Crystallinity in %

eff. isotropic elastic modulus in MPa

- simple Voigt av.
- laminate Voigt av.
- laminate geom av.
- simple geom. av.
- laminate Reuss av.
- simple Reuss av.
On the effective elastic properties of isotactic polypropylene

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Abstract
Calculating the effective elastic properties of semi-crystalline polymers is challenging due to a pronounced phase stiffness contrast, complex micro-structures and extreme anisotropies of the crystalline phases. To estimate the effective Young modulus of isotactic polypropylene depending on the crystallinity, we construct complex and simple homogenization schemes that unify the micro-scale interaction mechanisms that have been identified by Bartenev and Valishin \cite{4}, Bédoui et al. \cite{5}, Parenteau et al. \cite{38}. This is achieved by a two-step homogenization approach, namely a local laminate stiffness that is then subjected to orientation averaging. The resulting estimates show good agreement to experimental results. They further suggest that the relatively high effective stiffness of isotactic polypropylene when compared to polyethylene may in part be a result of the stronger lateral confinement effect on the laminate level.

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1. Introduction

Polymers display a complex micro-structure: One finds usually several coexisting phases. These are the amorphous phase, which is composed of entangled polymer chains, and crystal phases. Above the glass transition temperature, the properties of these phases are markedly distinct: The crystals are much stiffer than the amorphous phase and highly anisotropic, while the amorphous phase is rubber-like, i.e. isotropic and almost incompressible. We are concerned with isotactic polypropylene (iPP), which has three crystal phases labeled as the $\alpha$, $\beta$ and $\gamma$ crystals. Moreover, the phases form structures at different scales, which depend on the processing conditions. The most common structure is the spherulitic superstructure, with lamellar crystals aligned with their long axes parallel to the radius, and separated by interlamellar amorphous phase, see, e.g. Carraher [12] Sect-2.3. The spherulitic grains exhibit a sub-structure: embedded in the amorphous phase, one finds crystal lamellae aligned with the radial (growth) direction in case of $\beta$-crystal (see Fig. 1) and lamellae aligned parallel and perpendicular to the radial direction in case of $\alpha$-crystal.

Naturally, since the phases' stiffnesses differ extremely, the effective stiffness depends strongly on the micro-structure arrangement, which is why the effective stiffness of iPP can take values in a very broad range. The elastic moduli of regular grade-iPP fall into the range of 1.4 GPa to 1.5 GPa, a special grade-iPP may attain a stiffness from 2.4 GPa to 2.5 GPa [23].

There are several methods to adjust the elastic properties of iPP, the most common are

- nucleation agents,
- the molecular chain regularity,
- the molecular chain length distribution,
- the thermal processing conditions,
- mixing with other constituents.
All of these affect the final structure and phase distribution, such that experimental results display a wide range of effective properties.

Further, iPP shows ductile behavior, i.e. the stress-strain-curve is notably curved from the very beginning. This makes the measurement of the elastic modulus a source for errors. For our own measurements, we found a difference of approximately 16% when taking the tangent and the secant at $\varepsilon = 1$. Therefore, it is often more convenient to measure Young’s modulus in bending experiments, often termed as the flexural modulus. As one can see in Guan and Xu [19] Tab. 8, when measured in bending tests, there is a clear tendency observable, while there is much more scattering when Young’s modulus is measured directly in tension tests. Nevertheless, while the tensile modulus weighs every layer equally, the flexural modulus is biased towards the elastic properties of the skin, since the surface layers are stretched more than the central layers. Thus, the flexural modulus may tend to overestimate the stiffness.

A deeper understanding of the complex mechanical interactions on the microscale may hint on how to reliably produce stiffer iPP parts. We will shortly review the models of [5] and [38], who both identified important aspects that affect the effective elastic properties of iPP.

• [5] address the paradox why Polyethylene (PE) has in effect a lower stiffness ($E_{\text{PE}} \approx 0.8$ GPa) than iPP ($E_{\text{iPP}} \approx 1.5$ GPa to 2 GPa) although all its phases have similar stiffnesses. It appears that some difference in the micro-structure must be responsible for this. They argue that the iPP crystallites have more extreme aspect ratios than the PE crystallites. In fact, homogenization schemes that rely on Eshelby’s ellipsoidal-inclusion solution give, in combination with orientation averaging, higher effective stiffnesses as the aspect ratio is increased [20]. The final model that gives the best fit is a crystallite-inclusion-in-amorphous-matrix scheme, specifically the differential scheme is most successful, as it is known to give better results for higher volume fractions than the self consistent scheme (Gross and Seelig [18], Chapt. 8). The same results but with more experimental reconciliation are reported in [6]. As with most anisotropic materials in matrix-inclusion schemes, simplifying assumptions need to be made, which may decouple the material anisotropy from the microstructure’s morphological anisotropy, as discussed in Sect. 1.2.

• [38] approached similarly the effective stiffness of iPP with a matrix-inclusion scheme. They take into account the extremely anisotropic crystallites in conjunction with the short range order of the crystallites, which are aligned approximately parallel. Due to the aspect ratios of the crystallites and their arrangement, the connectivity among the crystals along the lamella growth direction (radial direction of the spherulite) is much higher than in the lamella chain direction (lamella normal direction, tangential direction of the spherulite, see Fig. 1). The paradox of a higher effective stiffness of iPP compared to PE is then explained by the fact that in the radial direction of the spherulite, iPP has a higher Young modulus than PE, namely approximately 5.97 GPa (iPP) in contrast to 4.85 GPa (PE). In the other in-plane-direction, the effect is even more pronounced, namely approx 9.27 GPa (iPP) in contrast to 4.92 GPa (PE). On the contrary, along the chain direction/lamella normal direction, PE has a much higher
Figure 1: Sketch of a spherulite with lamellar \( \beta \)-crystals. Although the overall lamellae orientation distribution is isotropic, a short range order between the crystallites prevails. Adjacent lamellae are practically parallel, which affects the effective elasticity through the strong anisotropy of the crystallites. In case of \( \alpha \)-crystals, a cross-hatched structure forms, which can be considered as two superimposed laminates.

Young modulus, namely 77.5 GPa (PE) compared to 40.0 GPa (iPP), see Fig. 2. However, the connectivity between the crystallites is high in the in-plane direction and low in the normal direction. According to this observation, [38] employ isotropic phase materials with the decisive Young modulus that is encountered in-plane. They find, contrary to Bédoui et al. [5, 6] the best model to be an amorphous-inclusion-in-crystalline-matrix-scheme. However, at high volume fractions, the experimental result for PP160 (annealed at 160°C), which has the highest crystallinity, lies outside the Hashin-Shtrikman and even the Voigt/Reuss bounds.

As becomes apparent by comparing these two approaches, we need to combine ingredients from both. While the extreme aspect ratios of the crystallites are important for the effective properties, the short range order inhibits the application of orientation averages of matrix-inclusion based approaches. Due to the almost parallel local alignment of the crystallites, we have different connectivities in the three main directions of the lamellae. In combination with the extreme elastic anisotropy in these directions, this leads to a strongly nonlinear dependence of the stiffness on the phase volume fractions.

This is best explained in laminate theory. Young’s modulus is largest parallel to the laminate normal. The effective Young modulus in this direction is obtained by the Reuss average of the Young moduli in this direction, which corresponds to a sequential arrangement of springs. Thus, as the amount of crystalline phase increases, a hyperbolic increase of the effective Young modulus along the laminate normal is observed. For tension inside the laminate plane, Young’s modulus is obtained by the linear mixture rule of Voigt, which corresponds to a parallel arrangement of springs. This has been observed firstly by Tsai and Pagano [45] and employed apparently independent on their findings by Bartenev and Valishin [4] for iPP. Thus, the effective Young modulus
Figure 2: Young’s modulus is plotted as the radius over the tension direction, which is parametrized by two angles. The resulting Young-moduli-bodies [8] for iPP and PE show the extreme anisotropy, which is more severe for PE than for iPP. In the lamella normal direction, PE is much stiffer than iPP, inside the plane iPP is much stiffer than PE.
is not simply obtained by Voigt or Reuss averages, but a combination of both. However, the Tsai-Halpin-models always contain a scaling parameter, which is hard to interpret physically. Further, they tend to overestimate systematically the effective stiffness [20].

