Determining the orientation, distributions, and concentration of glass fibers in polymer matrix using X-ray computed tomography and optical coherence tomography images

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Abstract

We report on the characterization of glass fiber-filled polypropylene compounds imaged by X-ray computed tomography and optical coherence tomography. During processing, the fibers can adopt complex patterns of orientation, which influence the mechanical properties of the final product. Gathering information about the flow behavior of polymer melts is important for the design of both extrusion dies and extruded parts. We show the application of X-ray computed tomography and optical coherence tomography to selected polymer extrusion samples. To analyze fiber breakage, fiber orientation, distribution, and the influence of fiber orientation on viscosity, we examined samples with a variety of fiber volume fractions, fiber lengths, and processing conditions.

Keywords: XCT, SD-OCT, FF-OCM, extrusion, glass fiber, elongation die, fiber length, fiber breakage

1 Introduction

Maximum reinforcement of glass fiber-filled polymers is achieved when the fibers are properly oriented. During processing, the fibers are dispersed in a polymer matrix. They influence the rheological properties of the melt and can adopt complex patterns of orientation. To predict and calculate polymer melt flow, we analyzed polymer-fiber interaction and coupling effects of flow kinematics and fiber orientation using X-ray computed tomography (X-CT), full-field optical coherence microscopy (FF-OCM), and spectral domain optical coherence tomography (SD-OCT). The selected geometries were used as preliminary studies for complex FEM simulations.

X-CT has become a very important tool for the three-dimensional characterization of materials and components. Density and atomic number determine the degree to which X-rays penetrate a specimen. A series of attenuation images is taken while the specimen rotates by 360°. Industrial X-CT scanners that are available on the market can achieve resolutions down to a few 100 nm. The result of an X-CT scan is a three-dimensional volumetric data set consisting of voxels. Each voxel has a gray value that depends on material composition. A voxel generated by an industrial X-CT scanner is usually a cube, which means that the resolution is isotropic. The characterization of filled polymers works well for material systems with reasonable differences in density. Fillers such as fibers, particles, platelets, and
polymer mixtures can be characterized by 3D image processing tools with the goal of extracting quantitative information, for example, about size, distribution, orientation, shape, and volume. OCT and FF-OCM are based on the physical phenomenon of low coherence or white light interferometry (WLI). The probe beam is focused onto the object, and photons are back-scattered from structures such as interfaces, impurities, pores, or fibers at different depths within the sample. By comparing the arrival times of the scattered photons with those from a reference beam, a depth scan can be obtained. Depth-resolved cross-sections (2D images) or volumes (3D images) are reconstructed by scanning the probing beam laterally across the sample with the aid of galvanometer mirrors and/or translation stages, and subsequent acquisition of depth scans at adjacent lateral positions. In OCT, the sample is commonly illuminated with light in the near infrared (NIR) using special broadband light sources such as superluminescent diodes (SLD) or supercontinuum lasers. The choice of the appropriate light source is crucial. On the one hand, the best resolution is achieved for high bandwidth sources centered at shorter wavelengths. On the other hand, the penetration depth is limited by the attenuation properties in the wavelength range used. It was shown that for most turbid polymers, especially for highly scattering ones, measurements at 1550 nm center wavelength resulted in more than double the penetration depth of measurements performed at 800 nm [1].

2 Experimental

2.1 Material

A Borealis RA130E polypropylene random copolymer was used as a base polymer, and two types of glass fiber were investigated. The fiber types and dimensions are summarized in Tab. 1. The glassfiber compounds were prepared by means of a ZSK 25 laboratory twin-screw extruder with a length of 42 times the diameter and one vacuum venting unit in combination with a strand pelletizing system. Each compound was available in the form of cylindrical pellets with a diameter of 2.5 mm and a length of about 4 mm. The compounds were processed in a second processing step with a single screw extruder with a length of 33 times the diameter from Thermo Scientific (Karlsruhe, Germany). For sample production, the single screw extrusion process was stopped, the elongation die from Thermo Scientific was cooled down, and samples were taken directly from the converging section [2].

