MAN-MADE CELLULOSE FIBER REINFORCED POLYPROPYLENE – CHARACTERIZATION OF FRACTURE TOUGHNESS AND CRACK PATH SIMULATION

Jan-Christoph Zarges\textsuperscript{a},* Maik Feldmann\textsuperscript{a}, Hans-Peter Heima, Paul Judt\textsuperscript{b}, Andreas Ricoeurb

\textsuperscript{a} Institute of Material Engineering, Polymer Engineering, University of Kassel, Germany
\textsuperscript{b} Institute of Mechanics, Engineering Mechanics / Continuum Mechanics, University of Kassel, Germany

Abstract
This investigation focuses on the fracture toughness of injection molded man-made cellulose fibers reinforced composites with PP as their matrix and 30wt% fiber content. The influence of the fiber orientation and the addition of a coupling agent on the fracture toughness was determined using SEM and a micro computer tomography. It was verified that a reinforcement with man-made cellulose fibers leads to significantly higher values of the critical $J_c$-integral in comparison to glass fiber reinforcement. A notch direction parallel to the flow direction shows higher values which is a result of less local strains around the crack path, as well as of a higher amount of fiber pull-outs in the fractured surface. The coupling agent MAPP creates stronger fiber-matrix adhesion, which results in a decreasing of the $J_c$-values due to less fiber pull-outs. The determined values of the critical $J_c$-integral and the crack deflection due to the materials anisotropy were used to apply a crack deflection criterion. The resulting calculated crack paths achieved a good approximation to the experiments.

Introduction
During the last decade the use of short, natural fiber reinforced composites with PP as the matrix material in serial production e.g. in the field of automotive parts has risen. This is based on an increasing demand for renewable resources and the possibility to combine the lightweight potential of the lower density fibers with the good mechanical properties. Together with the rising demand for natural fiber composites in industry, the number of publications increased as well. A large number of these investigations used the compression molding to prepare the specimen [1-3], but injection molding is of greater importance for industrial applications, especially for the production of serial parts.

In addition to plant fibers, man-made cellulose fibers, have been used as reinforcement in previous studies, and created a significant increase in the mechanical properties [5-8]. Especially the values of the notched impact strength are about four times higher in comparison to glass fiber reinforced composites using the same fiber weight percentage [4,9-16]. In comparison to conventional glass fibers, cellullosic fibers also have a significant potential for use in lightweight applications, due to their lower density [11-13]. Furthermore the fibers show a higher elongation at break that results in a ductile fracture behavior of the composites, which results in a less spontaneous fracture behavior [4,10].

In this investigation, the injection-molded CT specimens were examined in tensile tests regarding the crack resistance or fracture toughness $J_c$. Composites with 30 wt% of regenerated cellulose fibers and a coupling agent (MAPP) that were compounded on a twin-screw extruder were investigated. Composites with 30 wt% glass fibers were investigated for reference purposes. The CT specimens were manufactured with different flow directions and, in turn, different preferred fiber orientations. The fiber-matrix adhesion and the fiber orientation of the specimen were investigated using SEM microscopy and the micro computer tomography.

Materials
The polymer PP (575P), provided by the company Sabic, was used as the matrix material. Chopped, regenerated cellulose fibers (RCF), also called viscose fibers, with a diameter of approx. 12 µm and an initial length of 2 mm were used for reinforcement. The fiber rovings were coated with a PPL sizing to increase the pourability for use in a gravimetric feeding system. In addition to that, glass fibers (GF) (Lanxess CS 7952) with a sizing suitable for polypropylene, a diameter of 14 µm and an initial length of 4.5 mm were investigated for reference purposes (Table 1). Composites with maleic anhydride grafted PP (MAPP) were also investigated in order to illustrate the influence of a coupling agent.

Table 1. Properties of the matrix material and the reinforcement fibers.

<table>
<thead>
<tr>
<th></th>
<th>RCF - Cordenka CR-Type</th>
<th>GF - Lanxess CS 7952</th>
<th>PP - Sabic 575P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm$^3$]</td>
<td>1.5</td>
<td>2.6</td>
<td>0.905</td>
</tr>
<tr>
<td>Diameter [µm]</td>
<td>12</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Tensile Strength [MPa]</td>
<td>740</td>
<td>2600</td>
<td>34 (Yield)</td>
</tr>
<tr>
<td>Tensile Modulus [MPa]</td>
<td>19</td>
<td>73</td>
<td>1470</td>
</tr>
<tr>
<td>Elongation at Break [%]</td>
<td>14</td>
<td>3.5</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>
Compounding
The composites were compounded using a twin screw extruder ZSE 18 HPE (Leistritz) with a screw diameter of 18 mm and a process length of 40 D. Before the materials were compounded, the cellulosic fibers were dried in an air convection oven until their moisture content was less than 1%.