The following route in setting up a model is followed: Our approach is to approximate the semi-crystalline structure locally inside the spherulites as a laminate. We determine the effective laminate stiffness as a function of the crystal volume fraction based on the well known closed-form solution, see, e.g., Glüge and Kalisch [17]. Then, we take the Voigt, Reuss and geometric orientation averages over an isotropic orientation distribution of this laminate stiffness to obtain estimates for the effective isotropic stiffness, from which the effective Young modulus is extracted. We abstain from using any fitting parameter.

To assess the effect of the laminate intermediate solution, we consider also the pure volume averages of the local stiffnesses, disregarding the local lamellar arrangement. This requires only the orientation average of the crystalline stiffness. A similar comparison can also be found in [9] for the case of PE and a slightly different homogenization approach (Fig. 2 therein).

Since these approaches yield very complex expressions, we then examine a simpler Tsai-Halpin like ad-hoc model for the effective stiffness, but without a fitting parameter. Finally we compare the different estimates to our experimental results and to measurements from the literature. The simplified approach allows us to identify the lateral confinement effect to contribute considerably to the effective stiffness. This observation is in agreement with the lower stiffness of PE.

1.1. Simplifying assumptions

In this section we will briefly address three idealizations that we employ, namely the lamellar phase arrangement and the homogeneity of the crystal and the amorphous phase.

1.1.1. Cross-hatched structure in α-iPP and the laminate reference solution

We have tacitly assumed that the micro-structure is locally almost lamellar. For α-iPP, this assumption may be too strong, since there we encounter locally a structure which is best described as two superimposed laminates that are perpendicular to each other, see Liu et al. [28] Fig. 4 for a micrograph. This structure evolves due to the fact that the interface of α-crystal serves well as a nucleation site for new crystals, such that a structure similar to the sketch in Fig. 3 evolves. They are are also termed as “dendritic structures”. The applicability of an orientation average of the laminate reference solution depends strongly on how dense the connections between the two superimposed laminates are. If we have a high density of junctions, we can hardly speak of two superimposed laminates, but need a better fundamental “lattice” solution. Conversely, it may be admissible to use the laminate orientation average if the density of junctions is not so high, and sufficiently large parts are well approximated as laminates. On viewing Fig. 4a in Liu et al. [28], one can argue that this is indeed the case: large parts of the structure are locally lamellar, and the number of actual junctions is much smaller than the number of potential lamella crossings.

It should be noted that the same discussion applies in case of the ellipsoidal fundamental solution.
1.1.2. The rigid-amorphous phase and homogeneity of the amorphous phase

Another source of error is the idealized interface between the crystal and the amorphous phase. The transition from the aligned polymer chains inside the crystal to the entangled polymer chains in the amorphous region is discussed for iPP (among many other polymers) in Wunderlich [50]. The transition phase has some characteristics from the crystal phase (rigid, compared to the amorphous phase) as well as the amorphous molecular structure, hence it is denominated as the rigid-amorphous fraction (RAF). In this context, the pure (soft) amorphous phase is referred to as the mobile amorphous fraction (MAF).

Little is known about the RAF. It may be very pronounced when polymer chains that leave the crystal cross large parts of the MAF and then enter the crystal again, or it may be nonexistent when the polymer chains are neatly bend back into the crystal without entangling with the MAF. Typically, one assumes that the RAF has a thickness of 1 to 2 nm, see Fig. 4.

Wunderlich [50], Menczel and Jaffe [30], Zia et al. [53] determined the RAF by differential scanning calorimetry (DSC) in combination with wide- and small angle X-ray diffraction, and found for iPP a RAF in the range of 0 to approximately 30%, where high RAFs are obtained at very low cooling rates. Re-heating or annealing usually reduces the RAF. Zia et al. [53] examined as well the RAF in iPP, and found a relationship between the glass transition temperature of the MAF and the RAF. The RAF/MAF-ratio takes values between 1 and 1.7, with the highest values at crystallinities around 55%. In Zia et al. [53], among the polymers that have been examined, iPP showed the highest RAF/MAF-ratio, which may well explain the comparatively high stiffness of iPP.

The presence of the RAF explains well why very different effective stiffnesses are found for similar crystallinities. Sedighiamiri et al. [39] use a three-layer laminate to address this issue. In case of a matrix-inclusion model, a nested-ellipsoid approach like presented in Gueguen et al. [21] allows to include the RAF when estimating the effective properties. Nevertheless, the RAF is beyond the scope of this work for several reasons. Firstly, few is known about the elasticity of the RAF. Secondly, the gradient structure in the RAF requires a continuous parametrization of the material properties, which complicates the modeling considerably. Since the elastic properties of the RAF lie between the
crystalline and the amorphous elasticities, it may sufficient to slightly increase
the crystallinity if a large RAF is expected.

1.1.3. Granular crystal lamellae

Among the phenomena not taken into account is the inhomogeneity inside
the crystal structure, which may consist of a mosaic block substructure [42].
The transition from homogeneous to granular lamellae is gradual. The presence
of grains inside the crystal lamellae opens up the possibility to alternative de-
formation modes. Being embedded in a soft amorphous matrix, the grains may
reorient themselves easily in response to deformation, breaking up the apparent
lamellae. Although this effect is more important for the plasticity of polymers,
it may affect as well the primary response to straining.

1.2. Eshelby solution vs. laminate solution

It should be noted that the lamellar structure is often approximated as
oblate ellipsoidal inclusions. There is in fact some competition between the
two fundamental solutions of Eshelby and of laminates, with the Eshelby fun-
damental solution enjoying more popularity among scholars. Some researchers
find the orientation averaging over ellipsoidal inclusion schemes with extreme
aspect ratios to give better results, e.g. Janzen [24], Guan and Pitchumani [20],
which makes this approach quite popular, e.g. Bédouli et al. [5], Guéguen et al.
[21], Parenteau et al. [38]. The popularity may in part be due to the fact that
this approach offers more tuning parameters. For example, Guan and Pitchu-
mani [20], Bédouli et al. [5] adjust the aspect ratios of the ellipsoidal inclusion
to fit the estimate to the experiments, such that they find a ratio of 18/5=3.6
for the two longer half axes to give a good fit (Bédouli et al. [5], Sect. 3) while
Guan and Pitchumani [20] (Fig. 9 therein) find the best fit at a ratio of 30, both
considering pure PE. Other fine tuning is possible by using different inclusion
schemes, like Mori-Tanaka, differential scheme, and others, see Gross and Seelig

Figure 4: A crystal layer with no RAF (bottom) and a pronounced RAF (top).
[18] Chapt. 8 for an overview. Thus, it should be always possible to adjust the estimate more or less to the experiments, but due to the fitting parameters, the physical significance is questionable.

However, there are some arguments that should make one cautious regarding these approaches.

• Firstly, ellipsoids with extreme aspect ratios are unlikely to satisfy the assumptions that underly Eshelby’s solution, which presumes a homogeneous far-field in the matrix. Additionally, the unavoidable interaction between the stretched inclusions is excluded in the Eshelby solution. Only the self-consistent scheme that relies on the fundamental Eshelby solution allows in a sense the interaction between inclusions. Further, very long ellipsoids may basically break the scale separation. Bédoui et al. [5] worked with largest-to-smallest half axes ratios of up to 140, but experimental results indicate thicknesses of PP lamellae of 10 nm at length values up to 4 \( \mu m \) [6]. One can see that there is a considerable scale separation between these two dimensions, i.e. a violation of the Micro-Mini-Macro principle [22], which may render the oblate ellipsoid model with extreme aspect ratios unfit.

• Secondly, although Eshelby’s result holds for anisotropic phases, the Eshelby tensor that relates the matrix far-field strain to the inclusion’s eigenstrain can only be given as a closed form solution for isotropic phases. This assumption is far from realistic, see Fig. 2. Therefore, researchers often employ isotropic orientation averages for the individual phases before applying the fundamental solution. However, such a proceeding decouples the crystal orientation from the lamella orientation, basically presuming an unrealistic micro-structure.

