growth, perpendicular to the direction of the maximum principal stress (Kramer, 1983), is parallel to
For integration point D, which is located in a high tensile triaxial stress area, lamellar separations remain small.

In polymeric materials, the principal mechanisms leading to deformation and fracture (Kausch et al., 1999) are shear yielding of matrix material, voiding and the occurrence of crazelike features (Michler and Godehardt, 2000; Narisawa and Ishikawa, 1990) under triaxial stress conditions, and brittle fracture of the matrix by chain scission, induced by high tensile principal stresses. Whether or not the material will show toughened behavior will depend on which of these phenomena will predominantly occur. Massive shear yielding, with energy-absorbing inelastic deformation, has a beneficial effect on toughening. However, for the transcristallized orientation currently considered, the increase of matrix shear yielding (replacing strain localization) is limited. Intralamellar deformation...
is favored over interlamellar deformation. In the quasi isotropic material, crazelike features may be initiated in the equator region, where the peak tensile triaxial stresses are maximal, and significant interlamellar separation occurs. Since they will grow perpendicular to the direction of maximum principal stress, the growth direction will be...
transversely to the macroscopic tensile direction. These crazes may act as precursors to cracks, ultimately leading to failure. For the material having transcry stallized preferential orientations, in this region the negative hydrostatic pressures and interlamellar separation are reduced, diminishing the chance of craze initiation. On the other hand, in the polar region, for this material, relatively large tensile triaxial stresses are found, possibly initiating voids. However, interlamellar separation remains small at this location. In this area, the growth direction of possible crazes will be in the direction of macroscopic loading, and crazing may become an energy-absorbing mechanism. Therefore, transcry stallized orientations may lead to some degree of toughening, however, the effect is limited by the relatively small amount of anisotropy.

4.5 Influence of processing conditions

In the foregoing, a fully radially oriented, transcry stallized, microstructure was shown to have a beneficial, but limited effect on the mechanics of deformation in particle-modified systems. This was due to the relatively small reduction in yield strength in the local 12 and 13 shear directions. A further decrease of these shear yield strengths would increase matrix shear yielding. Alternatively, an increase of the local 22 tensile yield strength, would have a similar effect, since concurrently it reduces the strengths in shear.

As small flow-related crystallographic orientation was found by Bartczak et al. (1999b) in HDPE with calcium carbonate fillers. The importance of process conditions was demonstrated by Schrauwen et al. (2001a,b, 2002), who found toughness to be dominated by flow-induced effects, see figure 28. Compression molded specimens, having a transcry stallized microstructure, showed only a minor increase in impact toughness. However, a substantial increase in toughness was found for injection molded samples, indicating the presence of flow-induced effects. Moreover, the actual toughness was found to depend on the location of the Izod specimen in the mold, confirming Bartczak’s original results. A row structure of polyethylene lamellae was found in extruded alternating high density polyethylene and polystyrene thin layers by Pan et al. (1990). The long axes of the lamellae, which are the crystallographic b-axes, were oriented in the plane of the layers and perpendicular to the extrusion direction. The a-directions were found to be predominantly normal to the layer surface and lamellar surface normals were aligned with the direction of flow. Moreover, only partial twisting was observed. In thicker layers, an unoriented structure was observed, similar to bulk polyethylene, with the corresponding lamellar twisting.

The effect of a hypothetical microstructure, with preferential orientations that may be the result of an influence of the process conditions on the anisotropic crystallization of matrix material, is now investigated for a voided macrostructure. The transcry stallized preferential orientations as used previously, were axisymmetric with respect to the local 1-direction, i.e. within the plane of the particle/matrix interface, the orientation was assumed to be random. Here, an additional preferential orientation of the molecular chains and the lamellar normals in the local
2-direction is assumed. The lamellar row structure obtained thereby may be the result of an influence of the flow on the crystallization behavior, and resembles the structure that was reported by Pan et al. (1990). Again, the crystallographic $\{102\}$ planes are assumed to constitute the crystalline/amorphous interface, with an initial tilt angle of $9.7^\circ$. In Figure 29, a generated set of 125 composite inclusion orientations of this type are displayed. The stress–strain behavior obtained when this aggregate of composite inclusions is subjected to tension and shear

![Graph showing the influence of processing conditions on toughness](image)

**Figure 28:** Influence of processing conditions on toughness. Reproduced from Schrauwen et al. (2002).

![Diagram of equal area projection pole figures](image)

**Figure 29:** Equal area projection pole figures representing (a)–(c) the principal crystallographic lattice directions, and (d) the lamellar normals of an anisotropic set of orientations with an assumed influence of processing conditions and (e), (f) the normalized equivalent mesoscopic stress $\tilde{\sigma}/\tau_0$, vs. the imposed deformation for tension and shear, respectively, in the basic material directions as predicted by the composite inclusion model.