Injection Molding
Prior to the injection molding process, the compounds containing cellulosic fibers were dried using an air dryer until a moisture content of max. 0.1% was obtained.

An injection molding machine (Arburg Type 470) with a screw diameter of 30 mm was used to manufacture the plates for the compact tension (CT) specimen (see Figure 1). A plate with a dimension of 72 x 72 x 10 mm makes it possible to mill out specimens with 0° and 90° melt flow direction in relation to the notch. This enables the investigation of the influence of the preferred fiber orientation on the fracture toughness.

![Figure 1. CT specimen with positions of the μCT and SEM investigations.](image)

Specimen Preparation
The CT specimens used to determine the crack resistance behavior were manufactured according to ASTM D5045. For this purpose holes for clamps were drilled into the injection molded plates and the samples were milled out using a computer-controlled milling machine subsequently. To create a notch into the specimen, a circular saw blade with an angle of 30° at the tip was used. A pre-crack with a length of 1.5 mm was furthermore initiated into the notch base using a razor blade with a thickness of 0.09 mm. According to ASTM D5045, the crack length (a) was chosen so that the ratio was a/w = 0.45.

Characterization
All composites were conditioned and characterized in a standardized climate (23°C, 50% relative humidity).

Fracture Toughness (J_{fc}-integral)
The crack resistance behavior was measured using the J-integral. The values of J_{fc} depend on the force-displacement curve, which is integrated until the displacement belonging to the maximum load occurs. J_{fc} should be used to characterize the crack resistance of thermoplastics materials with their elastic-plastic behavior [17].

The fracture toughness of the composites was evaluated by means of the compact tension (CT) method using a testing machine (Zwick Roell UPM 1446) at a cross-head speed of 10 mm/min according to ASTM D5045. J_{fc}-values are calculated using the approximated method of Rice, Paris and Merkle and the simplification by Begley and Landes shown in the following equation (1). The geometry factor for CT specimen f\left(\frac{a}{w}\right) specified in ASTM D5045 is shown in equation (2).

\[ J_{fc} = \frac{f\left(\frac{a}{w}\right) \cdot A_{c}}{B\cdot(W-a)} \]

\[ f\left(\frac{a}{w}\right) = \frac{(-0.866 + 4.64 \left(\frac{a}{w}\right) - 13.32 \left(\frac{a}{w}\right)^2 + 14.72 \left(\frac{a}{w}\right)^3 - 5.6 \left(\frac{a}{w}\right)^4)}{(-1+\frac{2\pi}{\sqrt{3}})^2} \]  

If the conditions in the following equation (3) are met, the J_{fc}-values according to equation (1) are regarded as real material properties by definition in ASTM D5045 and do not depend on the geometry of the specimen. All specimen regarded in this investigation met this requirement.

\[ B\cdot a\cdot(w-a) \geq \varepsilon \cdot \frac{J_{fc}}{\sigma_{y}} \text{ with } \varepsilon = 224 \cdot J_{fc}^{0.94} \]

Scanning Electron Microscopy (SEM)
To investigate the morphology of different CT specimen a scanning electron microscope (SEM) MV2300 by CamScan Electron Optics was used. Prior to the observation of the area directly behind the pre crack, the fractured surfaces of tested CT-samples were sputter coated with gold (see Figure 1). Images with a low level of magnification were taken to obtain an overview of the fiber distribution. In order to examine the interfacial adhesion between the fiber and the matrix, images with a high level of magnification were taken.

Micro Computer Tomography
In order to investigate the resulting fiber orientation throughout the cross section of the CT specimen, the micro computer tomograph Xradia 520 Versa provided by Zeiss was used. Subsequently the graphical analysis of the results was performed using the software Avizo 9.0.1 provided by FEI. The use of an objective with a 4x magnification resulted in a voxel size of 5.05 μm. With an exposure time of 2 seconds the duration of the tomography was 1.5 hours. Due to the size of the CT specimen, a small sample measuring 10 x 10 mm was cut out of an area next to the notch in the middle of a tested specimen (see also Figure 1).
Results and Discussion

The calculated values of the fracture toughness \( J_{ik} \) of
the different composites and flow directions are shown in
Figure 2a. The composites reinforced with man-made
cellulose fibers show significantly higher \( J_{ik} \) values than
the composites with glass fiber reinforcement. This result
can be explained by the force-path diagrams (in Figure 2
(b) and (c)) where the cellulose fiber reinforced specimens
reach the maximum force at much higher values of
elongation. In regards to equation (2), this fact results in
an increase of the work \( A_{fc} \) as an integral of load and
elongation, and leads to higher \( J_{ik} \) values.