Therefore, it may be rewarding to incorporate the laminate structure directly. It is most apparent in the works of Tsai and Pagano [45], Bartenev and Valishin [4], Boyd [9], Sedighiamiri et al. [39]. Especially Boyd [9] appears to be the first one to have applied the orientation averaging to the laminate solution with anisotropic phases. The laminate fundamental solution is simpler than Eshelby’s solution and uses less assumptions. For example, no restrictions regarding the material symmetry is made, but still an explicit expression for the effective laminate stiffness can be given (see Milton [32] Chapt. 9 or Sect. 3.1 in this work). For PE, such approaches have been used successfully by Lee et al. [26, 27] to model the effective plastic behavior. Guan and Pitchumani [20], Bédoui et al. [5] state that the laminate structure needs to be incorporated, but do this by considering extreme aspect ratios in matrix-inclusion schemes.

It is worth noting that Doyle [15] examined the effective stiffness of a spherulite finite element simulations. He found the Halpin-Tsai approach, which accounts for the laminate structure in a mechanism-based manner, to be in good agreement, unlike the self-consistent method.

1.3. Notation

A direct notation is preferred. Vectors are denoted as bold minuscules (like \( \mathbf{u} \)), second-order tensors as bold majuscules (like \( \mathbf{F} \), \( \mathbf{H} \), \( \mathbf{T} \)), and higher-order tensors as blackboard bold majuscules (like \( \mathbf{T} \), \( \mathbf{H} \)). The dyadic product and scalar contractions are denoted like \( (\mathbf{a} \otimes \mathbf{b} \otimes \mathbf{c}) : (\mathbf{d} \otimes \mathbf{e}) = (\mathbf{b} \cdot \mathbf{d}) (\mathbf{c} \cdot \mathbf{e}) \mathbf{a} \),
with a dot being the usual scalar product between vectors. If multiple scalar contractions are carried out, the order is such that the inner-product property is maintained, i.e. \( A : A = A_{ij}A_{ij} > 0 \). If the index notation is required, we will make use of implicit summation over the indices 1 to 3. Components are then given w. r. t. an orthonormal basis \( \{ e_i \} \), for which we can write \( e_i \cdot e_j = \delta_{ij} \), with the Kronecker delta \( \delta_{ij} = 1 \) if \( i = j \) and 0 if \( i \neq j \).

When working with stiffness tensors, we make use of the normalized Voigt notation,

\[
\begin{align*}
E_1 &= e_1 \otimes e_1, & E_2 &= \frac{1}{\sqrt{2}}(e_1 \otimes e_2 + e_2 \otimes e_1), \\
E_2 &= e_2 \otimes e_2, & E_3 &= \frac{1}{\sqrt{2}}(e_1 \otimes e_3 + e_3 \otimes e_1), \\
E_3 &= e_3 \otimes e_3, & E_6 &= \frac{1}{\sqrt{2}}(e_2 \otimes e_3 + e_3 \otimes e_2).
\end{align*}
\]

(1) (2) (3)

also referred to as Mandel notation, see Brannon \[10\] Chapt. 26. With respect to this basis, the stresses \( \sigma \) and the strains \( \varepsilon \) are 6-dimensional vectors, and the stiffness tensor \( C \) is a 6\times6-matrix. Then, Hooke’s law \( \sigma = C : \varepsilon \) can be written as

\[
\begin{pmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sqrt{2}\sigma_{12} \\
\sqrt{2}\sigma_{13} \\
\sqrt{2}\sigma_{23}
\end{pmatrix} = \begin{bmatrix}
C_{1111} & C_{1122} & C_{1133} & \sqrt{2}C_{1112} & \sqrt{2}C_{1113} & \sqrt{2}C_{1123} \\
C_{2222} & C_{2233} & \sqrt{2}C_{2212} & \sqrt{2}C_{2213} & \sqrt{2}C_{2223} \\
C_{3333} & C_{3312} & \sqrt{2}C_{3313} & \sqrt{2}C_{3323} & \sqrt{2}C_{3333} \\
\sqrt{2}C_{1212} & 2C_{1213} & 2C_{1223} & 2C_{1323} & 2C_{1333} \\
\sqrt{2}C_{1312} & 2C_{1313} & 2C_{1323} & 2C_{2323} & 2C_{2333}
\end{bmatrix} \begin{pmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\sqrt{2}\varepsilon_{12} \\
\sqrt{2}\varepsilon_{13} \\
\sqrt{2}\varepsilon_{23}
\end{pmatrix} = E_{i} \otimes E_{j} : E_{k}.
\]

The \( \sqrt{2} \)-factor comes from the normalization of the symmetric basis, such that \( E_i : E_j = \delta_{ij} \). It may appear cumbersome to work with this normalized basis, and is not customary. But since we need to operate on the stiffness tensors, we want the usual matrix operations for inversion, scalar contractions, eigenvalue calculation to apply, which is only the case if we use a normalized basis.

For an \( n \)-th order tensor \( \mathbb{A} = A_{i_{1}...i_{n}} e_{i_{1}} \otimes ... \otimes e_{i_{n}} \), the Rayleigh product with a second-order rotation tensor \( \mathbb{Q} \) is defined via \( \mathbb{Q} \mathbb{A} := A_{i_{1}...i_{n}}(\mathbb{Q} e_{i_{1}}) \otimes ... \otimes (\mathbb{Q} e_{i_{n}}) \).

This is a generalization of the rotation of a vector to tensors of arbitrary order.

It can be written as a linear mapping \( \mathbb{Q} \mathbb{A} = \sum_{n \text{ dots}} \mathbb{Q}_{n} \mathbb{A} \). The rotation is an element of the special orthogonal group \( SO(3) \).

We will make use of the isotropic projectors \( \mathbb{P}_1 = \frac{1}{3} \mathbb{I} \otimes \mathbb{I} \) and \( \mathbb{P}_2 = \mathbb{I} - \mathbb{P}_1 \), with \( \mathbb{I} \) the fourth order identity tensor that maps symmetric second order tensors onto themselves. \( \mathbb{P}_{1,2} \) form an orthogonal basis for isotropic stiffness tensors, i.e. every isotropic stiffness tensor can be written as \( C_{\text{iso}} = 3K\mathbb{P}_1 + 2G\mathbb{P}_2 \), where \( K \) and \( G \) are the compression modulus and the shear modulus, respectively. \( \mathbb{P}_{1,2} \) have the projector properties \( \mathbb{P}_1 : \mathbb{P}_j = \delta_{ij} \mathbb{P}_j \). \( \mathbb{P}_1 \) maps every symmetric second order tensor into its dilatioric part \( \mathbb{P}_1 : \mathbb{A} = \text{tr}(\mathbb{A})/3 \mathbb{I} =: \mathbb{A}^\circ \). \( \mathbb{P}_2 \) extracts the deviatoric part \( \mathbb{P}_2 : \mathbb{A} = \mathbb{A} - \mathbb{A}^\circ =: \mathbb{A}' \).
we have
\[
P_1 = \begin{bmatrix}
1/3 & 1/3 & 1/3 & 0 & 0 & 0 \\
1/3 & 1/3 & 1/3 & 0 & 0 & 0 \\
1/3 & 0 & 0 & 0 & 0 & 0 \\
sym & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix} \quad P_2 = \begin{bmatrix}
2/3 & -1/3 & -1/3 & 0 & 0 & 0 \\
2/3 & -1/3 & 2/3 & 0 & 0 & 0 \\
2/3 & 0 & 0 & 1 & 0 & 0 \\
sym & 1 & 0 & 0 & 1 & 0 \\
\end{bmatrix} \quad E_i \otimes E_j, \quad E_i \otimes E_j.
\]

2. Material parameters for amorphous and single crystalline iPP

There are few direct measurements of these material parameters, since samples of the pure phases are hard to obtain. Most measurements are indirect, like hardness-measurements in nano-indentation. In view of these problems, researchers often estimate the elastic properties by molecular static simulations.