<table>
<thead>
<tr>
<th>type of glass fiber</th>
<th>coding</th>
<th>diameter</th>
<th>max. length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type 1</td>
<td>short fibers</td>
<td>10-19 µm</td>
</tr>
<tr>
<td></td>
<td>Type 2</td>
<td>long fibers</td>
<td>14 µm</td>
</tr>
</tbody>
</table>

Nine different types of compound with different fiber contents and fiber lengths were prepared and investigated in this study:

- S01: 10 w% short fibers,
- S02: 20 w% short fibers,
- S03: 10 w% long fibers,
- S04: 20 w% long fibers,
- S05: 5 w% short and 5 w% long fibers,
- S06: 10 w% short and 10 w% long fibers,
- S07: 24 w% short fibers,
- S08: 4.8 w% short and 19.2 w% long fibers,
- S09: 7.2 w% short and 16.8 w% long fibers.
2.2 X-ray computed tomography (X-CT)

A Phoenix X-ray Nanotom 180NF CT device was used for quantitative sub-µm analysis of fiber length and diameter distributions and for determining the orientation in three spatial dimensions. Data quality must be high for length and diameter calculation and can be slightly lower for orientation. Scans with 5 µm voxel size were used to determine fiber orientation, and with 2 µm voxel size for fiber length and diameter. For the quantitative data analysis, an in-house software tool that allows characterization of each individual fiber [3] was used.

2.3 Full-field optical coherence microscopy (FF-OCM)

The FF-OCM setup was realized in a Mach-Zehner interferometric configuration. A ns-pulsed super continuum source (Leukos, with a spectral bandwidth of 210 nm and a central wavelength of 800 nm) chosen for illumination provided an axial resolution of about 1 µm. The lateral resolution was determined mainly by the incorporated microscope objectives and also reached about 1 µm. A scientific CMOS camera (ANDOR Neo, 16 Bit), achieving a frame rate of 100 fps (at full frame) and equipped with a 5 megapixel detector, was used as a suitable area detector [4]. The FF-OCM images were acquired to a depth of 150 µm.

2.4 Spectral domain optical coherence tomography (SD-OCT)

In our experiments, the commercially available Telesto SD-OCT system from Thorlabs (Lübeck, Germany) operating at 1325 nm was used. The spectral bandwidth of the light source amounts to 150 nm, which translates into an axial resolution of 5 µm in materials with a refractive index around n=1.5. The lateral resolution is about 15 µm. The SD-OCT system can be operated at three different depth-scan rates (5.5 kHz, 28 kHz, and 91 kHz). The choice of such a system operating at a wavelength of 1325 nm is well justified by the presence of highly scattering species in the samples measured in this work. In general, scattering is a non-isotropic process that depends on the orientation of the scattering particles with respect to the direction of the incident light beam. Slight tilting of the sample was necessary in order to detect the majority of fibers. The drawback of tilting the sample is a reduction in penetration depth (i.e., the depth at which glass fibers can still be sufficiently resolved) perpendicular to the surface direction. An angle of approximately 5° was found to be a good compromise between contrast of glass fibers in the OCT images and penetration depth. Because of scattering, the penetration depth was about 230 µm.

2.5 Oscillatory rheometry

The rheological properties were measured using a stress- and strain-controlled rheometer from Anton Paar (Paar Physica UDS 200, Graz, Austria) equipped with an electrically heated thermostating unit. The experiments were carried out in parallel plate mode at 220°C under nitrogen with a plate diameter of 25 mm. Strain sweeps were carried out in the strain range from 0.01 to 10% at a fixed frequency of 1 rad/s. All frequency sweep tests were conducted in the linear viscoelastic region as confirmed by an independent strain sweep test, and the angular frequency range was 0.1-100 rad/s.

