Micro-mechanical modelling of Young’s modulus of semi-crystalline polyamide 6 (PA 6) and elastomer particle-modified-PA 6

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Abstract
In this study semi-crystalline polyamide 6 (PA 6) and its composites consisting of a semi-crystalline PA 6 matrix filled with up to 32.9 vol.% submicron elastomeric copolymer particles are investigated. The aim of this paper is to show how micro-mechanical modelling can predict the elastic behaviour of these composites from the experimentally observed morphology and determined parameters. Semi-crystalline PA 6 possesses a spherulitic morphology, consisting of a radial assembly of amorphous layers and nano-sized crystalline lamellae. In the continuum mechanical representation of semi-crystalline PA 6, nano-sized crystallite lamellae are considered as a phase which is additionally embedded into the amorphous matrix. The 2D self-consistent embedded cell model was chosen to predict the Young’s modulus of the semi-crystalline PA 6 material. In this model a rectangular lamella is surrounded by an amorphous matrix, which is again embedded in the semi-crystalline PA 6 material with the mechanical behaviour to be determined iteratively in a self-consistent manner. The Young’s modulus of PA 6 has been calculated by an appropriate integration of results of all orientations of the crystalline lamellae. The Young’s modulus of PA 6/elastomer composite is also predicted by a 3D self-consistent embedded cell model. In this model a circular inclusion is surrounded by the PA 6 polymer matrix, which is again embedded in the PA 6/elastomer composite. Good agreement is obtained between experiments and the prediction with the self-consistent embedded cell models.

1. Introduction
Polyamide 6 (PA 6) is an important engineering semi-crystalline thermoplastic. It offers a unique combination of high mechanical strength, low wear and abrasion with good chemical resistance. Since the 1940s polyamides have become one of the most important engineering thermoplastics [1]. In the recent years there are more increasing demands in using PA 6 to replace certain metals in structural applications. Its mechanical behaviour has attracted increasing scientific and industrial interest. Characterization and prediction of the mechanical behaviour of PA 6 is indispensable to enable their wide use. The toughness of PA 6 can be improved by a dispersion of additional second phase elastomer particles. The main goal of the present paper is to predict the elastic behaviour of semi-crystalline PA 6 and elastomer particle-modified-PA 6. The paper deals with micro-mechanical modelling of elastic properties of both materials with the self-consistent embedded cell model in conjunction with the finite element method based on the experimentally determined Young’s modulus and morphology of composites. This classical embedded cell model was developed and used by Dong and Schmauder in 1996 to successfully predict the elastic–plastic behaviour of metal matrix composites (MMCs) [2]. In the present research work this model will be used for the first time to predict the property of the polymer materials. As we know polymers are viscoelastic materials. They possess the properties of solids and viscous liquids. But for small strains the viscoelastic and viscoplastic effects can be neglected [3]. We calculate the Young’s moduli of the semi-crystalline PA 6 and the PA 6/elastomer composite at ambient temperatures for very small deformations (0.05–0.25%).

2. Investigated materials
The material under study is a polyamide 6 (Ultramid® B40) provided by BASF. The elastomer particles are obtained by milling PA 6/polyether block copolymer plates with a polyether soft phase of 30 mass% (Nyréns® 3000), delivered by Brüggemann Chemical. Elastomer particle-modified-PA 6 is formed by melt compounding using a twin screw extruder followed by injection moulding. For the simulation of the overall mechanical properties of the composites the parameters of the constitutive components (morphology

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and the mechanical properties) should be known. The sample preparation and the characterization were provided by the institute of polymer technology (IKT, Uni Stuttgart).

### 2.1. Morphology

The morphology of the semi-crystalline PA 6 and the elastomer particle-modified PA 6 were taken by polarized light microscopy, transmission electron microscopy (TEM) and atomic force microscopy (AFM). Fig. 1a and b shows the expected spherulitic microstructure of the semi-crystalline PA 6. Fig. 1c shows the distributed spherical elastomer particles in the PA 6 matrix.

### 2.2. Mechanical properties

#### 2.2.1. Tensile tests

Tensile tests were performed according to DIN EN ISO 527-2 at room temperature (25 °C) on dry-as-molded samples. The stress–strain behaviour of the semi-crystalline PA 6 and the elastomer particle-modified PA 6 is given in Fig. 2.