2.1. \( \alpha \)-crystalline iPP

For \( \alpha \)-iPP, there appears to be a well-established agreement that the atomistic simulations of Tashiro et al. [43] (Eq. 5 therein) are a quite good approximation. \( \alpha \)-iPP has a monoclinic symmetry, hence the stiffness tensor has 13 independent components,

\[
C_{\text{cryst}} = \begin{bmatrix}
7.78 & 3.91 & 3.72 & 0 & \sqrt{2} \times 0.9 & 0 \\
11.55 & 3.99 & 0 & -\sqrt{2} \times 0.36 & 0 \\
42.44 & 0 & -\sqrt{2} \times 0.57 & 0 \\
2 \times 4.02 & 0 & -2 \times 0.12 & & \end{bmatrix} \quad \text{GPa} \quad E_i \otimes E_j.
\]

The much higher stiffness in the \( e_3 \)-direction is due to stretching of the polymer chains along the chain direction, in which primary (covalent) bonds prevail. Perpendicular to the chain direction the elasticity is considerably smaller due to the weaker secondary (intermolecular) bonding. A graphical representation of this highly anisotropic stiffness in terms of Young’s modulus is given in Fig. 2.

2.2. \( \beta \)-crystalline iPP

Surprisingly, we were unable to find material parameters for hexagonal \( \beta \)-iPP. However, the stiffnesses of \( \alpha \)- and \( \beta \)-iPP seem to be very similar. Our own experiments show that the effective elasticities of iPP are more sensitive to the overall crystallinity than to the \( \alpha \) to \( \beta \)-ratio.

We have cut thin section of 50 \( \mu \)m thickness from an injection-molded cuboid of Borealis HJ120UB iPP. The phase fractions of the layers have been characterized by wide angle X-ray scattering. Depending on the depth, the volume content of \( \alpha \) and \( \beta \) varied, with more \( \alpha \) phase near the rapidly cooling surface. We further characterized the mechanical properties of the strips in tension tests, from which we extracted Young’s modulus.

The main conclusion is that the effective Young-moduli of \( \alpha \)- and \( \beta \)-nucleated iPP are very similar, namely approximately 2.2 GPa for \( \alpha \)-nucleated iPP and
Table 1: Our measurements of Young’s moduli and crystal phase fractions for pure-, α- and β-nucleated iPP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>α/β-distribution in %</th>
<th>crystallinity in %</th>
<th>E in GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP</td>
<td>100 / 0</td>
<td>30 to 35</td>
<td>1.53</td>
</tr>
<tr>
<td>α-nucleated iPP</td>
<td>80 to 85 / 15 to 20</td>
<td>50 to 55</td>
<td>2.2</td>
</tr>
<tr>
<td>β-nucleated iPP</td>
<td>10 to 20 / 80 to 90</td>
<td>≈ 45</td>
<td>2.3</td>
</tr>
</tbody>
</table>

2.3 GPa for β-nucleated iPP (see Tab. 1). On the other hand, Tordjeman et al. [44] showed that the substitution of α-iPP by β-iPP at otherwise constant crystallinity has an adverse effect on Young’s modulus. They found an approximately linear decrease from approximately 2.5 GPa at a value of 40% β-content of the crystalline phase to 1.78 GPa at a value of 90% β-content of the crystalline phase, at a constant overall crystallinity of 57% ±2%. Our measurements lie well in this range. Regarding the scattering that is observed (Fig. 6 in Tordjeman et al. [44]), our results agree with these of Tordjeman et al. [44]. The higher stiffness of the α-nucleated iPP is due to the formation of the cross-hatched lamellar morphology in α-crystals, which increases the connectivity of the stiffer crystalline phase. Hence, the α-dominated iPP is stiffer and less ductile than the β-dominated iPP. Thus, the overall stiffer α-nucleated iPP does not imply that the α crystal is itself stiffer than the β crystal, but is primarily the result of the differing morphology. It is not easy to separate these effects, more so since the difference between the stiffnesses of the α- and β-crystals is probably small.

Additionally, the α- and β-crystals exhibit molecular similarity as well as a similarity of other physical properties. Both are built from parallel chain helices of period 3 with all methyl groups pointing either up or down in each chain. The α-phase consists of alternating stacks of only left- and only right-handed helices, and has the monoclinic symmetry. The β-phase consists of isochiral domains that are combined at phase boundaries, such that the overall statistical coexistence of left- and right-handed helices holds [46, 29]. The α-crystal is the more ordered phase. It has a higher density (0.945 g/cm$^3$ vs. 0.925 g/cm$^3$) and a higher melting temperature (186°C vs. 177°C) than the β phase. Since it is more ordered and has a lower stored energy, it’s growth rate is lower than that of the β-phase. Nevertheless, the structure is very similar. Most important, along the chain direction, Young’s modulus depends on the presence of α- or β phase mostly through a differing density, i.e. number of chains per cross section. However, the densities differ only by approximately 2%. In absence of material parameters for the β crystal and because of the small stiffness difference between the α and β crystals, we used the stiffness of the α-crystal and the overall crystallinity, in effect not distinguishing the stiffnesses of α- and β-crystals.

2.3. Amorphous iPP

It is also hard to find reliable material parameters for amorphous iPP, although the material is isotropic. Amorphous polymers consist of entangled polymer chains, the properties are rubber-like above and glass-like below the glass transition temperature, which is approximately -10°C for iPP and -20°C for atactic polypropylene (aPP). This implies a much smaller overall stiffness compared to the crystalline phase. In absence of reliable data we resorted to the...
crystalline iPP | see Eq. 6
amorphous iPP | $E = 1.13$ MPa, $K = 1.76$ GPa

Table 2: Material parameters

stiffness of aPP. Atactic PP solidifies without prior crystallization, by vitrification of the amorphous phase, since the irregularity of the monomer group orientation inhibits a crystalline chain arrangement. Thus, it is much easier to obtain large samples of pure, amorphous aPP. It is not unrealistic to assume that amorphous iPP and amorphous aPP have a similar stiffness. We rely on the experimental data of De Rosa et al. [14] for aPP (Fig. 8 therein) and estimate Young’s modulus of aPP to be 1.13 MPa at room temperature. The second elastic constant that needs to be determined is related to the compressibility. The compressibility of aPP at room temperature is given by Andersson and Andersson [2] as $K = 1.76 \pm 0.06$ GPa (see Tab. 1 therein). This combination of $E$ and $K$ leads to a Poisson ratio of

$$\nu = \frac{1}{2} \frac{E}{6K} \approx 0.499893,$$  

which is quite realistic for polymers in the rubbery state. The shear modulus is

$$G = \frac{3KE}{9K-E} \approx 0.377 \text{ MPa}.$$  

With $K$ and $G$, we can write the stiffness of the amorphous phase with the isotropic projectors

$$C_{\text{amorph}} = 3KP_1 + 2GP_2.$$  

3. Complex model

3.1. The effective laminate stiffness

The effective elastic properties of laminates can be given in closed form for arbitrary phase stiffnesses, provided that the layers are homogeneous and the elastic strains remain small. The basic mechanism is to exploit the jump balances algebraically, which has been done for isotropic phases by Backus [3] and then later in different settings and notations, see Milton [32] Chapt. 9 for an exhaustive summary. An interesting method is to use projection tensors that extract the continuous and discontinuous parts of the stresses and strains across the interface, see Sedighiamiri et al. [39].

A more descriptive derivation of the effective laminate stiffness for the case of an orthotropic crystal phase is presented in Boyd [9] Eqs. 3 to 12. The underlying assumptions are the same as used here, but the calculations are explicit on stiffness matrix components.