In the basic material directions, is shown in Figures 29(e) and (f). Because of the lack of a fiber symmetry in this material, large differences between the 22 and 33 tensile loading configurations are found. With respect to the transcrystallized orientations (Figure 20), the yield strength in the 22-direction has considerably increased, whereas the 33 yield strength is reduced. At $\ln(\lambda) = 0.05$ and $\frac{2}{\sqrt{3}}\gamma = 0.05$, the ratio of the 22 tensile and 12 shear yield
strength is 3.4. The ratio of the 22 tensile resistance and the 12 shear resistance of transcrystallized material is 3.0. When material with this microstructural morphology would, in a particle-dispersed system, be oriented appropriately with respect to the loading conditions, an additional beneficial effect on the amount of matrix shear yielding may be expected, based on the simple analyses of Section 2.

A microstructure of matrix material around well-dispersed voided particles is hypothesized that consists of lamellar crystals that are nucleated at the particle/matrix interface. An influence of processing conditions is assumed for the matrix material in the equatorial regions (with respect to the flow direction). This hypothetical morphology is realized by assigning aggregates of composite inclusions with crystallographic and morphological orientations similar to the orientation set in Figure 29 to specific elements of the finite element meshes which were previously used for the ID model and the SA model. These elements are located in the equatorial areas with respect to the flow direction. For the remaining elements, again transcrystallized orientations are assumed (similar to Figure 20).

In Figure 30, the assigned flow-influenced areas are shown for both models, for either flow in the loading direction or flow perpendicular to the loading direction. In each integration point, the local 1-directions are assumed to be radially oriented with respect to the nearest particle, as was previously used for the transcrystallized situation. In Figure 31, the effect of this microstructure on the obtained field of plastic deformation is shown for the ID model at $\dot{\varepsilon}_t = 0.035$. In this figure, also the fully transcrystallized situation is represented. When the macroscopic loading is applied perpendicular to the flow direction, no significant effect of the flow-influenced orientations can be observed, compared to fully transcrystallized material. However, when the RVE is loaded in the direction of the flow, the plastic deformation is no longer localized in the relatively thin interparticle ligaments, but occurs predominantly in the matrix material, away from the particle surfaces and at the particle surface at an inclined location.

In Figure 32(a), the normalized hydrostatic pressure field is represented for the SA model, loaded in the flow direction. Results for the material loaded perpendicular to the flow direction are not shown because of the simi-
particles relies on the presence of a layer of anisotropic transcrystallized material around the particles (Murato et al., 1995c; Bartczak et al., 1999a,b). A multiscale model was used to investigate the effect of preferentially oriented matrix material in HDPE blended with rubber particles, which were assumed to be cavitated. The particle-dispersed system was described by both a plane strain RVE model with irregularly dispersed voids and by an axisymmetric RVE model with an assumed regular stacking of voids, which were loaded in constant strain rate tension. In each integration point of the finite element model, an aggregate of composite inclusions was used as a representative microstructural element that provides the constitutive behavior of the material at the mesoscopic level. Constitutive properties were assigned at the microstructural level to the amorphous and the crystalline domains. Besides these properties, the mesoscopic constitutive behavior was affected by the crystallographic and lamellar orientations of the composite inclusions. By using preferential initial orientations, a mesoscopically anisotropic constitutive behavior was obtained.

