Retrieving the spatially resolved preferred orientation of embedded anisotropic particles by small-angle X-ray scattering tomography

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Experimental nondestructive methods for probing the spatially varying arrangement and orientation of ultrastructures in hierarchical materials are in high demand. While conventional computed tomography (CT) is the method of choice for nondestructively imaging the interior of objects in three dimensions, it retrieves only scalar density fields. In addition to the traditional absorption contrast, other contrast mechanisms for image formation based on scattering and refraction are increasingly used in combination with CT methods, improving both the spatial resolution and the ability to distinguish materials of similar density. Being able to obtain vectorial information, like local growth directions and crystallite orientations, in addition to scalar density fields, is a longstanding scientific desire. In this work, it is demonstrated that, under certain conditions, the spatially varying preferred orientation of anisotropic particles embedded in a homogeneous matrix can be retrieved using CT with small-angle X-ray scattering as the contrast mechanism. Specifically, orientation maps of filler talc particles in injection-moulded isotactic polypropylene are obtained nondestructively under the key assumptions that the preferred orientation varies slowly in space and that the orientation of the flake-shaped talc particles is confined to a plane. It is expected that the method will find application in *in situ* studies of the mechanical deformation of composites and other materials with hierarchical structures over a range of length scales.

1. Introduction

Functional materials have properties deriving from their underlying design, and tend to involve organized anisotropic molecules that respond to external stimuli. Indeed, it is well known that the preferred orientation of embedded anisotropic nano- and microparticles can strongly affect a material's macroscopic properties. This fact is strikingly exemplified by the high charge-carrier mobility dependence on the orientation of crystallites within thin films for organic electronics (Sirringhaus *et al.*, 1999; Kline *et al.*, 2006). A textbook example of orientation dependence is liquid-crystal displays, which control light transmission by actively changing the molecular orientation (Clark & Lagerwall, 1980). Similarly, advanced *structural* materials also increasingly involve nano- and microstructured features to improve their mechanical properties, an example of high commercial relevance being talc particles added to polypropylene to improve the mechanical characteristics of the polymer. The microscopic embedded talc particles serve to reinforce the polymer (Phillips & Wolkowicz, 2005), in addition to reducing shrinkage and warpage, and they reduce thermal expansion

and cycle time during production (Naiki *et al.*, 2001; Ferrage *et al.*, 2002).

Measurement of the spatially averaged orientation distribution function of embedded particles or crystallites in homogeneous samples is traditionally carried out using texture analysis, usually with X-rays (Bunge, 2013; Breiby & Samuelsen, 2003; Lutterotti *et al.*, 2004) or NMR (Eletr & Inesi, 1972). However, in the important cases when the preferred orientation varies with spatial position, traditional texture analysis will only be able to give the spatially averaged orientation distribution. Highly desirable information might not be retrieved, for example whether the crystallites near the surfaces of the specimen are oriented differently from those at the centre (Kline *et al.*, 2006). Measuring spatially varying orientations by texture analysis normally requires destructive sample preparation, where thin sample cross sections have to be cut. Obtaining a full understanding of how embedded particles affect the meso- and macroscopic mechanical properties must be done with *in situ* measurements where the material response can be monitored and related to how the particles reorient during external loading, which clearly precludes physical cutting.

Computed tomography (CT) is well established in the medical and scientific communities for nondestructive three-dimensional imaging of the interior of samples. CT is widely used in the natural sciences, including materials science, biology, medicine, and even the electronic and food industries (Midgley & Weyland, 2003; Möbus & Inkson, 2007; Maire & Withers, 2014; Fløystad *et al.*, 2015). Traditionally, material-specific absorption has been used for image contrast in X-ray tomography, relying on differences in the attenuation of the X-ray beam for different materials in the sample. As synchrotron and detector technologies have improved, more advanced tomographic techniques have emerged, such as propagation-based phase contrast (Cloetens *et al.*, 1999). Micro- and nanotomography based on coherent X-ray diffraction imaging (Chapman *et al.*, 2006; Rodenburg *et al.*, 2007; Dierolf *et al.*, 2010; Jiang *et al.*, 2013; Esmaili *et al.*, 2013), X-ray fluorescence (de Jonge & Vogt, 2010; Cheong *et al.*, 2010; Cong *et al.*, 2014) and transmission electron microscopy (Midgley & Weyland, 2003; Van Aert *et al.*, 2011) are other notable examples of recent developments. Different X-ray CT techniques make it possible to investigate sample structures across length scales ranging from nanometres (Holler *et al.*, 2014) to metres (Murphy *et al.*, 2003). Some of the new CT techniques give access to the refractive index, allowing quantitative imaging of the electron-density distribution (Dierolf *et al.*, 2010; Diaz *et al.*, 2012), but all of the techniques mentioned above share the limitation that they only measure three-dimensional scalar fields (absorption and/or phase contrast).