We use here the symbolic derivation in Glüge and Kalisch [17]. The jump conditions for strains and stresses on both sides ($+$ and $-$) of the interface, the
mixture rule and the material laws are

\[ \varepsilon^+ - \varepsilon^- = \text{sym}(n \otimes a), \]

\[ (\sigma^+ - \sigma^-) \cdot n = 0, \]

\[ \sigma = v^+ \varepsilon^+ + v^- \varepsilon^-, \]

\[ \sigma = v^+ \sigma^+ + v^- \sigma^-, \]

\[ \sigma^+ = C^+ : \varepsilon^+, \]

with the stresses and strains \( \sigma^\pm, \varepsilon^\pm \), the volume fractions \( v^+ + v^- = 1 \) and the stiffnesses \( C^\pm \). We have 12 independent strain components, which give 12 dependent stress components. The jump conditions constitute 6 additional equations. They are just the dynamic compatibility, i.e. equilibrium of tractions across the interface, and kinematic compatibility, i.e. equality of the in-plane strains. Because of the linearity of all equations we can recast this as a linear system of size 6, which can be brought into the form \( \overline{\sigma} = \overline{C}_{\text{lamine}} : \overline{\varepsilon} \), where one can compare coefficients to identify \( \overline{C}_{\text{lamine}} \). Inserting the material laws into the stress jump condition gives

\[ (\sigma^+ - \sigma^-) \cdot n = (C^+ : \varepsilon^+ - C^- : \varepsilon^-) \cdot n, \]

where we can eliminate either \( \varepsilon^+ \) or \( \varepsilon^- \) with the strain jump condition,

\[ (C^+ : \text{sym}(n \otimes a) + \Delta C : \varepsilon^+) \cdot n = 0, \]

\[ (C^- : \text{sym}(n \otimes a) + \Delta C : \varepsilon^-) \cdot n = 0, \]

with \( \Delta C = C^+ - C^- \). We can drop the sym(…)-function due to the symmetrization property of \( C^\pm \). We can rewrite then

\[ A^+ \cdot a = -(\Delta C : \varepsilon^-) \cdot n \]

\[ A^- \cdot a = -(\Delta C : \varepsilon^+) \cdot n, \]

where \( A^\pm = n \cdot C^\pm \cdot n \) is usually referred to as the acoustic tensor. Multiplying with \( v^\pm \) and summing up gives with \( v^+ \varepsilon^+ + v^- \varepsilon^- = \overline{\varepsilon} \)

\[ (v^- A^+ + v^+ A^-) \cdot a = -(\Delta C : \overline{\varepsilon}) \cdot n. \]

With the abbreviations

\[ Z = (v^- A^+ + v^+ A^-)^{-1} \]

\[ Z = n \otimes Z \otimes n \]

we can give \( n \otimes a \),

\[ n \otimes a = -Z : (\Delta C : \overline{\varepsilon}). \]

Next we obtain the effective stresses from the mixture rule for the stresses and the elasticity laws,

\[ \overline{\sigma} = v^+ \sigma^+ + v^- \sigma^- \]

\[ = v^+ C^+ : \varepsilon^+ + v^- C^- : \varepsilon^-. \]
Again, we can replace either $\varepsilon^+$ or $\varepsilon^-$ with the strain jump condition,

$$\underline{\sigma} = (v^+ C^+ + v^- C^-) : \epsilon^+ + v^- C^- : \text{sym}(\mathbf{n} \otimes \mathbf{a}), \quad (26)$$

$$\underline{\sigma} = (v^+ C^+ + v^- C^-) : \epsilon^- - v^+ C^- : \text{sym}(\mathbf{n} \otimes \mathbf{a}). \quad (27)$$

Again, the symmetrization of $\mathbf{n} \otimes \mathbf{a}$ may be dropped. Combining again linearly with $v^\pm$ and using $v^+ + v^- = 1$ and further replacing $\mathbf{n} \otimes \mathbf{a}$ by Eq. (23) gives finally

$$\underline{\sigma} = \underline{\sigma}_\text{laminate} : \underline{\epsilon} \quad (28)$$

with

$$\underline{\sigma}_\text{laminate} = \underline{\sigma}_\text{Voigt} - v^+ v^- \Delta C : \underline{Z} : \Delta C. \quad (29)$$

For the material parameters given in Sec. 2 we obtain the effective laminate stiffness as a function of the crystal volume fraction. Unfortunately, due to the involved computations, in conjunction with material parameters that differ by orders of magnitude, the overall expressions for the components are not manageable by hand, but best dealt with by the aid of a computer algebra system. It is rather futile to reproduce here the lengthy polynomial expressions. Instead, we refer to the supplementary material and the Appendix, and have a look at the following numeric example. For the specific volume fraction 0.5 we get

$$\underline{\sigma} = \begin{bmatrix}
4.588 & 2.835 & 1.845 & 0 & 1.594 \times 10^{-4} & 0 \\
6.581 & 1.846 & 0 & -5.705 \times 10^{-5} & 0 \\
3.38 & 0 & -7.82 \times 10^{-6} & 0 \\
4.016 & 0 & -3.023 \times 10^{-5} & 0 \\
sym & 1.507 \times 10^{-3} & 0 & 1.507 \times 10^{-3} \\
\end{bmatrix} \text{GPa} \ E_i \otimes E_j. \quad (30)$$

Note that the 13- and 23-shear stiffnesses (fifth and sixth principal diagonal entries) practically vanish, because shear parallel to the laminate normal is accommodated by the shear-compliant amorphous phase. This already hints to problems that may occur with this reference solution. These tiny values are not effective on the macro scale due to the complexity of the microstructure. However, when applying the harmonic average, these tiny stiffnesses dominate the effective stiffness.

Another important observation is that the longitudinal modulus along the 33-direction (the third principal diagonal entry) is not affected by this, although the serial alignment along this direction suggests a dominance of the soft phase tensile modulus. This is not the case because of the lateral confinement effect. The amorphous phase buttresses tensile loading in the 33 direction due to its relatively large compression modulus, together with the large in-plane crystal stiffness.

### 3.2. Orientation averages

With the effective laminate stiffness at hand we are ready to consider the orientation averaging.
3.2.1. Isotropic orientation distribution

Since we are concerned here with an isotropic distribution, the orientation averaging collapses to the very simple application of the isotropic projectors $P_{1,2}$ in the following form

$$C_{\text{iso}} = (P_{1} :: C_{\text{laminate}})P_{1} + \frac{1}{5}(P_{2} :: C_{\text{laminate}})P_{2}$$

(31)

$$= P_{\text{iso}} :: C_{\text{laminate}}$$

(32)

with

$$P_{\text{iso}} = P_{1} \otimes P_{1} + \frac{1}{5}P_{2} \otimes P_{2}.$$ 

(33)

The latter formula is nothing but a projection of the laminate stiffness into its isotropic part. The fraction $1/5$ comes from normalizing the second isotropic projector. One may have an intuition about this: With the isotropic projectors forming an orthonormal basis for the space of all isotropic stiffness tetrads, one can decompose the laminate stiffness into its isotropic and anisotropic parts, and argue that the anisotropic part vanishes when orientation-averaging is carried out over an isotropic orientation distribution, while the isotropic part remains unaltered. Applying this projector to $C_{\text{laminate}}$ reduces to taking some traces of $C_{\text{laminate}}$, as detailed in Walpole [48]. Nevertheless, the derivation of this equation from general orientation averaging is somewhat involved, see, e.g., Walpole [48], Guan and Pitchumani [20], and we shall sketch it here for completeness. We firstly introduce an abstract orientation averaging over the space of all possible orientations,

$$C_{\text{iso}} = \int_{SO(3)} p(Q) Q * C_{\text{laminate}} dQ.$$ 

(34)

The space of all orientations is the special orthogonal group $SO(3)$, $dQ$ is a differential volume element of this space and $Q$ a rotation that orients the laminate stiffness w.r.t. the reference stiffness $C_{\text{laminate}}$ with a fixed normal vector $n$. The orientation distribution is captured by the probability distribution function $p(Q)$, which can be thought of as a weighing function. It is normalized, i.e. $\int_{SO(3)} p(Q) dQ = 1$. For example, it becomes a sum of Dirac distributions if a discrete number of orientations is present. In case of isotropy, it is constant and equal to $1/V_{SO(3)}$, where $V_{SO(3)}$ is the volume of the orientation space. This rather abstract volume depends on the parametrization of the orientation space. For example, when integrating over Euler angles in the usual $e_{z}$-$e_{x}$-$e_{z}$ convention with the respective angles $\phi_{1}$, $\Phi$, $\phi_{2}$ and with the Jacobian $\sin(\Phi)$ we get

$$V_{SO(3)} = \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} \sin(\Phi) d\phi_{1} d\Phi d\phi_{2} = 8\pi^{2}$$ 