The addition of the coupling agent MAPP leads to a
decrease of \( J_{ik} \), which is founded in a decrease of the
elongation when a higher maximum force is reached. The
reason for this result can be seen in the SEM pictures in
Figure 4, where the use of MAPP leads to a significantly
reduced quantity of fiber pull-outs due to improved fiber-
matrix adhesion. This reduced amount of pull-outs leads
to less frictional energy during the failure of the specimen,
and results in a lower value of \( J_{ik} \). Figure 2 furthermore
shows the reduced, resulting values of \( J_{ik} \) due to the
rectangular flow direction whereas the flow direction
parallel to the direction of the notch leads to higher
values. This phenomenon can be explained with the
images obtained from the SEM and the micro computer
tomography analyses.

![Figure 2](image)

Figure 2. Values of \( J_{ik} \) of different composites and flow
directions (a) and load-crosshead travel curve of the
reinforced composites with parallel (b) and perpendicular
(c) flow direction.

Those images on the left side of Figure 3 show the
results of different slices of a specimen made of PP
30wt% RCF with a parallel flow direction. The fibers in
the edge region (a) are oriented parallel to the flow
direction (arrow), and, thus also, in the direction of the
notch. In contrast to that preferred fiber orientation in the
core shows a direction nearly perpendicular to the edge
region and the flow direction (b). Thus, the fibers in a
wide area around the core of the CT specimen show an
orientation perpendicular to the notch and the fractured
surface. The \( \mu \)CT scans of specimen of PP 30wt% RCF
with a perpendicular flow direction on the right side of
Figure 3 show the expected contrary results regarding the
fiber orientation. The fibers in the edge region (c) are
mainly oriented in the flow direction (arrow), and,
therefore, are perpendicular to the notch. Again, the fibers
in the core of the specimen show an orientation parallel to
the notch and the resulting fractured surface in a wide
range (d). The orientation of the glass fibers in the
specimens of PP 30wt% GF is similar to the orientation of
the CRF, with the difference of the straight form of the
GF in contrast to the curved shape of the CRF. These
resulting orientations can be explained by the flow
processes in the mold during injection molding.

![Figure 3](image)

Figure 3. Fiber orientation in slices of PP 30wt% RCF with a parallel flow direction (left) and a perpendicular flow direction (right). Slice (a) and (c) are near the edge, slice (b) and (d) near the core of the specimen.

The determined fiber orientation resulting from the
two flow directions also shows an influence on the
fractured surface of the CT specimen shown in the SEM
images (Figure 4). The majority of the fibers in specimens
with a parallel flow direction stick out of the fractured
surface, caused by the orientation perpendicular to the
notch (a). In contrast to that and according to the results of
the \( \mu \)CT, the specimens with a perpendicular flow
direction show fibers situated parallel to the fractured
surface which are peeled out of the matrix (b).
orientations of the composites with the coupling agent MAPP show similar fiber orientations, but the amount of pulled-out fibers is significantly lower and the amount of ruptured fibers is higher due to the resulting higher fiber-matrix adhesion.

The fractured surfaces of the GF reinforced specimen are significantly deviant to those reinforced with CRF. Figure 4 (c) and (d) show that there are nearly no measurable pull-outs of the GF. This can be explained by the shorter fiber length of the GF and the lower elongation at break that lead to a higher amount of broken fibers. Compared to the CRF reinforced composites the different flow directions furthermore do not result significant deviations of the fractured surface.

![Figure 4](image.png)

**Figure 4.** SEM pictures of the fractured surface of PP 30wt% CRF at parallel (a) and perpendicular flow direction (b) and 30wt% GF at parallel (c) and perpendicular (d) flow direction.

In Figure 5, the crack paths of the different compounds and flow directions are shown. The compound with cellulosic fiber reinforcement displays a straight crack path and a small plastic zone at a perpendicular flow direction (a). In contrast to that, the crack path in the specimen with a parallel flow direction is deflected with an angle of approx. 60° from the notch base to the outer edge, and displays a significantly larger plastic zone (b). Independent of the flow direction, the glass fiber reinforced composites show straight crack paths nearly parallel to the direction of the notch with nearly no plastic deformation around the crack path (c and f).