Small-angle X-ray scattering (SAXS) is often employed for studying systems where the structures of interest are too small for conventional imaging. Standard SAXS is typically applied to study the conformation of molecules in solution or disordered multicomponent solid-state systems, covering structures from about 10 Å to 1 µm. The structural information

retrieved includes shapes, phase fractions, orientations and inter-particle spacing distributions. The SAXS signal is averaged over the effective volume, defined by the intersection between the incoming beam and the sample. This averaging is often considered one of the advantages of SAXS: in a single exposure, an ensemble average comprising a large number of scatterers is probed, yielding statistically reliable data. Still, multiple efforts have been made to probe spatial variations using SAXS, as we shall now describe.

It is instructive to consider the number of dimensions involved in SAXS experiments. By applying raster scanning to a thin physically cut specimen, information is retrieved in two dimensions in real space and two dimensions in reciprocal space, in total four dimensions. Position-resolved scanning SAXS has been used for the past three decades to study hierarchically structured materials (Ascenzi *et al.*, 1985; Fratzl *et al.*, 1997). A theoretical framework for analysing the measured scattering patterns has been developed (Fratzl *et al.*, 1996; Cave, 1997; Paris & Müller, 2003). Materials suitable for analysis include wood (Cave, 1997; Reiterer *et al.*, 1998), dentine (Kinney *et al.*, 2001; Märten *et al.*, 2010) and the cornea (Boote *et al.*, 2004; Meek & Boote, 2009). Another material thoroughly studied by scanning SAXS is bone, owing to its relevance for medicine and industry (Rinnerthaler *et al.*, 1999; Jaschouz *et al.*, 2003; Giannini *et al.*, 2012). Granlund *et al.* (2013, 2014) have recently published detailed studies of the spatially resolved orientation of talc particles in extruded isotactic polypropylene, also demonstrating that modern area detectors make it feasible to collect the necessary data in a practical amount of time ($\leq$ hours) even in home laboratories.

In the case of isotropic scattering, every SAXS pattern is of course rotationally symmetric [$I = I(q)$]. By introducing *one* rotation axis into the experimental setup, (3 + 1) dimensions, *i.e.* three dimensions in real space and one dimension in reciprocal space, can be obtained, as demonstrated by Schroer *et al.* (2006) on injection-moulded polyethylene. In other reports, the SAXS patterns from anisotropic scatterers with preferred orientation have been intentionally azimuthally averaged prior to further analysis to reduce the huge amount of data, thus deliberately dispensing with the orientation information on the particles (Jensen *et al.*, 2011). This again effectively gives (3 + 1) dimensions, where different choices of q allow different three-dimensional scalar fields to be visualized.

In fact, by using one rotation axis, up to five-dimensional data can be obtained by (i) studying a thin sample (giving two dimensions in real space and three in reciprocal space) or (ii) assuming that the scattering exhibits rotational symmetry about an axis (giving three dimensions in real space and two in reciprocal space). SAXS-CT based on the first approach is exemplified by the work on bone carried out by Liu *et al.* (2010) and Wagermaier *et al.* (2007).

Several research groups, including ours, have recently been working on methods towards extending SAXS-CT to retrieve six-dimensional (three real-space dimensions and three reciprocal-space dimensions) information. Georgiadis *et al.* (2015) have demonstrated that six-dimensional information on

collagen fibrils in bone can be retrieved by combining the above-mentioned thin-slice (2 + 3 dimensions) approach with multiple contiguous *physically cut* slices, but their technique is obviously destructive, making further studies of the same sample impossible. Most recently, it was demonstrated (Schaff *et al.*, 2015; Liebi *et al.*, 2015) that, by using *two* orthogonal rotational axes, six-dimensional information can be retrieved numerically from data sets comprising $\sim 10^6$ scattering patterns.