(35)

as the volume of $SO(3)$ in terms of the Euler-angle parametrization of $SO(3)$, see Morawiec [35] Sects. 2.4 and 3.1. We can now examine the orientation averaging in case of isotropy. Sticking to the Euler angle parametrization, we see that $p$ is constant with $(8\pi^{2})^{-1}$, and the reference stiffness is also constant with respect to
the Euler angles. The Rayleigh product can be written as a linear transformation with an eighth order tensor whose components are

$$Q_{im} Q_{jn} = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \sin(\Phi) d\phi_1 d\Phi d\phi_2$$

$$C_{\text{iso}}(\Phi) = \langle \mathbf{P} \rangle \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l,$$

where $$Q_{ij}$$ are the components of an orthogonal matrix parametrized by the three Euler angles with the components

$$Q_{ij} = \begin{bmatrix} c_1 c_2 & -c_2 s_1 & c_1 s_2 & c_1 c_2 \sin \Phi \\ c_2 s_1 & c_1 & -c_1 s_2 & \cos \Phi \\ s_1 & 0 & 0 & 0 \\ \cos \phi_1 & \sin \phi_1 & 0 & 0 \end{bmatrix},$$

$$c_1 = \cos \phi_1, \quad c_2 = \cos \phi_2, \quad s_1 = \sin \phi_1, \quad s_2 = \sin \phi_2, \quad \Phi = \sin \phi_1.$$

The integration over a product and sum of trigonometric functions over multiples of $$\pi$$ gives rational coefficients. For example, for $$P_{33333333}$$ we get

$$P_{33333333} = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \sin \Phi \cos^4(\Phi) d\phi_1 d\Phi d\phi_2 = \frac{1}{5},$$

which corresponds to

$$\left(\frac{1}{3}\right)^2 + \left(\frac{2}{3}\right)^2 = \frac{1}{5},$$

where 1/3 and 2/3 are the 3333-components of $$P_1$$ and $$P_2$$, respectively (see Eqs. 5 and 33).

3.2.2. Voigt, Reuss and geometric averages

In the last section, we found that the isotropic orientation average of the effective stiffness is obtained by applying the projector $$\langle \mathbf{P} \rangle \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l$$ to the laminate stiffness $$C_{\text{laminate}}$$ (Eq. 29). This is referred to as the Voigt orientation average [47, 7],

$$\overline{C}_{\text{LV}} = \langle \mathbf{P} \rangle \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l,$$

where "LV" stand for laminate and Voigt. On the other hand, one might consider the orientation average of the compliance, and then take the inverse to obtain the effective stiffness, which is the laminate Reuss average,

$$\overline{C}_{\text{LR}} = \langle \mathbf{P} \rangle \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l,$$

These averages constitute energetic bounds in the theory of linear elasticity (Gross and Seelig [18], Chapt. 8). An intermediate estimate is the geometric average

$$\overline{C}_{\text{LG}} = \exp\left(\langle \mathbf{P} \rangle \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l \right),$$

17
which gives the same result when applied to the stiffness or the compliance, i.e. applying it to $\mathbf{C}_{\text{laminate}}$ gives the same result as applying it to $\mathbf{C}_{\text{laminate}}^{-1}$ with a successive inversion [1].

Naturally, the Voigt average is easiest to evaluate, since it does not involve operations like inversion, exponentiation and the logarithm. These operations can be approximated by series expansions, but are most easily evaluated by the spectral decomposition of the argument tensor, in which the eigenvalues are subjected to the operation. Unfortunately, closed form expressions for the eigenvalues are not readily obtained, since the $6\times6$ matrix representation produces a sixth-order polynomial, for the roots of which no general closed form expression exist. On the other hand, the laminate stiffness is already not manageable as a closed form expression, so we have to resort to numerical calculations in any case.

Additional to the orientation averages over the laminate solution, we consider the naïve volume averages of the isotropic crystal orientation distribution, which completely neglects the micro-structure. By comparing with the laminate orientation averages, we can assess the advantage of approximating the microstructure locally as a laminate over the simple orientation averages. The simple Voigt, Reuss and geometric averaging procedures are given by applying the orientation averaging to the crystal stiffness, in conjunction with the corresponding rule of mixture,

$$\mathbf{C}_{\text{SV}} = v_{\text{amorph}} \mathbf{C}_{\text{amorph}} + v_{\text{cryst}} \mathbb{P}_{\text{iso}} \mathbb{C}_{\text{cryst}}, \quad (45)$$

$$\mathbf{C}_{\text{SR}} = \left( v_{\text{amorph}} \mathbf{C}_{\text{amorph}}^{-1} + v_{\text{cryst}} \mathbb{P}_{\text{iso}} \mathbb{C}_{\text{cryst}}^{-1} \right)^{-1}, \quad (46)$$

$$\mathbf{C}_{\text{SG}} = \exp \left( v_{\text{amorph}} \log(\mathbf{C}_{\text{amorph}}) + v_{\text{cryst}} \mathbb{P}_{\text{iso}} \log(\mathbb{C}_{\text{cryst}}) \right), \quad (47)$$

where "S" stands for simple and "V", "R" and "G" for the Voigt, Reuss and geometric average. Since the amorphous phase is isotropic, the orientation average needs not to be applied to $\mathbf{C}_{\text{amorph}}$. It is noteworthy that at 100% amorphous phase, all the presented averages coincide. This does not hold for the pure crystalline case: due to the anisotropy of $\mathbb{C}_{\text{cryst}}$, the orientation averages differ in that case.

4. The ad-hoc model

We have already established that the lamellar arrangement calls for the Reuss-average when Young’s modulus is determined perpendicular to the laminate and for the Voigt average when Young’s modulus is determined parallel to the laminate,

$$E_{\text{normal}} = (v_{\text{cryst}} E_{\text{cryst}}^{-1} \mathbb{C}_{\text{normal}} + v_{\text{amorph}} E_{\text{amorph}}^{-1})^{-1}, \quad (48)$$

$$E_{\text{in-plane}} = v_{\text{cryst}} E_{\text{cryst in-plane}} + v_{\text{amorph}} E_{\text{amorph}}. \quad (49)$$

The material parameters are already collected in section 2. To obtain the Young moduli in different directions, one needs to invert the stiffnesses. However, there is a catch to the Young modulus of amorphous iPP perpendicular
to the laminate. While in tension parallel to the laminate each layer can freely adjust its lateral straining, in tension perpendicular to the laminate, both layers must undergo the same lateral straining. Since the crystal phase is much stiffer, the lateral straining of the amorphous phase is constraint. Thus, for tension perpendicular to the laminate, we need to use Young’s modulus as if lateral straining is inhibited. Due to the very large compression modulus of the amorphous phase, the elongation in tension perpendicular to the laminate without lateral straining in the amorphous phase is countered almost exclusively by the compression modulus of the amorphous phase. This is illustrated in Fig. 5. This effect depends obviously on the volume fractions, it vanishes at zero crystallinity and is strongest at crystallinities close to 100%. This is referred to as the reinforcement or contiguity factor, originally introduced by Tsai and Pagano [45]. Other denominations are structural confinement effect and oedometric effect. The elastic modulus with confined lateral straining is also referred to as the longitudinal modulus. Its contribution to the overall reasonable quality of the Tsai-Halpin-estimate is demonstrated by [15, 9], among others. [51] (see the summary point 3 therein) showed for PE experimentally that this structural confinement effect is relevant for PE. It should be noted that the laminate stiffness takes automatically care of this, at the price of producing involved expressions. In the ad-hoc model, we may include the constrained lateral straining manually by using corrected values for Young’s modulus in the amorphous phase: in-plane we use the values

\[ E_{\text{amorph in-plane}} = 1.13 \text{ MPa (unconstrained tension test)} \]  
\[ E_{\text{cryst in-plane 1}} = 6 \text{ GPa} \]  
\[ E_{\text{cryst in-plane 2}} = 9 \text{ GPa} \]

and perpendicular we use

\[ E_{\text{amorph normal}} = 1.76 \text{ GPa} = K_{\text{amorph}} \text{ (constrained tension test)} \]  
\[ E_{\text{cryst normal}} = 40 \text{ GPa}. \]

We can now assemble an estimate for the effective Young modulus by averaging the response of the material in the three considered directions:

\[ E_{\text{adhocVoigt}} = \frac{v_{\text{cryst}}E_{\text{cryst in-plane 1}} + (1 - v_{\text{cryst}})E_{\text{amorph in-plane}}}{3} + \frac{v_{\text{cryst}}E_{\text{cryst in-plane 2}} + (1 - v_{\text{cryst}})E_{\text{amorph in-plane}}}{3} + \frac{v_{\text{cryst}}( \frac{v_{\text{cryst}}}{E_{\text{cryst normal}}} + \frac{1 - v_{\text{cryst}}}{K_{\text{amorph}}} )^{-1} + (1 - v_{\text{cryst}})( \frac{v_{\text{cryst}}}{E_{\text{cryst normal}}} + \frac{1 - v_{\text{cryst}}}{E_{\text{amorph in-plane}}} )^{-1}}{3}. \]  