3 Results and Discussion

3.1. Detection of fibers

In X-CT the signal is given by the change in absorbance caused by the included structures. In FF-OCM and OCT the signal is proportional to the refractive index changes at interfaces. Therefore, in X-CT the included glass fibers appear clearly as “filled” structures (with a volume/diameter dependent on the chosen threshold). In FF-OCM (and also in OCT) signals from the front and back interfaces of the
structure are recorded, resulting in a “double” line appearance of fiber structures. The fiber diameter can be accurately estimated by auto-correlation [5].

In the (demodulated) FF-OCM images (taken as en-face reflectivity map), fibers and spherical inclusions are clearly recognizable, as shown in Figure 2. In FF-OCM, due to the large difference in refractive index between air and polymer material, very tiny air bubbles and defect structures can also be visualized. The almost spherical defect structures are caused mainly by air inclusions (voids) introduced to the material during cooling.

Figure 1 – FF-OCM image (en-face reflectivity map) of coextruded polymer specimens filled with glass-fiber components of different length and concentration, corresponding to: (a) S01, (b) S03, (c) S05 (measured at a depth of about 150 µm; the image field is 735x550 µm).

3.2 Detection of fiber length distribution

From X-CT data sets, start and end points of each fiber are determined. The distance between these two points is defined as fiber length. To obtain accurate values for start and end points, a series of 3D image processing filters is applied. By calculating the Hessian matrix for each voxel, information about local fiber orientation can be acquired and is used in the next step to determine the center line of each fiber. Combining local orientation with the fact that the gray value peaks at the center of the fiber enables extraction of a single line of voxels for the center of the fiber. In the ideal case, all fibers would be separated after this step. In reality, there are some cases where fibers are very close or touch in some way. In some cases “connections” persist between center lines of different fibers. These are eliminated by an additional step in the image processing chain. After identification of critical coordinates, the branches connected to a critical point are analyzed according to the angles between them. The property of straightness of glass fibers within the matrix is taken as a constraint for connected branches. The final result contains separated fibers that are characterized by start and end points and information about diameter, surface, and volume.

The two processing steps (proc. step 01: compounding, proc. step 02: single screw extrusion) lead to a reduction of approximately 50% in maximum fiber length compared to the manufacturer's specifications [2]. Changes in melt pump speed (MPS) and melt temperature (MT) in the single screw extrusion step do not have a substantial influence on fiber length distribution. The small impact of melt pump speed can be attributed to the fact that pump volume rather than pump speed is the critical parameter for fiber breakage. The cause of the minor influence of melt temperature on fiber breakage is not clear. An increase in processing temperature should lead to a reduction in melt viscosity and better flow conditions, and should therefore normally lead to reduced fiber breakage.
Table 2 - Fiber properties of PP-GF compounds after the first processing step (compounding)

<table>
<thead>
<tr>
<th>Sample</th>
<th>S01</th>
<th>S03</th>
<th>S05</th>
</tr>
</thead>
<tbody>
<tr>
<td>weighted av. fiber length µm</td>
<td>321</td>
<td>729</td>
<td>551</td>
</tr>
<tr>
<td>av. fiber length µm</td>
<td>198</td>
<td>565</td>
<td>317</td>
</tr>
<tr>
<td>max. fiber length µm</td>
<td>1037</td>
<td>3323</td>
<td>2234</td>
</tr>
<tr>
<td>total number of fibers in the measurement area (2.5 x 2.2 x 3.6 mm³)</td>
<td>-</td>
<td>5990</td>
<td>4212</td>
</tr>
</tbody>
</table>

Table 3 - Fiber properties of 3 different PP-GF compounds after the second processing step