In this article, we demonstrate that, using CT with small-angle X-ray scattering as the contrast mechanism, under certain conditions the spatially varying preferred orientation of embedded flake-shaped talc particles in isotactic polypropylene (iPP) can be retrieved nondestructively. Our approach is a variant of the five-dimensional acquisition scheme, where instead of assuming rotationally symmetric scattering, the orientation of the platelets is confined to a plane perpendicular to the rotation axis, effectively reducing the dimensionality of reciprocal space to two. The method presented is fast compared with the six-dimensional approach, requiring only 15 min exposure time of the sample and <5 h computation time for the reconstruction, using a single rotation axis.

2. Tensorial SAXS tomography model

The method described here for retrieving the spatial variation in the preferred orientation of embedded anisotropic particles is generic but relies on the following assumptions. First, the particles need to be relatively monomorphous and monodisperse. Second, the particles need to be uniaxial, in the sense that their individual orientation can be described by a single directional vector, which will be denoted the director from now on. This is the case for instance for discs, rods, cones, tori, and oblate and prolate spheroids. Here we will work with oblate spheroids and therefore relate the method to this shape. Third, we assume the system to be dilute yet of uniform density of scattering particles and that scattering from the matrix material can be ignored. Fourth, in the case presented, we further have the prior knowledge that, for the area we are investigating, the director is confined to lie in a plane, which effectively reduces the problem to two dimensions, and we exploit the fact that the orientation changes slowly with position. Finally, we assume that the X-ray radiation is monochromatic.

To retrieve the orientation distribution of the embedded particles in a material, we fit a theoretical model of the X-ray scattering to the experimental

scattering pattern. In a dilute system, the inter-particle scattering can be ignored and the structure factor is thus unity, $S(\mathbf{q}) = 1$. The SAXS signal from one particle is then essentially proportional to the absolute square of the Fourier transform of the shape of the particle (Guinier & Fournet, 1955):

$$I^{\text{SAXS}}(\mathbf{q}) \propto (\rho_{\text{sl,p}} - \rho_{\text{sl,0}})^2 \left| \int_{V_p} \exp(i\mathbf{q} \cdot \mathbf{r}) dV \right|^2 = (\rho_{\text{sl,p}} - \rho_{\text{sl,0}})^2 |F(\mathbf{q})|^2. \quad (1)$$

Here, $\rho_{\text{sl,p}}$ and $\rho_{\text{sl,0}}$ are the scattering length densities of the particle and the matrix material, respectively. The scattering vector is given by $\mathbf{q} \equiv \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}}$, where $\mathbf{k}_{\text{in}}$ and $\mathbf{k}_{\text{out}}$ denote the incoming and outgoing wavevectors, respectively, and has magnitude $q = |\mathbf{q}| = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle 2θ . V_p is the volume of the particle and F denotes the form factor of the particle. For a spheroid, as sketched in Fig. 1, the form factor is given by (Guinier & Fournet, 1955)

$$F(\mathbf{q}) = \int_0^{H/2} 4\pi R_y^2 \frac{J_1(q_{\parallel} R_y)}{q_{\parallel} R_y} \cos(q_{y'} y') dy'. \quad (2)$$

Here, $J_1(u)$ is a Bessel function of first order, H is the total height of the spheroid, $q_{y'}$ is the scattering vector along the director axis, $q_{\parallel} = (q_x^2 + q_z^2)^{1/2}$ and $R_y = R(1 - 4y'^2/H^2)^{1/2}$. The axis directions and other variables are indicated in Fig. 1(b). Particle polydispersity will tend to smear out the SAXS signal and can be accounted for by convoluting the theoretical intensity $I^{\text{SAXS}}(\mathbf{q})$ with a Gaussian distribution.