The last summand is the most complicated one: for small crystal volume fractions the lateral straining constraint effect described above is gone, and we use the ordinary Young modulus of amorphous iPP, for large crystallinities the lateral straining inhibition is strong, hence we use the compression modulus instead of Young’s modulus. A linear transition between the two effects is assumed. The expression for \( E_{\text{adhocVoigt}} \) cannot be simplified much. Inserting the numbers allows to summarize to a rational polynomial (we reduced to 4 significant digits}
Figure 5: The layers can freely adjust their lateral straining when extended in-plane (upper left), where the contraction of the almost incompressible amorphous phase is sketched. When stretched normal to the laminate direction, the much stiffer crystal phase practically inhibits lateral straining, forcing the stress-strain relation in the amorphous phase to be dominated by the amorphous compression modulus (lower right). The amorphous compression modulus is approximately 1500 times larger than the amorphous Young modulus, but still approximately 23 times smaller than the Young modulus of the crystalline phase along the laminate normal.
in the following equation)

\[ E_{\text{adhoc Voigt}} = \frac{1.182 + 5841v_{\text{cryst}}^2 - \frac{1084v_{\text{cryst}}^3}{1.046 - 2.046v_{\text{cryst}} + v_{\text{cryst}}^2} + 4999v_{\text{cryst}}^3}{MPa} \]  

(58)

As shown later, it is somewhat revealing to consider also the ad-hoc Reuss average, where we just take the harmonic mean of the Young moduli along the three directions,

\[ E_{\text{adhoc Reuss}}^{-1} = [v_{\text{cryst}}E_{\text{cryst in-plane 1}} + (1 - v_{\text{cryst}})E_{\text{amorph in-plane}}]^{-1}/3 + \]

\[ [v_{\text{cryst}}E_{\text{cryst in-plane 2}} + (1 - v_{\text{cryst}})E_{\text{amorph in-plane}}]^{-1}/3 + \]

\[ [v_{\text{cryst}}(\frac{v_{\text{cryst}}}{E_{\text{cryst normal}}} + \frac{1 - v_{\text{cryst}}}{K_{\text{amorph}}})^{-1} + (1 - v_{\text{cryst}})(\frac{v_{\text{cryst}}}{E_{\text{cryst normal}}} + \frac{1 - v_{\text{cryst}}}{E_{\text{amorph in-plane}}})^{-1}]^{-1} \]  

(59)  

(60)  

(61)

5. Comparison to experimental findings

5.1. Source of experimental data

We have compiled experimental data from a variety of articles. We consider only iPP homo-polymer with spherulitic micro-structure. Naturally, the samples differ in the chain length, volume fractions of the crystalline \( \alpha \), \( \beta \) and \( \gamma \) phases, nucleation agents, processing conditions and many other parameters. Also, the measurement methods for Young’s modulus are not always specified. When stress-strain curves are given, we extract Young’s modulus as the slope of the stress-strain-curve at the origin, which is indicated by an asterisk next to the citation. Our own measurements are included as well.

Often, researchers examine directly the effect of the crystallinity, which is controlled either by nucleation agents or a heat treatment. In these cases we used all relevant data points. When some modifications where studied, like UV irradiation or additional copolymers, we used only the reference value of the pure iPP. In Tab. 3, these are the lines with only one data point.

Regarding the data of Menyhárd et al. [31], we employed a correction of the crystallinity by a factor of 146/207, which is due to a too low enthalpy of fusion of 146 J/g that has been used in this work. The low value has been reported by Monasse and Haudin [34], and has been improved later to 207 J/g by Bu et al. [11]. The latter value is more realistic and better established, see e.g. van der Meer [46]. For \( \beta \)-iPP one finds values between 100 J/g and 190 J/g. However, the reported cooling conditions and the WAXS graphs suggest a dominance of the \( \alpha \)-phase.

Regarding the data of Horváth et al. [23], very large crystallinities are reported. The methodology is a little bit unorthodox: The crystallinity has been estimated from the lamella thickness, Young’s modulus has been estimated with the aid of a very simple empirical formula. Nevertheless, the data fits well into the overall tendency. It should be used nevertheless with caution, which is indicated in Fig. 7.
Table 3: Experimental data taken from literature

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<td>5 TVK iPP grades of varying isotacticity</td>
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<td>Horváth et al. [23], Tab. 3</td>
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<td>Parenteau et al. [38], Fig. 7,16</td>
<td>3 annealed Basell Polyolefins Moplen HP501H</td>
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<tr>
<td>also Zia et al. [52]</td>
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<td>9</td>
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<td>Tordjeman et al. [44], Fig. 6</td>
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</table>

5.2. Quality of the orientation averages

The experimental results collected in Sec. 5.1 are plotted together with the estimates from Sec. 3.2 in Figs. 6 (full plot range) and 7 (zoom on experiments). Due to the extreme spread of the results over three orders of magnitude, a logarithmic scale is used. This spread is a consequence of the extreme stiffness contrast. The simple Voigt and Reuss averages give extremely wide bounds, and the Voigt and Reuss laminate orientation averages give a smaller but still a wide range. In numbers, when considering a crystallinity of 50\%, the laminate Voigt orientation average estimates \( E_{LV50\%} = 2551 \) MPa, while the laminate Reuss orientation average estimates \( E_{LR50\%} = 5.644 \) MPa. The simple Voigt and Reuss averages give \( E_{SV50\%} = 6941 \) MPa and \( E_{SR50\%} = 2.26 \) MPa, respectively. At extremal volume fractions, the laminate estimates coincide with the simple estimates. At 100\% crystallinity we get 13.5 GPa for the Voigt estimates, 10.4 GPa for the geometric estimates and 8.9 GPa for the Reuss estimates. At 0\% crystallinity we obtain 1.13 MPa for all estimates. This is expected, since the amorphous phase is isotropic, hence the orientation average does not effect it at all.

Further, we observe that the laminate Voigt average is relatively close to the experimental results. Some measurements come very close to this estimate. As mentioned before, this may be expected, since the underlying assumptions (locally perfect laminate inside perfectly isotropic spherulitic meso-structure) are not met exactly. Also, we know that the laminate orientation averaging falls inside the second-order Hashin-Shtrikman bounds [25]. The values of the Hashin-Shtrikman bounds are in principle attainable by a real micro-structure.
Figure 6: Experimentally observed Young moduli (dots) and orientation average estimates (solid curves). The ad-hoc-approaches (Eqs. 58 and 61) are the dotted lines, where the upper one is the ad-hoc Voigt and the lower one the ad-hoc Reuss approach. The dashed line is a cubic regression polynomial fitted to the experimental results.

Figure 7: Experimentally observed Young moduli (symbols) and orientation average estimates (solid curves). The ad-hoc-approaches (Eqs. 58 and 61) are the dotted lines, where the upper one is the ad-hoc Voigt and the lower one the ad-hoc Reuss approach. The dashed line is a cubic regression polynomial fitted to the experimental results.
Thus, we need not be surprised that some values are very close or even exceed the Voigt laminate orientation average, given the fact that numerous other effects may affect the effective stiffness. It is noteworthy that the laminate Voigt orientation average can well retrace the upper limit of the experimental results (see Fig. 7), without the use of any tuning parameters. This shows that the laminate reference solution in conjunction with a Voigt-orientation averaging gives a relatively safe upper bound for the true effective Young modulus. Since it may be of use for others, we therefore give the following Padé-approximant around the point $\nu_{\text{cryst}} = 0.6$ of this otherwise involved function,

$$
E_{LV} \approx -7468(\nu_{\text{cryst}} - 0.6)^3 - 10910(\nu_{\text{cryst}} - 0.6)^2 + 1309(\nu_{\text{cryst}} - 0.6) + 3100
$$

and include the computer algebra script needed to reproduce the estimates from scratch in the supplementary material.