Simulations on voided polymeric material with a large average interparticle matrix ligament thickness, having quasi isotropic constitutive behavior at a mesoscopic level, showed a strongly localized deformation, along a path through the matrix, perpendicular to the loading direction. Large tensile triaxial stresses were found in the equator region (with respect to the loading direction) near the particles. In this area, interlamellar separations were relatively large. A particle-modified system having a relatively small average interparticle matrix ligament thickness has been realized by using initially preferentially oriented lamellae, with the crystallographic (100) planes approximately parallel to the void/matrix interface. For this system, a more dispersed field of plastic deformation was found, induced by a small relative reduction of the shear yield strength. Moreover, a relocation of the tensile triaxial stresses in the polar region, where deformation by interlamellar separation remains small, was observed, diminishing the likeliness of initiation and growth of critical crazelike features in the amorphous domains. These phenomena could indeed lead to some degree of toughening of the particle-modified material if the interparticle distance is small. However, with the level of anisotropy as predicted by the composite inclusion model, the effects of these locally preferential orientations remain limited. Simulations on idealized polymeric materials, modeled by anisotropic Hill plasticity (Section 2), showed a much larger potential of local anisotropy for toughening of particle-dispersed semicrystalline materials, if the amount of anisotropy would be sufficiently large (ζ > 3).

4.6 Conclusions

A physically-based mechanism for the toughening of semicrystalline polymeric materials by the dispersion of particles relies on the presence of a layer of anisotropic transcrystallized material around the particles (Muratoğlu et al., 1995c; Bartczak et al., 1999a,b). A multiscale model was used to investigate the effect of preferentially oriented matrix material in HDPE blended with rubber particles, which were assumed to be cavitated. The particle-dispersed system was described by both a plane strain RVE model with irregularly dispersed voids and by an axisymmetric RVE model with an assumed regular stacking of voids, which were loaded in constant strain rate tension. In each integration point of the finite element model, an aggregate of composite inclusions was used as a representative microstructural element that provides the constitutive behavior of the material at the mesoscopic level. Constitutive properties were assigned at the microstructural level to the amorphous and the crystalline domains. Besides these properties, the mesoscopic constitutive behavior was affected by the crystallographic and lamellar orientations of the composite inclusions. By using preferential initial orientations, a mesoscopically anisotropic constitutive behavior was obtained.

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The level, and thereby the effect of local anisotropy was found to be improved if an additional hypothetical possibly flow-induced row structure of the transcryallized lamellae was assumed in certain regions. When loaded in the direction of the macroscopic flow, plastic deformation was no longer localized in relatively thin interparticle ligaments, but was dispersed through the matrix. This massive shear yielding, in combination with the effects on craze-initiating conditions, has a further beneficial influence on the behavior of this material, however, only if loaded in the appropriate direction. Although the employed microstructure was hypothetical, the calculations demonstrated the important role of processing conditions in particle-toughening of semi-crystalline polymers.

5 Discussion

The hypothesis that local anisotropy in particle-modified polymeric systems may lead to macroscopically toughened behavior was investigated by numerical methods. The anisotropy is assumed to be induced by a specific microstructure, which results from preferred crystallization of the polymeric matrix material. The role of the particles in this mechanism is (i) to create a microstructure with anisotropic constitutive behavior during crystallization, and additionally (ii) to provoke local stress concentrations during loading, thereby inducing extensive matrix shear yielding, meanwhile (iii) decreasing or relocating critical triaxial stresses that induce crazes. The validity of this hypothesis has been investigated by micromechanical modeling methods. The precise crystallization behavior was left out of consideration, and the starting-point was an estimated microstructure for the particle-modified system.

The effect of a matrix material with a reduced yield strength in the local shear directions around well-dispersed voids was investigated by finite element simulations for idealized systems. The fictitious polymeric material was modeled in the context of anisotropic Hill plasticity. The three-dimensional structure of the voided material was simplified by using two different micromechanical models. The calculations confirmed that the mechanism as proposed by Muratoğlu et al. (1995c) could indeed lead to toughened material behavior. Required for toughening by this mechanism is apparently (i) a structure of well-dispersed voided particles; (ii) locally anisotropic material, radially oriented with respect to the nearest void surface; and (iii) sufficiently reduced shear yield strengths. If these requirements are satisfied, local plastic anisotropy of matrix material around the voids can effectively replace localization by dispersed shear yielding and can relocate the occurring tensile triaxial stresses from the equator to the particle poles, potentially leading to toughened material behavior.

A similar modeling approach was used to investigate the influence of mineral filler particles on this toughening mechanism. These systems require debonding in order to prevent excessive negative hydrostatic pressures. These debonded hard particles show a relocation of tensile triaxial stresses to the particle polar areas by local anisotropy, similarly to anisotropic voided systems, with the maximum principal stresses directed such that crazes or microcracks are expected to propagate parallel to the loading direction. Moreover, the anisotropy-induced shear yielding mechanism is affected by the presence of stiff inclusions. Although some effect of the anisotropy was observed, the mechanism of toughening by local anisotropy is considered to be less effective for nonadhering hard particles, which have the advantage of increasing the blend modulus, than for low stiffness rubber fillers.