Figure 1

(a) A sketch of the experimental SAXS-CT measurement procedure. The sample is scanned laterally through the beam, along the x axis, for each projection angle ψ about the z axis. A typical raw data image is given in the detector plane. Only the intensity from the equatorial scattering, collected in the unhatched detector areas, is used for the SAXS-CT analysis. The fixed laboratory frame is given by (x, y, z) , with the incoming beam $\mathbf{k}_{\text{in}} = \hat{\mathbf{y}}2\pi/\lambda$. For modelling, the two-dimensional sample cross section is divided into voxels. Each voxel (i, j) contains one representative particle, shown here as a dark grey ellipsoid, with its director confined to the xy plane and making an angle φ_{ij} with the sample edge. φ_{ij} will in general be different for different voxels, thus modelling the spatial dependence of the orientation. When the sample is rotated, the particle at voxel (i, j) will thus have an orientation $\alpha_{ij} = \varphi_{ij} + \psi$ with respect to the incoming X-ray beam. (b) A sketch of an oblate spheroid indicating the radius R , total height H and director $\mathbf{n}$. The internal coordinate system (x', y', z') of the talc particle as used in equation (2) is also indicated.

A scheme for modelling the orientation of the embedded particles with respect to the overall sample and the X-ray setup is illustrated in Fig. 1(a). The sample is rotated by an angle ψ around the laboratory z axis, which coincides with the long axis of the sample, and the embedded particles have a fixed angle φ_{ij} with respect to the sample.

If we assume that the particle orientation gradient is low (*i.e.* the orientation varies slowly with position, $w|\nabla\varphi| \ll 1$, where w is the voxel size in the reconstruction), we can take the particles within each voxel to have a uniform orientation, whereby the orientation of voxel ij is characterized by a single director $\mathbf{n}_{ij}$. Motivated by our prior knowledge about the injection shear alignment of the talc particles, all directors $\{\mathbf{n}_{ij}\}$ are taken to be confined perpendicular to the flow direction $\mathbf{z}$ and thus confined to the xy plane (Granlund *et al.*, 2013, 2014). In other words, the z' component of $\mathbf{n}_{ij}$ is set to zero. We assume that, for each voxel in the reconstruction, an effective scattering spheroid can be assigned, oriented by an angle $\alpha_{ij} = \varphi_{ij} + \psi$ with respect to the laboratory. Because the form factor tends to vary slowly with orientation, it is not necessary to have a large number of allowed orientations to extract the main features of the spatially varying preferred orientation. For simplicity and numerical stability, we further discretize the different allowed directions to a low number, typically just four, *i.e.* $\varphi_{ij} \in \Phi = \{-45^\circ, 0^\circ, 45^\circ, 90^\circ\}$, to extract the essential orientation features of the sample. With the oblate spheroid oriented with its director in the xy plane, the SAXS signal will be most sensitive to the particle orientation in the equatorial plane, which was thus used for the subsequent analysis, as indicated in Fig. 1(a).

We model the scattering as the intensity sum of the scattering from all the voxels encountered on a straight line along the incoming beam through the sample. Neglecting absorption, for any given sample orientation ψ and lateral sample position x we assume the scattering intensity to be the incoherent sum of the scattering from the different voxels traversed by the beam. If the X-ray beam at position x travels a distance $a_{\varphi_k, x, \psi}$ through regions with an orientation φ_k with respect to the sample, and the sample is rotated by an angle ψ , then the total scattering intensity recorded at the detector will be

$$I_{x, \psi}(\mathbf{q}_{\text{lab}}) \propto \sum_{k=1}^n a_{\varphi_k, x, \psi} |F_{\varphi_k, \psi}(\mathbf{q}_{\text{lab}})|^2. \quad (3)$$

Here, n is the number of different orientations in the set Φ . The subscripts on the form factor emphasize the fact that one needs to transform the scattering vector $\mathbf{q}_{\text{lab}}$, which is the one measured in the fixed laboratory frame, to the scattering vector $\mathbf{q}$, which is that measured with respect to the internal coordinate system of the particle. If the absorption is not negligible, the modelled scattering intensity has to be multiplied by Beer–Lambert correction factors $\exp(-\mu l)$ for the incoming and scattered beams (Breiby & Samuelsen, 2003; Schroer *et al.*, 2006) to obtain the measured scattered intensity from the sample, where μ is the effective attenuation coefficient and $l = l(x, \psi)$ is the length of the path the X-rays travel through the sample. Approximating all the scattered rays to

follow the same path as the unscattered ray is valid as long as the scattering angle 2θ is small.