The addition of the coupling agent MAPP into the composite with 30wt% man-made cellulose fibers leads to a reduction of the plastic zone, which is indicated by a smaller, whitened area around the crack path (c and d). This can be explained by the higher level of fiber-matrix adhesion that is created by the MAPP, which, in turn, leads to more fiber breakage and less fiber pull-outs. The form of the crack path itself is not influenced by the MAPP, and is similar to that of composites without coupling agent. These results match closely to the results of the fracture toughness $J_{lc}$ in Figure 2.

![Figure 5](image.png)

**Figure 5.** Deviating crack paths of the different composites and flow directions.

The values of $J_{lc}$ determined in the experiments were applied to simulate the deviating crack paths at the different flow directions using a characterized crack deflection criterion which is explained in the following.

During the experiment the CT-specimens are exposed to a mode-I crack opening and thus a straight crack path is expected. The crack deflection, as observed in the experiments, is explained by anisotropy of the crack resistance attributed to the orientation of the fibers due to the flow direction. This anisotropy is characterized by the ratio of the crack resistance $\chi = \frac{J_{lc}^{para}}{J_{lc}^{perp}}$, obtained from specimens with the notch parallel and perpendicular to the flow direction. A crack deflection criterion is introduced, assuming the crack to grow into the direction where the ratio of the crack tip loading ($J$-integral) and the crack resistance $J_{lc}$ is a maximum [18]. The ratio $J_{lc}$ is a function of the angle $\varphi$ of a polar crack tip coordinate system and provides the crack deflection angle $\alpha$ depending on $\chi$ as depicted in Figure 6. For a crack initiating parallel to the flow direction, a bifurcation is observed at $\chi \geq 1.22$ providing two possible crack deflection angles with positive or negative sign, thus $\pm \alpha$.
From Figure 6 it becomes clear, that a crack with mode-I loading can only deflect if the notch is parallel to the flow direction and the ratio $\chi \geq 1.22$. This result is consistent with the experiment, as the ratio related to PP 30wt\% CRF is $\chi_{\text{CRF}} = 1.43$ and the one related to to PP 30wt\% GF is $\chi_{\text{GF}} = 1.13$.

Crack paths in CT-specimens are calculated applying the above introduced crack deflection criterion. Figure 7 shows the crack paths from the simulation (red line) and the tested specimens (blue line). For PP 30wt\% CRF, the straight crack paths in specimens with the notch perpendicular to the flow direction as well as the deflection of the crack paths in specimens with the notch parallel to the flow direction are reproduced. Furthermore, the simulated crack paths in glass fiber reinforced specimens are independent of the flow direction remaining straight, thus matching the real crack paths very well.

Figure 7. Crack paths from experiment and simulation in CT-specimens of PP 30wt\% CRF with perpendicular (a) and parallel (b) flow direction and PP 30wt\% GF with perpendicular (c) and parallel (d) flow direction.

Conclusions

The investigation evaluated the influence of a coupling agent, as well as the orientation on the fracture toughness $J_{ik}$ of injection molded specimen made of man-made cellulose fiber reinforced polypropylene.

A comparison of the employed reinforcement fibers verified that a reinforcement of PP with man-made cellulose fibers leads to significantly higher $J_{ik}$-values than glass fibers.

The flow direction and the resulting orientation of the fibers significantly influence $J_{ik}$, especially those of cellulose fiber reinforced composites. Here, the majority of the fibers displayed an orientation perpendicular to the flow direction. That, in turn, means that specimen with a notch parallel to the flow direction achieved higher values due to fiber pull-outs in the fractured surface. Furthermore, the specimens with a parallel flow direction displayed a deflected crack path with an angle of approx. $60^\circ$ to the notch.

The occurring local strains measured with an optical measurement system and the plastic zone around the crack tip and crack path also showed a significant dependence the resulting fiber orientation of PP 30wt\% RCF. The specimen with a parallel flow direction reached a 20\% higher maximum load after which the crack propagated.

The coupling agent MAPP leads to an increase in the fiber-matrix adhesion, a higher amount of fiber breakage, and less fiber pull-outs. This fiber-matrix interaction leads to a reduction of the plastic zone around the crack path, but also lower $J_{ik}$-values.

The calculated crack paths are in good agreement with the experiment, if the measured values of the crack resistance $J_{ik}$ are considered in the model. An improvement of the prediction is expected, additionally taking into account the anisotropy of elastic constants.

References