#### 2.2.2. Nanoindentation

To simulate the overall mechanical properties of the semi-crystalline PA 6, it is desirable to know the properties of each component (amorphous phase and crystalline lamellae). For the determination of the Young’s modulus of the amorphous PA 6 a sample with amorphous surface (the thickness of the film is approximately 50 µm) was produced by very fast cooling down from the PA 6 melt (Fig. 3a). The Young’s modulus of the amorphous PA 6 film was measured by a quasi continuous stiffness measurement method with the nanoindenter UNAT (company ASMEC) (Fig. 3b). Unfortunately, because of the size of the individual crystalline lamella, it is realistically not possible to get their mechanical properties from experiment. The Young’s modulus of the crystalline PA 6 was therefore determined by an inverse modelling technique. The amorphous phase in the semi-crystalline PA 6 is able to absorb water from the air. It leads to softening of the material (Fig. 3b). The Young’s modulus of each component is summarized in Table 1.

### 3. Description of the self-consistent embedded cell model

In the present work, self-consistent embedded cell models will be applied to model the Young’s moduli of the semi-crystalline PA 6 and the PA6/elastomer composite. According to the observation from the experiments semi-crystalline PA 6 consists of amorphous and crystalline components with spherulite structure. In one spherulite the crystalline lamellae grow radically from a common centre, with amorphous phase filling in the inter regions. In the simulation semi-crystalline PA 6 will be taken as a composite with amorphous PA 6 as matrix and crystalline PA 6 lamellae as inclusions. Due to the random orientation of the lamellae the overall behaviour of the semi-crystalline PA 6 is assumed to be isotropic at scales larger than the spherulite diameter, although the lamellae themselves are highly anisotropic. In the model for semi-crystalline PA 6 a rectangular lamella is surrounded by an amorphous matrix, which is again embedded in the semi-crystalline PA 6 material with the mechanical behaviour to be determined in a self-consistent manner. Due to the random orientation of the crystalline lamellae the embedded unit cell will be rotated by steps of 10° with respect to the applied loading (Fig. 4a). The Young’s modulus can then be calculated by an appropriate integration of results of all lamellae orientations.

The matrix in the elastomer particle-modified composite is the PA 6 and the inclusion is the approximately spherical soft elastomer phase. In the model for this polymer composite a circular
inclusion is surrounded by the PA 6 polymer matrix, which is again embedded in the PA 6/elastomer composite with unknown properties. Due to the symmetry of the geometry a quarter of the model will be taken for the calculation (Fig. 4b). Moreover, good adhesion between the dispersed elastomer soft phase and the PA 6 matrix is assumed in the model because of a high chemical affinity between the PA 6 and the copolymer soft phase.

The finite element analysis (FEA) was used for the prediction of the elastic behaviour of the materials under study. A two-dimensional model was created and meshed using the PATRAN software. The dimension of the embedding composite was sufficiently large compared with that of the embedded cell \((D = 5d)\). It ensured that there would be no influence on the composite behaviour of the inner embedded cell. Plane strain eight-node biquadratic elements (for 2D) as well as axially symmetric biquadratic elements (for 3D) with full integration points were used (Fig. 5). Mesh refinement was performed in the region at the interface of the embedded unit cell and the embedding composite. The nodes lying at the bottom of the mesh in the model were fixed along the vertical directions. The calculations were carried out with ABAQUS at the Gauss integration points by integrating exactly the polynomial terms in the element’s stiffness matrix.

The experimentally determined Young’s modulus, Poisson’s ratio and volume fraction of the matrix and inclusions will be at first assigned to the inner embedded cell while the initially assumed material data of the composite is assigned to the embedding composite. The embedded cell model will then be stretched under axial displacement loading. The mechanical stress–strain behaviour of the embedded cell and the surrounding embedding composite are then compared with each other. If they are not identical the
improved stress–strain curve of the composite from the previous iteration will be assigned to the embedding composite for the next iteration step until the stress–strain curves of the embedded cell and the surrounding embedding composite are found to be identical within a pre-given limit. Thus the found overall stress–strain curve is assumed to predict the mechanical behaviour of the composite.