Thereafter, to investigate whether the requirements for the toughening mechanism can be achieved by a transcryallized microstructure, a micromechanically-based numerical model for the elasto-viscoplastic deformation and texture evolution of semicrystalline polymers was developed and used to simulate the behavior of particle-modified high density polyethylene (HDPE). For these blended polymeric systems, a distinction between three different scales has been made. The constitutive properties of the distinguishable material components were characterized at the microscopic scale. At the mesoscopic scale, an aggregate of individual phases was considered. To bridge between those scales, a composite inclusion model has been formulated. The model is based on a simplified representation of the underlying morphology and deformation mechanisms of this material. As a representative microstructural element, a two-phase layered composite inclusion has been used, with a lamellar structure as is commonly observed in semicrystalline polymers. Both the crystalline and the amorphous phase are represented in the composite inclusion model and are mechanically coupled at the interface. For both phases, micromechanically-based constitutive models have been used. The local inclusion-averaged deformation and stress fields are related to the mesoscopic fields of the aggregate using an interaction model. In the model, the effect of transcryallization on microscopic properties other than orientation, such as crystallinity and amorphous and crystalline constitutive behavior (e.g. as a result of the lamellar thickness), are not accounted for.

A full multiscale model was used to investigate the effect of preferentially oriented matrix material in HDPE blended with rubber particles, which were represented by voids. In this model, the structure–property relation-
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ship is addressed at various levels: (i) the arrangement of chain segments, represented in the constitutive behavior of the individual phases; (ii) the arrangement of the lamellae, influencing the response of the polymeric matrix material; and (iii) the particle-modified macroscopic structure. Simulations on voided polymeric material with a large average interparticle matrix ligament thickness, having quasi isotropic constitutive behavior at the mesoscopic level, showed strongly localized deformation. Maximum tensile triaxial stresses were found in the equator regions near the particles. A particle-modified system having a relatively small average interparticle matrix ligament thickness was realized by using initially preferentially oriented lamellae, with the crystallographic (100) planes approximately parallel to the void/matrix interface. For this system, a more dispersed field of plastic deformation was found, induced by a relative reduction of the shear yield strength. Moreover a relocation of the peak tensile triaxial stresses to the polar region was observed, diminishing the initiation and growth of critical crazelike features in the amorphous domains. These phenomena could indeed lead to some degree of toughening of the particle-modified material when the interparticle distance is small. However, with the level of anisotropy as predicted by the composite inclusion model, the effects of these locally preferred orientations remained limited. The simulations on idealized polymeric materials, modeled by anisotropic Hill plasticity, showed a substantially increased potential capacity of local anisotropy for toughening of particle-dispersed semicrystalline materials, if the amount of anisotropy was sufficiently large.

The level, and thereby the effect of local anisotropy was made more pronounced by assuming a hypothetical additional row structure of the transcrysallized lamellae in certain regions, which represents the result of the processing history. When loaded in the direction of the macroscopic flow, plastic deformation was no longer localized in relatively thin interparticle ligaments, but was largely distributed through the matrix. This shear yielding, in combination with the effects on craze-initiating conditions, has a further beneficial effect on the mechanical behavior of this material, however only when loaded in the appropriate direction.

Based on these simulations, Figure 3, which was the starting-point of this work, illustrating the potential of rubber and mineral fillers for improving mechanical properties by the hypothesized mechanism, can be further refined. This refinement is displayed in Figure 33. Whereas in the reference (large scale) isotropic system, tensile triaxial stresses were found in the particle equator areas, for all anisotropic (small scale) systems, maximum negative pressures were observed in the polar area. For these systems, crazelike events are expected to propagate in the loading direction. For rubber-filled systems, transcrysallized layers had a limited effect on matrix shearing, whereas the presence of row-structured material more efficiently changed the mode of deformation to dispersed shear yielding. However, the mechanism of toughening by local anisotropy was concluded to be less effective for nonadhering hard particles.

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Figure 33: The influence of voids (cavitated rubber) vs. hard (mineral) particles in combination with microstructure-induced anisotropy on the mechanical properties.
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