3. Experimental details

The sample used in this study was a specimen of injection-moulded isotactic polypropylene (iPP) containing talc particles, chosen because we have previously performed raster scanning wide- and small-angle X-ray scattering of physically cut specimens of the same material (Granlund *et al.*, 2013, 2014). The fact that the spatially resolved preferred orientation of the embedded talc flakes is known in advance makes it possible to compare the results from the SAXS-CT technique with the true orientation distribution. In particular, it is known that all the talc particles, to a good approximation, are oriented about a common z' axis inside the iPP sample. Moreover, the inorganic talc particles have a high scattering cross section compared with the polymer, which gives high scattering contrast.

The experiment was performed on the cSAXS beamline (X12SA) at the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland, and the setup is sketched in Fig. 1(a). A monochromatic beam with photon energy 12.4 keV (wavelength $\lambda = 1.00 \text{ \AA}$) was used, focused by the beamline optics to a beam of dimensions $20 \times 20 \mu\text{m}$. After the sample, the X-rays passed through an evacuated flight tube to reduce air scattering before being collected by a PILATUS 2M detector (Henrich *et al.*, 2009) placed 7.119 m downstream of the rotation axis. The measurement was performed on the narrow part of the dogbone sample, which had dimensions $\sim 10.2 \times 4.2 \text{ mm}$ and was mounted with the long axis vertical, as illustrated in Fig. 1(a). Each tomography scan consisted of rotating the iPP sample around the z axis from 0 to 179° in 1° steps, while for each angular step horizontal scans along the x axis were performed with 101 measuring points of 0.120 mm distance between each point, *i.e.* for each horizontal scan we scanned a total distance of 12.0 mm , which is slightly longer than the diagonal of the cross section. This gave a total of $180 \times 101 = 18180$ scattering patterns, each with an exposure time of 0.05 s , totalling about 15 min of beam exposure. For the reference raster scan experiment, a cross section of 1 mm thickness was physically cut, and the X-ray beam, being in this case parallel to the long axis of the original sample, was raster scanned in two dimensions along the x - and z -axis directions with a $15 \mu\text{m}$ step length, recording the scattering pattern at each position of the beam on the sample. Further experimental details regarding the sample material and preparation can be found in the paper by Granlund *et al.* (2014).

4. Analysis

The talc particles in the iPP sample were modelled as oblate spheres of average height $H = 2.3 \mu\text{m}$ and radius $R = 3.0 \mu\text{m}$, as this gave the best fit to the experimental data, and these dimensions are of the same order of magnitude as indicated by scanning electron microscopy images (Granlund *et al.*, 2013). The model included an absorption correction, with the effective absorption coefficient measured experimentally to be $\mu = 2.85 \text{ cm}^{-1}$. As expected, this is in between the absorption

coefficients of pure talc ($\mu = 23.1 \text{ cm}^{-1}$) and pure polypropylene ($\mu = 0.94 \text{ cm}^{-1}$) for the given wavelength (Henke *et al.*, 1993).

From each scattering pattern the 'equatorial' part of the detector was chosen, consisting of two sectors of 45° , as illustrated in Fig. 1(a). The chosen sectors were azimuthally averaged to give one-dimensional curves of scattering intensity $I(q)$. The experimental scattering patterns were compared with the theoretical scattering according to the cost (or 'energy') function

$$E = \sum_q \sum_x \sum_\psi \{ [I_{\psi,x,q}^{\text{expt}}(q) - I_{\psi,x,q}^{\text{model}}(q)] q^m \}^2. \quad (4)$$

Here, x is the projection position at each angle, and I^{expt} and I^{model} are the experimental and theoretical calculated scattering patterns, respectively. Because the SAXS intensity drops rapidly by several orders of magnitude with increasing q , it is necessary to multiply the intensity by a factor q^m , $m > 1$, to be more sensitive to high- q scattering. In this work $m = 3$ was used.

The orientation distribution was retrieved using simulated annealing (Press *et al.*, 2007), which is a numerical method for searching global minima in optimization problems. For each iteration, a new randomly modified configuration is tested and the corresponding 'energy' calculated. If the energy is reduced, the new state is accepted. If the energy is increased, the new state is accepted if the current simulated annealing 'temperature' T_{SA} via a Boltzmann-like factor is sufficient to jump the energy barrier. This method reduces the chances of being trapped in a local minimum. The parameter T_{SA} is gradually reduced during the search, hence the name simulated annealing. The procedure can be summarized with the following pseudo-code:

Initialize:

Choose the allowed orientations, e.g. $\Phi = \{-45^\circ, 0^\circ, 45^\circ, 90^\circ\}$.