4. Results and discussion

The elastic behaviour of semi-crystalline PA 6 was found to depend strongly upon the crystalline lamellae orientation with respect to the applied loading. After each rotation of 10° the Young’s modulus was calculated with the self-consistent unit cell model. The results are presented in Fig. 6.

The Young’s modulus can be calculated using Eq. (1) by an appropriate integration of results of all lamellae orientations [4] (the results are shown in Fig. 7):

$$E(\theta) = \frac{1}{2\pi} \frac{\int_0^{2\pi} E(\phi) f(\theta) d\phi}{\int_0^{2\pi} f(\theta) d\phi}$$

with $E$: Young’s modulus in dependence on the lamellae orientation $\theta$ angle between lamella and applied loading direction; $f(\theta)$: weighting function, which describes the distribution density of lamellae. In the case of random distribution $f(\theta) = 1$.

With the geometry of a standard tensile bar is hardly possible to vary the crystallinity of the semi-crystalline PA 6 due to the limitation of the cooling procedure in the moulding tool (IKT). For this reason the moulded test bars possess a constant crystallinity which amounts to around 28%. Therefore, there are no other experimental values except the Young’s modulus of the PA 6 with 28% crystallinity available to be compared with the predicted values. According to Seymour’s conclusion the Young’s modulus increases with the increase in crystallinity [7]. The simulation shows the same tendency. In semi-crystalline PA 6 there are two kinds of PA 6 crystals present, i.e. a monoclinic $\alpha$-form and a pseudo hexagonal $\gamma$-form [8]. They differ from each other in polymer chain alignment. The polyamide chains of the $\alpha$-form are joined by hydrogen bonds and fully planar extended. The polymer chains are oriented in an anti-parallel zigzag fashion. In the $\gamma$-form crystal of PA 6 the polymer chains are parallel. The hydrogen bonds lie between two parallel chains. The difference of the crystalline structures reflects on the difference in the mechanical properties between the two crystal forms. The modulus in the chain direction derived by the X-ray method of the $\alpha$-form amounts to 165 GPa while for the $\gamma$-form the modulus is found to be 27 GPa [9]. The predicted Young’s modulus of the crystalline PA 6 obtained by the inverse modelling procedure (51.5 GPa) lies between these two values. Due to this finding the magnitude of the predicted value is plausible.

The predicted and measured Young’s moduli of elastomer-modified-PA 6 are given in Fig. 8.

The results in Fig. 8 show perfect agreement between experiment and prediction of the Young’s modulus of the elastomer particle-modified-PA 6 with the embedded cell model, even if the elastomer soft phase particles are not perfectly spherical and the particle sizes are not uniform. This self-consistent unit cell model can predict the Young’s modulus of the spherical particle-modified material quite well.

5. Conclusion

In this paper the semi-crystalline thermoplastics and elastomer soft phase particle-modified thermoplastics were investigated. The 2D and 3D self-consistent embedded unit cell model was used to predict the Young’s modulus of semi-crystalline PA 6 and PA 6/ elastomer composites. Some conclusions from the present research are summarized as follows:

- Semi-crystalline PA 6 has a spherulitic morphology, consisting of an assembly of amorphous layers and nano-sized crystalline lamellae.
- The mechanical properties of semi-crystalline PA 6 depend strongly on the crystallinity and the orientation of the crystalline lamellae.
- The unmeasurable Young’s modulus of the crystalline PA 6 is calculated by inverse 2D simulations. Its value was derived to be 51.5 GPa which is plausible based on the literature data.
- The particle shape of the elastomer is approximated to be spherical.
Good agreement between experiment and prediction of the Young’s modulus of the elastomer particle-modified-PA 6 with the 3D embedded cell model is obtained, although the elastomer soft phase in the experiment is not perfectly spherical.

The results indicate that the self-consistent embedded unit cell model can be used to successfully simulate the elastic behaviour of the semi-crystalline polymer and polymer composites with randomly arranged spherical inclusions.

For the large deformation regime the double yielding behaviour of semi-crystalline PA 6 [10] should be taken into account. The built-in plasticity model in the ABAQUS software can not capture this special behaviour. A user subroutine should be written and implemented in the model to capture for this elastic plastic material behaviour.

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Reference