The good quality of the Voigt laminate orientation average and the bad quality of the Reuss laminate orientation average indicate that the assumption of a homogeneous strain field is much more realistic than the assumption of a homogeneous stress field. It is in fact easy to accept that the very soft amorphous phase simply follows the average deformation of the stiff crystalline phase, which gives the load carrying capacity to the material. Conversely, a homogeneous stress field is far from realistic, since this would require the strains in the amorphous phase to be orders of magnitude larger (approximately $10^3$ times) than the strains in the crystalline phase. Such a deformation is far from kinematically compatible, hence the bad quality of the Reuss estimate.

It is rather surprising that even the intermediate geometric orientation average considerably underestimates the effective Young modulus. In numbers, at a crystallinity of $50\%$ we find $E_{LG50\%} = 211.3$ MPa. Usually, one would assume that any compromise between the extremal Voigt and Reuss estimate is closer to the reality than the extreme cases. However, the very low shear resistance of the laminate against parallel gliding renders the Reuss approximation really bad, such that the intermediate geometric average is drawn too far away from the experimental findings.

5.3. Contribution of the laminate reference solution to the quality of the orientation averages

It is clear from Figs. 6 and 7 that the laminate intermediate solution improves the estimates considerably. The simple averages are virtually useless. We therefore confirm that the model assumption of a local laminate structure inside the spherulites is a good approximation of the structure inside the spherulites, which has been similarly shown for PE by Boyd [9].

5.4. Quality of the ad-hoc approach

The ad-hoc Voigt approach is close to but above the laminate Voigt orientation average. As one may expect from this Tsai-Halpin like approach, the stiffness is overestimated. Nevertheless, it contains all the features of this approach qualitatively, most notably the super-linear stiffening at high crystal volume fractions due to the lateral constraining effect described above. However, somewhat unexpectedly, the ad-hoc Reuss average is just slightly below the
the ad-hoc Voigt approach, but still overestimating the experimental results, instead of being close to the Reuss estimates (see Fig. 7). This is exactly what Boyd [9] found (see the paragraph around Eq. 31 in Boyd [9]). It allows us to identify the main mechanism that causes the Tsai-Halpi-approach to overestimate the experimental results. The only term common to the ad-hoc Voigt and ad-hoc Reuss estimates that can bring these approaches close to the laminate Voigt orientation average is the linear interpolation of the transition from the amorphous to the crystalline phase. Mostly referred to as $\xi$, the reinforcement factor or contiguity factor enters linearly, just like the volume fractions in the Voigt estimate.

This underlines the importance of the lateral constraining effect of the amorphous phase: the higher the compression modulus of the amorphous phase and the in-plane Young moduli of the crystal phase, the higher is the lateral constraining effect. It should be noted that both are in iPP considerably larger than in PE. The in-plane Young moduli of iPP lie direction-dependent between 6 GPa and 9 GPa for iPP, for PE the in-plane Young modulus lies around 5 GPa. Regarding the compression modulus of the amorphous phase, reliable values are hard to find for both phases. Nevertheless, the glass transition temperature $T_g$ is around -80°C for PE and -10°C for iPP. Most polymers display more or less the same master curve for the compression modulus over the temperature, centered around $T_g$ at approximately 2.5 GPa [36, 37]. Following the rather simple thermodynamical free-volume approach, $K$ decays exponentially beyond $T_g$, i.e. amorphous iPP must have at room temperature a considerably larger compression modulus than PE. A reasonable estimate gives a factor of $2 = K_{\text{amorphous iPP}} / K_{\text{amorphous PE}}$ [36]. Putting these observations together, one must conclude that the lateral confinement effect is much more pronounced in iPP than in PE.

5.5. Potential influence of a rigid-amorphous fraction

The RAF is a stiff fraction of the amorphous phase. As a first approximation, we could include the RAF by simply increasing the crystallinity in our model. For example, if we believe 30% of the amorphous phase to be rigid, we could calculate corrected volume fractions $v^*_{\text{cryst}} = v_{\text{cryst}} + 0.3v_{\text{amorph}}$ and $v^*_{\text{amorph}} = 0.7v_{\text{amorph}}$, which enter then the homogenization approach. This would result in a shift and stretch of the curves in Figs. 6 and 7 parallel to the horizontal axis to the left, driving the Voigt-estimates further away from the measurements, and bending all other estimates towards the measurements. Thus, the tendency is reasonable. Nevertheless, one can see that this would have almost no effect on the diagnosis given here, since the curves as well as the experiments are approximately plateau-like for crystallinities between 20% and 80%. In fact, the stretch needs to be extreme to get one of the non-Voigt estimates near the results, except for the simple geometric orientation average. This leaves us to conclude that the RAF has not that much of an influence on the effective stiffness as one might suspect.

6. Summary

The main problems when estimating the effective elastic properties of polymers are the following:

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• complex micro-structure in at least two scales
• strong anisotropy of the crystalline phase, isotropy of the amorphous phase
• strong correlation between the crystalline anisotropy and the microstructure
• strong stiffness contrast between the isotropic and the anisotropic shear moduli,
• vanishing shear modulus of the amorphous phase above the glass transition temperature.

We have shown here that the characteristic spherulitic micro-structure can be approached very well by a local laminate inside the spherulites.

We argue for preferring the fundamental laminate solution over an oblate ellipsoidal inclusion scheme with extreme aspect ratios. The main advantage is that one can give the closed form fundamental solution of the laminate for arbitrary phase stiffnesses, while the ellipsoidal inclusion solution can only be given explicitly for isotropic phases. This is in contrast to the strong anisotropy of the crystalline polymer phases.

The isotropic orientation Voigt average of the laminate stiffness gives then a reasonable estimate for the upper bound of the stiffness that is attainable. Comparisons to experiments show that all measured Young-moduli are below but relatively close to the estimate.

Further, we observed that all other isotropic orientation averages (simple Voigt, simple Reuss, simple geometric, laminate Reuss and laminate geometric) produce results that drastically over- or underestimate the effective stiffness. This is explained by the fact that the very soft amorphous phase simply follows the deformation of the load-carrying crystal phase, i.e. Voigt’s iso-strain assumption works well, while an iso-stress assumption, implying strain differences of three orders of magnitude between the stiff and soft phases, is unrealistic. Further, the laminate reference solution contributes significantly to the quality of the estimate.

We also constructed an ad-hoc model for the effective Young modulus in the way of Tsai-Halpin from engineering considerations of the laminate, which is qualitatively in accordance with the Voigt laminate orientation average, but overestimates the experiments. The approach consists in averaging the effective Young moduli in three main directions (two in plane and one perpendicular). These anisotropic Young moduli take the laminate structure and the lateral confinement effect into account. Surprisingly, the Reuss average of these moduli is between the ad-hoc Voigt average and the experiments, i.e. it still overestimates the experiments, but less than the ad-hoc Voigt approach. The same has been found by Boyd [9]. This underlines the importance of the lateral confinement effect over the type of averaging.

The importance of the lateral confinement effect also gives an explanation why the effective Young modulus of iPP (around 1.5 GPa to 2 GPa) is relatively large compared to PE (around 0.8 GPa for HDPE), although most local stiffnesses are very similar. The lateral confinement effect relies on two ingredients: the in-plane crystal stiffness and the compression modulus of the amorphous phase. Both are larger in iPP than in PE. The in-plane crystal stiffness is by
a factor of 1.2...1.8 bigger. The same value holds for the amorphous compression moduli. Amorphous polymers display more or less the same compression-modulus–temperature dependence with respect to the normalized temperature, with $K \approx 2.5$ GPa near the glass transition temperature. Beyond $T_g$, $K$ drops exponentially, but not as dramatic as the shear modulus. At room temperature, PE is approximately 100°C above its $T_g$, while iPP is only approximately 30°C above its $T_g$, which indicates that the amorphous compression modulus of iPP is larger than for PE.

Therefore, to the following list of explanations for why iPP has a favourable stiffness over PE, namely

- the more extreme aspect ratios of the lamellae [5],
- the higher in-plane stiffness of the crystal phase [38],
- the large rigid amorphous fraction [53],

we may add the more pronounced lateral confinement effect.

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1. An ad-hoc homogenization scheme for the elasticity of iPP is presented
2. Laminate orientation averages are calculated
3. The ellipsoidal-inclusion approach is critically discussed
4. The lateral confinement effect contributes to the high stiffness of iPP