Choose the voxel size and assign to each voxel (i, j) a randomly chosen orientation $\varphi_{ij} \in \Phi$.

Calculate the initial energy E using equation (4).

Set the initial simulated annealing 'temperature' T_{SA} .

Repeat N times

$E_{\text{set}} \leftarrow E$

Repeat M times

A random subset of voxels is chosen and tentatively assigned new orientations $\varphi_{ij} \in \Phi$.

A new value of E_{new} is calculated using equation (4).

If $\exp(-E_{\text{new}}/T_{\text{SA}}) / \exp(-E/T_{\text{SA}}) > r$, then $E \leftarrow E_{\text{new}}$

and

$\{\varphi\} \leftarrow \{\varphi_{\text{new}}\}$.

If $E < E_{\text{set}}$, then $T_{\text{SA}} \leftarrow T_{\text{SA}}\delta$, (the temperature is reduced)

Here, r denotes a random number between 0 and 1, and $\delta \in (0, 1)$ is a constant governing the rate of temperature decrease. In the work presented here, the reconstructed voxel size was

taken to be equal to the CT step length of $20 \mu\text{m}$, and the values of $N \simeq 10^4$, $M \simeq 10^3$ and $\delta \simeq 0.95$ were found to work well.

After the simulated annealing has converged, the resulting map of preferred orientations necessarily has a discrete set of orientations. Because the real sample has a continuous orientation distribution, an averaging filter was used to smooth out the transitions between the different orientation domains, replacing voxel (i, j) with the average of the elements within the box $i \pm 1, j \pm 1$. This smoothing procedure made the general trends in the distribution clearer, and is justified as long as the preferred orientation varies slowly with position. In this work the set of orientations used was $\Phi = \{-45^\circ, 0^\circ, 45^\circ, 90^\circ\}$, the code was written in MATLAB (The MathWorks Inc., Natick, MA, USA) and each reconstruction took around 4.5 h on a computer with an Intel i5-3570 CPU operating at 3.40 GHz. It should be noted that the speed might be increased significantly by writing the code more efficiently, and possibly by parallelization.

5. Results and discussion

The representative experimental and fitted data shown in Fig. 2 correspond to five paths of the X-ray beam through the sample, showing the differences in intensity decay as a function of q . Note that the theoretical curves consistently follow the experimental data for the different projections, over several decades of intensity and for the full measured q range. The slopes of the five curves in the log-log plot of Fig. 2(b) are -3.8 ± 0.1 . This emphasizes that the measured scattered intensities are in the Porod regime, where the intensity is known to be proportional to the surface area of the talc particles and to follow $I \simeq q^{-4}$ (Porod, 1951). For a given path through the sample, the measured intensity thus clearly depends on both the length of the path and the angle by which the surfaces of the scatterers are aligned with the beam. Still, owing to the limited number of talc orientations allowed in the model, the theoretical curves should not be expected to

Figure 2

Comparison of theoretical and experimental data. (a) The coloured arrows indicate five paths of X-rays through the sample. The grey ellipses represent the talc particle orientation. (b) Comparison of the experimental and theoretical intensities from the five different paths through the sample (indicated by the colour of the curve) on a logarithmic plot. The intensity values are as they were measured and modelled. Noting that these curves are representative of a large number ($>18\,000$) of simultaneously fitted scattering configurations (variables ψ and x), there is generally good agreement between the experimental and theoretical data over several orders of magnitude. q_{max} represents the highest measured scattering vector, 0.39 nm^{-1} .

overlap completely with the experimental data. Other reasons for an imperfect overlap between the curves might include the talc particles not being perfectly spheroidal, the size distribution not being well enough accounted for, the particle orientations not being fully confined to a plane, and noise in the data.