### 2 rpm melt pump speed

<table>
<thead>
<tr>
<th>Sample</th>
<th>S01</th>
<th>S03</th>
<th>S05</th>
<th>S01</th>
<th>S03</th>
<th>S05</th>
</tr>
</thead>
<tbody>
<tr>
<td>weighted av. fiber length µm</td>
<td>272</td>
<td>432</td>
<td>367</td>
<td>273</td>
<td>459</td>
<td>353</td>
</tr>
<tr>
<td>av. fiber length µm</td>
<td>188</td>
<td>319</td>
<td>252</td>
<td>184</td>
<td>326</td>
<td>233</td>
</tr>
<tr>
<td>max. fiber length µm</td>
<td>945</td>
<td>1163</td>
<td>1265</td>
<td>1005</td>
<td>1608</td>
<td>1012</td>
</tr>
<tr>
<td>total number of fibers in the measured area</td>
<td>-</td>
<td>2532</td>
<td>2666</td>
<td>2241</td>
<td>2892</td>
<td>3095</td>
</tr>
</tbody>
</table>

### 25 rpm melt pump speed

<table>
<thead>
<tr>
<th>Sample</th>
<th>S01</th>
<th>S03</th>
<th>S05</th>
<th>S01</th>
<th>S03</th>
<th>S05</th>
</tr>
</thead>
<tbody>
<tr>
<td>weighted av. fiber length µm</td>
<td>267</td>
<td>420</td>
<td>377</td>
<td>270</td>
<td>442</td>
<td>350</td>
</tr>
<tr>
<td>av. fiber length µm</td>
<td>187</td>
<td>299</td>
<td>256</td>
<td>185</td>
<td>316</td>
<td>228</td>
</tr>
<tr>
<td>max. fiber length µm</td>
<td>855</td>
<td>1279</td>
<td>1174</td>
<td>951</td>
<td>1256</td>
<td>969</td>
</tr>
<tr>
<td>total number of fibers in the measured area</td>
<td>-</td>
<td>2554</td>
<td>3095</td>
<td>2431</td>
<td>2541</td>
<td>2232</td>
</tr>
</tbody>
</table>

Figure 2 – left: Maximum fiber length after different processing steps (PT 210°C); right: Fiber length distribution after different processing steps (PT 210°C).

### 3.3 Detection of the fiber orientation

The fiber orientation in FF-OCM was estimated using monogenic signal approaches in combination with scale space methods [5]; in particular, we employed the orientation toolbox EPFL, which delivers the local orientation of structures (shown in Figure 4), for orientation estimation and analysis [6]. For the analysis of the fibers imaged by FF-OCM orientation estimation is performed. The fibers are depicted with an overlaid orientation map encoding orientation in colours.
Figure 3 – Orientation map of fiber-reinforced extruded polymer structures (corresponding to Fig. 2 a) imaged by FF-OCM.

To detect fiber orientation using X-CT data, the elements of the orientation tensor can be computed using the start and end points of each fiber. A method of describing fiber orientation was originally developed by Advani and Tucker [7]. Each fiber \( i \) can be characterized by two angles \( \theta_i \) and \( \phi_i \) or the unity vector \( p \) parallel to the fiber:

\[
p = \begin{pmatrix} \sin \theta \cdot \cos \phi \\ \sin \theta \cdot \sin \phi \\ \cos \theta \end{pmatrix}.
\]

Furthermore, a group of \( n \) fibers can be described by means of an orientation tensor \( a \) as follows:

\[
a_{ij} = \frac{1}{n} \left( \sum_{k=1}^{n} p_{i,k} p_{j,k} \right) = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} = \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix},
\]

If start and end points of each fiber are known, the angles \( \theta_i \) and \( \phi_i \) can be calculated by the following relations:

\[
\theta_i = \cos^{-1} \left( \frac{dd_z}{\sqrt{dd_x^2 + dd_y^2 + dd_z^2}} \right) \quad \text{and} \quad \phi_i = \tan^{-1} \left( \frac{dd_y}{dd_x} \right),
\]

where \( dd_x, dd_y, \) and \( dd_z \) are the distances between the fiber start and end points. The direction along the thickness of the disc-shaped samples is represented by the \( y \)-coordinate.

