Biochar as processing agent in PBAT

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Biochar

Higher value applications enhances the economic viability of thermochemical conversion

- Product of thermochemical conversion of organic waste
- Agent of circular economy and carbon sequestration

Why is this important?

Experiment design and samples

Results

Biochar feedstocks

https://www.rit.edu/sustainabilityinstitute/blog/what-biochar-and-how-it-made

Conclusions

Biochar Markets

(Draper K, 2015)
Biochar in plastics

- Feedstock affects effect of biochar in the composite
- Additive proportions effects are an unexplored area

Zhang, Q. et al. (2020)
Hernandez-Charpak, Y et al. (2022)
What did we do?

Poly(butylene adipate-co-terephthalate) (PBAT)

Calcium Carbonate (CaCO₃)
- Anti-blocking
- Anti-slipping
- Widely used in industry
- Extractive
- Present in patents for agricultural films

Wood-based biochar (BC)
- Affects surface
- Affects degradability
- Wood-based BC has a good adhesion to PBAT
- Sustainable and renewable source
Masterbatch process

PBAT 1:1

Brabender

• Mixed for 5 min.
• 170 °C
• 60 rpm

PBAT 99:1

Carver

• Pressed for 3 min at 180 °C
• Load 3 tons
• Cooled with water

Filmblown process

Lab-tech three layer blown film line 250mm wide with 12.5mm extruders
Characterizations

Thermal properties
- Fourier transform infrared spectroscopy (FTIR-ATR)
- Differential scanning calorimetry (DSC)
- Thermogravimetric analysis (TGA)

Chemical properties
- Tensile properties (ASTM D882-18)
- Blocking force (ASTM D903-98 and ASTM D3354-21)
- Coefficient of friction (ASTM D1894)

Rheological properties
- Melt flow index (MFI) with ASTM D1238-A
- Viscosity measurements at 180ºC (HR-2)

Morphology
- Scanning electron microscopy (SEM)

Manufacture
(Lyondellbasel, 2009)
Mechanical properties

Lower modulus and higher strain at break (usually is the inverse when filling a polymeric matrix)
Blocking and slipping

ASTM D3354, is on the whole film and reports maximum force.

ASTM D903, is on a set width and reports an average force.
Morphology

PBAT-CaCO₃

200 x

PBAT-BC

200 x

PBAT

1000 x
Rheological properties

- Both increased MFI without affecting viscosity
- Additional secondary forces leading to higher blocking and friction
Additional formulations

- Additional loading did not show increased elongation but eliminated blocking
Additional experimentation

- MFI shows a different flow from the finer BC. Initial particle size affects the interaction.

- Viscosity did not increase with higher loading
Conclusions

Wood-based biochar (BC) and CaCO$_3$ in additive proportion within PBAT

- BC increased the strain at break, less than CaCO$_3$.
- BC barely affected processing properties, CaCO$_3$ had a significant impact on them.
- Neither BC nor CaCO$_3$ affected viscosity but increased the MFI of the PBAT.

BC, when added as an additive in PBAT, increased flow and elongation without affecting processing. Future research should be made to assess its potential for injection molding or other shape filling extrusions applications.

Next steps

- Explore the effects of BC on traditional, high-volume polymers (LDPE).
- Additional experimentation to pinpoint the mechanisms that lead additional interactions in the CaCO$_3$. 
Thank you!

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(Bartoli, 2020)
No differences on the blends despite the strong difference of the additives
Thermal properties

Second heat BC sample is more crystalline, and crystallization occurs at a lower temperature. But when the loading increases, little difference is seen.

<table>
<thead>
<tr>
<th></th>
<th>DSC-1st Heat</th>
<th>DSC-2nd Heat</th>
<th>DSC-Cooling</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi_c$ (%)</td>
<td>$\chi_c$ (%)</td>
<td>$T_c$ (°C)</td>
<td>$T_{offset}$ (°C)</td>
</tr>
<tr>
<td>PBAT</td>
<td>11.3 ± 0.7\textsuperscript{a}</td>
<td>8.8 ± 0.2\textsuperscript{b}</td>
<td>78.6 ± 1.4\textsuperscript{b}</td>
<td>367.2 ± 1.2\textsuperscript{a}</td>
</tr>
<tr>
<td>PBAT BC 0.5%</td>
<td>12.2 ± 0.5\textsuperscript{a}</td>
<td>9.5 ± 0.1\textsuperscript{a}</td>
<td>76.3 ± 0.2\textsuperscript{a}</td>
<td>368.0 ± 2.0\textsuperscript{a}</td>
</tr>
<tr>
<td>PBAT CaCO\textsubscript{3}</td>
<td>11.7 ± 0.3\textsuperscript{a}</td>
<td>8.7 ± 0.1\textsuperscript{b}</td>
<td>79.3 ± 1.4\textsuperscript{b}</td>
<td>369.1 ± 2.7\textsuperscript{a}</td>
</tr>
<tr>
<td>PBAT Gr-BC 0.5%</td>
<td>11.5 ± 1.0\textsuperscript{a}</td>
<td>9.0 ± 0.7\textsuperscript{ab}</td>
<td>77.8 ± 1.4\textsuperscript{a}</td>
<td>369.6 ± 1.1\textsuperscript{a}</td>
</tr>
<tr>
<td>PBAT BC 5%</td>
<td>11.8 ± 0.1\textsuperscript{a}</td>
<td>8.3 ± 0.4\textsuperscript{b}</td>
<td>81.6 ± 0.3\textsuperscript{b}</td>
<td>367.8 ± 2.8\textsuperscript{a}</td>
</tr>
<tr>
<td>PBAT BC 5% CaCO\textsubscript{3}</td>
<td>11.8 ± 0.1\textsuperscript{a}</td>
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</tr>
</tbody>
</table>
PBAT-BC PBAT-Gr-BC PBAT-5%-BC PBAT-5%-BC-CaCO3

MPa

Modulus MD Modulus CD Tensile Strength MD Tensile Strength CD
Effect of different loadings and particle size on cooling

- PBAT-BC
- PBAT-Grounded-BC
- PBAT-5% BC
- PBAT-5% BC-CaCO3

Effect of different loadings and particle size on the first heating

Effect of different loadings and particle size on the second heating

Effect of Biochar particle size and loading on film thermal stability
PBAT based composites Rheology, Arrhenius Equation

- Small particles, of nanoscale, are more efficient to hinder polymer structure evolution than large ones (Al-Itry, 2014).
- No physical interactions between the matrix and the microparticles have been detected. This is attributed to the polar nature of the wood-flour particles compared with the rather hydrophobic nature of the PLA/PBAT matrix. (Georgiopoulos, 2014)

\[
|\eta^*| = A^o \exp \left( - \frac{E_a}{RT} \right)
\]

Fig. 11. Effect of long chain branching (LCB) on the activation energy. (Al-Itry, 2014).