Two maps of retrieved preferred orientations are shown in Fig. 3, taken from different positions along the narrow part of the iPP dogbone sample as illustrated in Fig. 3(f). One can see that neighbouring voxels tend to form domains of constant orientation. The results from raster scanning a cut-out cross section of the sample can be found in the paper by Granlund *et al.* (2014) and are also shown in Fig. 3(e) to facilitate comparison with the orientation distribution retrieved by SAXS-CT. After application of the averaging filter there is excellent correspondence between the orientation distribution reported previously by raster scanning and that obtained by the present SAXS-CT method. In fact, even the small lateral offset of the central node of the spatial orientation distribution (Granlund *et al.*, 2013, 2014) is reproduced. Although the gross features of the preferred orientation patterns are faithfully retrieved, there is some mismatch with the finer details. This may be partly caused by how the retrieval algorithm was implemented. Because the experimental equatorial scattering curves are actually integrated over the two-dimensional scattering pattern, they will not be fully consistent with the theoretical model which gives the purely equatorial scattering intensity. The reason why the entire two-dimensional scattering pattern was not simulated is that this would be computationally heavy, slowing down the algorithm. In addition to the fact that only the equatorial part of the experimental scattering pattern was used, the model only had four different allowed orientations for the talc particles. As mentioned above, the justification for the low number of

allowed orientations in the set Φ is the slow angular variation of the form factor. In reality, the talc particles in the iPP sample have a continuous orientation distribution in the interval $[-90^\circ, 90^\circ]$. Regions in the sample with talc particles oriented around 22.5° would, in the fitted model of the sample, be given an orientation of either 0 or 45° . Both these orientations would give roughly equally good fits to the experimental data and the algorithm would not be able to distinguish them. As a result, close to the boundaries between different domains there will be ambiguity in the retrieved orientation distribution. Applying an averaging filter as described in the *Analysis* section will to some extent remedy this ambiguity and emphasize the general trend.

As discussed in the *Introduction*, the approach presented here is a variant of five-dimensional (three real-space and two reciprocal-space dimensions) SAXS-CT. The method has the practical advantage of being straightforward to implement, both experimentally and in terms of analysis. The actual experiment (15 min exposure time) and the reconstruction (<5 h) are both comparably fast compared with the recently published six-dimensional studies.

The micrometre-sized talc particles are large in the context of SAXS analysis, and thus much of the scattering signal is at inaccessible ultra-small angles. With the analysis based exclusively on the Porod signal, it seems likely that our SAXS-CT method would in fact work even better with significantly smaller particles, which would give additional Guinier scattering features that might increase the convergence rate of the fitting procedure.

We conjecture that extending the model to account for differently shaped particles and non-uniform distributions might be possible by adding additional variables to each reconstructed voxel, such as type of particle and density of particles. The condition of slowly varying orientation with position seems mandatory since it effectively gives regions of uniform orientation over several voxels. Finally, we note that, while other authors point to the necessity of using 'rotationally invariant' signals for the tomographic reconstruction (Schaff *et al.*, 2015), the current work is based on the equatorial scattering which in fact varies maximally during sample rotation. While a detailed comparison of the present work with the six-dimensional approaches remains to be carried out, we conclude that to release the 'full potential of SAXS tomography' there is still considerable refinement to be done.

6. Conclusion

In this study, maps of the spatially varying orientation of flake-shaped talc particles embedded in a polymer matrix have been retrieved nondestructively using SAXS combined with computed tomographic reconstruction methods. We have demonstrated using new algorithms that, given certain prerequisites, the spatial variations of the preferred particle orientation can indeed be retrieved to good fidelity. A condition for the method to work is that the representative dimensions of the scattering particles should be known so that the gross features of the form factor can be estimated. In addition, the particles should be rather monomorphous and

Figure 3
(a) and (b) Retrieved maps of the preferred orientation from two different cross sections of the iPP sample, using four allowed different orientations of the talc particles. (c) and (d) The same orientation maps after applying an averaging filter to better visualize the general trend of the director. The dominant direction of the talc flake director is colour coded and indicated by the colour wheel. (e) The corresponding preferred orientation maps of the talc particles in a physically cut iPP sample slice of 1 mm thickness as found by raster scanning SAXS (Granlund *et al.*, 2014). (f) A sketch of the iPP sample, with a measured cross section indicated.

monodisperse, and exhibit slowly varying orientation gradients. In this work only the equatorial scattering was used, since it was known *a priori* that all particles in the sample are aligned by the flow during injection moulding. Being able to retrieve spatially resolved orientation information in three dimensions is deemed to have important applications in a wide range of fields, and we consider the results reported here as a promising step towards realizing such analysis.

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