The orientation tensor was calculated at different sample positions, shown in Figure 4. At Position 1, more long than short fibers are oriented in the flow direction. At Position 3, where pressure transducers were located, all fibers - independent of fiber length - are oriented mainly in the flow direction. Increasing processing temperatures and melt pump speeds did not influence fiber orientation at Position 3, but increased the number of fibers (S01, S03) oriented in the flow direction at Position 1. A mixture of long and short fibers shows no dependency on processing temperature and screw speed and exhibits different flow behaviour.

Figure 4: left: Fiber orientation in three spatial directions at various positions (Pos.) (PT 210°C, MPS 25 rpm) [2]; right: Definition of the scan-positions in the sample.
3.4 Influence of fiber orientation on viscosity

Dynamic measurements of the PP and the PP-GF compounds in the specified range were performed. Storage and loss modulus were obtained, and the steady shear viscosity was determined from the complex viscosity using the Cox-Merz rule. In order to investigate initial wall effects, we varied the duration of different levels of pre-shearing to achieve a proper orientation of the fibers parallel to the plates. As shown in Figure 8, shear viscosity decreases with increasing levels of pre-shearing. In addition to the shear rate, the duration of pre-shearing also plays an important role, although its effect is less pronounced. An initial loading of 0.1 s\(^{-1}\) for 60 min turned out to be sufficient to reduce orientation effects to a level at which they can be neglected. Further pre-shearing damages samples, as indicated by a strong decrease in viscosity and results which cannot be reproduced.

To gain insights into the fiber orientation process, we employed X-CT measurements. The diagonal elements of the orientation tensors of three samples are illustrated in Figure 6. If pre-shearing is applied, more fibers adopt circumferential orientation, as indicated by decreasing \(a_{yy}\) values. In this direction, the sample with 10 min pre-shearing at 0.01 s\(^{-1}\) shows twice as many fibers with this orientation than the sample with 60 min pre-shearing at 0.1 s\(^{-1}\).

Figure 5 – left: Fiber orientation in three spatial directions at various temperatures (Pos. 1, MPS 2 rpm); right: Fiber orientation in three spatial directions at various melt pump speeds (Pos 1, PT 210°C).

Figure 6 – left: Comparison of viscosity curves at different degrees of pre-shearing; right: Comparison of fiber orientation with and without pre-shearing.
4 Conclusion
Due to large differences in refractive index between air and polymer material, very tiny air bubbles and defect structures can also be visualized. These defects are introduced to the material during the uncontrolled cooling process. In FF-OCM (and also in OCT) the signals from the front and back interfaces of a structure are recorded, resulting in a “double” line appearance of fiber structures. The fiber diameter can be estimated by auto-correlation. In X-CT, the signal is given by the change in absorbance caused by the included structures, which leads to the clearest pictures suitable for further data analysis. The two processing steps (compounding, single screw extrusion) lead to a reduction of approximately 50% in maximum fiber length compared to the manufacturer’s specifications. Changes in melt pump speed and melt temperature in the single screw extrusion step result in an increased number of fibers (S01, S03) orientated in the flow direction at Position 1. A mixture of long and short fibers shows no dependency on processing temperature and screw speed and exhibits different flow behaviour. We used parallel plate rheometry to study the shear viscosity of glass-fiber-reinforced polypropylene melts at shear rates between 0.1 and 100 s$^{-1}$. In order to investigate initial wall effects, the duration of different levels of pre-shearing was varied to achieve optimal orientation of the fibers parallel to the plates. Dynamic shear measurements highlight the importance of fiber orientation, as shown by the strong relationship between strain and viscosity. We have demonstrated that shear viscosity decreases with increasing levels of pre-shearing. We found that an initial loading of 0.1 s$^{-1}$ for 60 min sufficed to minimize the effects of initial fiber orientations. Further increase in the degree of pre-shearing damaged the samples.

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References