DUCTILITY OF POLYLACTIDE COMPOSITES REINFORCED WITH POLY(BUTYLENE SUCCINATE) NANOFIBERS

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PLA market in packaging, textile, agriculture, transportation, bio-medical, electronics and others.
How to increase the resistance to brittle failure?

- increasing the molecular mass;
- cross-linking;
- creating a branched structure;
- reducing the polydispersity;
- rapid cooling.

- rubber or void toughening;
- mechanical rejuvenation.
The basic strategy underlying the above-mentioned approaches is that the shear yield stress is lower than the craze stress. This leads to an increase in ductility and toughness and a decrease in strength and stiffness.
SEM micrographs showing crystalline filaments of PLA at PBS nanofibrils for (a) PLA/PBS (90/10), (b) PLA/PBS (80/20), and (c) PLA/PBS (60/40) composite.

Typical strain–stress curves of (a) pure PLA, (b) PLA/PBS (90/10), (c) PLA/PBS (80/20), and (d) PLA/PBS (60/40).
Materials and methods of preparation

- D-Lactide and L-lactide contents were 18 and 82 mol%, respectively. The presence of 18% DLA prevented PLA from crystallization during thermal treatment.

- Melt blends were prepared using a Brabender batch mixer operating at 170 C for 10 min at 100 rpm. Further blending was followed by extrusion of tapes using single-screw extruder equipped with the 12 mm wide, 0.8 mm thick and 100 mm long slit die.

- For examination of the properties of initial PLA and PLA/PBS composite 0.75 mm thick films of the materials were compression molded at 170 C for 3 min, and quenched between thick metal blocks kept at room temperature.
Stress-strain curves for PLA, PLA blended with PBS, PLA extruded and PLA/PBS extruded

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young modulus, GPa</th>
<th>Yield stress, MPa</th>
<th>Stress at break, MPa</th>
<th>Strain at break,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt-mixed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA</td>
<td>2.04</td>
<td>Brittle fracture</td>
<td>43.0</td>
<td>7.0</td>
</tr>
<tr>
<td>PLA/PBS</td>
<td>1.83</td>
<td>40.0</td>
<td>38.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Extruded</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA</td>
<td>2.11</td>
<td>38.0</td>
<td>36.0</td>
<td>17.2</td>
</tr>
<tr>
<td>PLA/PBS</td>
<td>2.19</td>
<td>36.6</td>
<td>33.1</td>
<td>70.0</td>
</tr>
</tbody>
</table>
The propagation goes from left to right. The principal stress acts in the up-down direction.
In situ observation of brittle crack of PLA originated by the crazing
In situ observation of brittle crack of PLA/PBS blend originated by the crazing
The slit die extrusion process at low temperature in a single screw extruder

Severe elongation deformation

170 °C  150 °C  135 °C  130 °C
Morphology of PLA/PBS extruded composite exposed by selective etching
SEM image of extruded tapes of PLA, PLA/PBS

Direction of extrusion is horizontal. Shear bands are tilted at ±30°.
In situ SEM micrograph of the structure evolution of extruded PLA subjected to tensile test

$e=0.0$

$e=0.08$

$e=0.16$
Example how the shear bands deflect, blunt, terminate or initiate crazes in PLA extrudate
In-situ SEM micrographs of the structure evolution of extruded PLA/PBS composite subjected to tensile test
In-situ SEM micrographs of the structure evolution of extruded PLA/PBS composite subjected to tensile test
Conclusions

• The slit die extrusion process at low temperature in a single screw extruder is an effective method of production “green nanocomposites”.

• Extrusion of PLA and composite of PLA with 3 wt.% PBS causes that the extruded material contains a large number of frozen-in dormant shear bands. These shear bands are inactive and uniformly distributed over the material volume. However, the main deformation mechanism remains crazing while dormant shear bands deflect, blunt, terminate or initiate crazes.

• Crazes in PLA/PBS extrudate become thicker with increasing strain reaching even few tens of μm. The craze surfaces are additionally span with nanofibers of PBS which are preferentially oriented perpendicular to craze planes in PLA/PBS extrudate. So, when the strength of PLA nanofibrils spanning a craze is overpowered the role of bridging the craze gap is overtaken by PBS nanofibrils and prevents for fracture. In pure PLA crazes do not thicken, they just fracture.

• Fragments of dormant shear bands locked between crazes may become activated even at strain just beyond yielding as it can be judged from curved undulated crazes.

• The formation of such structural features as pre-existing shear bands and nanosized PBS fibers provided an opportunity to substantially increase ductility and retain high strength and stiffness of PLA/PBS composite. All these were accomplished at low temperature (130 °C), medium shear rate (about 300 s⁻¹) but high elongational deformation (about 30 times) during extrusion.
• Thank you very much!
• Dziękuję bardzo!