AFM nanomechanical mapping to understand the structure and behavior of polymer blends compatibilized with ionic liquids

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How nanomechanics can help to understand macroscopic mechanical behavior of polymers/composites?
1 Materials / Methods
   • Materials, context
   • AFM setup

2 Results
   • Morphology
   • Nanoscale moduli
   • Interfaces
   • Modelization

3 Conclusions / Further work
Biopolymers tend to replace oil-based polymers

**Problem**: They have to match the same properties
Biopolymers tend to replace oil-based polymers

Problem: They have to match the same properties
Solution: Biopolymer blends
Biopolymers tend to replace oil-based polymers

Problem: They have to match the same properties
Solution: Biopolymer blends
Problem: Incompatibility of many polymers give poor results
**Context**

- **Biopolymers** tend to replace oil-based polymers
  - **Problem**: They have to match the same properties
  - **Solution**: Biopolymer blends
  - **Problem**: Incompatibility of many polymers give poor results
  - **Solution**: Compatibilization
Biopolymers tend to replace oil-based polymers
- Problem: They have to match the same properties
- Solution: Biopolymer blends
- Problem: Incompatibility of many polymers give poor results
- Solution: Compatibilization

 Ionic liquids are investigated here as a novel route for compatibilization of biopolymer blends

What are the mechanisms beyond ionic liquids compatibilization?
Polymer blends compatibilized with Ionic Liquids (ILs)

<table>
<thead>
<tr>
<th>Designation</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymers:</strong></td>
<td></td>
</tr>
<tr>
<td>PBAT</td>
<td><img src="image" alt="PBAT Chemical Structure" /></td>
</tr>
<tr>
<td>PLA</td>
<td><img src="image" alt="PLA Chemical Structure" /></td>
</tr>
<tr>
<td><strong>Ionic Liquids:</strong></td>
<td></td>
</tr>
<tr>
<td>il-Cl</td>
<td><img src="image" alt="il-Cl Chemical Structure" /></td>
</tr>
<tr>
<td>il-TMP</td>
<td><img src="image" alt="il-TMP Chemical Structure" /></td>
</tr>
</tbody>
</table>

**Extruded/Injected**

- PBAT/PLA (80/20 %wt)
- PBAT/PLA/il-Cl (80/20/1 %wt)
- PBAT/PLA/il-TMP (80/20/1 %wt)
Macroscopic tensile tests show a successful compatibilization:
AFM setup

- **AFM**: Multimode 8
- **Mode**: PeakForce QNM
- **TAP150 tips** (Spring constant: 5 N/m)
- **Contact model**: DMT
- **Sample preparation**: Cryofracture
- **Piezo Frequency**: 2 kHz
- **Typical PeakForce Setpoint**: 20 nN (adjusted depending on the tip)
- **Typical scan rate**: 0.5 Hz for 3.5 µm scan rate; 1 Hz for 1 µm scan rate or less
Probe calibration

- **Deflection sensitivity** on hard sapphire sample
  - Single ramp calibration
  - **Drive3 Amplitude Sensitivity** adjusting
  - Calibration in scanning conditions
  - Setting the value of **Sync Distance** for the whole session

- **Spring constant** calibration: Thermal tune

- **Tip radius** calibration: Relative method on PS film
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Blends morphology

PBAT/PLA

With il-Cl

With il-TMP

Topography

Modulus
Modulus Quantification

- Compatibilization achieved while each phase shows a modulus decrease
- \(\Rightarrow\) Modification of the interface?
Modulus quantification: Crystalline phase identification

IL-TMP induces the nucleation of crystalline structures into the PLA phase

⇒ Crystalline phase localized in the center of the PLA fibril
Interfaces : Modulus evolution

- Profile analysis: Evolution of the modulus across PBAT/PLA interfaces

- Thickness of the interfaces:

⇒ With ILs the interface becomes an interphase
Interfaces: Adhesion of ionic liquids

Materials / Methods

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Conclusions / Further work

Morphology

Nanoscale moduli

Interfaces

Modelization

Interfaces: Adhesion of ionic liquids

ADHESION PROFILE:

PBAT

PLA

IL location

PBAT

PLA

DMT MODULUS
Results:

<table>
<thead>
<tr>
<th>Blend</th>
<th>Interfacial adhesion evolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAT/PLA</td>
<td>Adhesion step (PBAT-PLA transition)</td>
</tr>
<tr>
<td>PBAT/PLA/il-Cl</td>
<td>Large adhesion peak! (more on PBAT side)</td>
</tr>
<tr>
<td>PBAT/PLA/il-TMP</td>
<td>Adhesion peak!</td>
</tr>
</tbody>
</table>

⇒ Both ionic liquids are preferentially localized in the generated interphase.
Model of the interfaces

**neat PBAT/PLA blend:**
- Steep modulus/adhesion transition between PBAT and PLA

**il-Cl:**
- Very thick interphase
- IL mostly in the interphase ⇒ **Local miscibility of polymers**

**il-TMP:**
- Cristalline PLA phase in the center of the fibril
- Tick interface
- IL mostly in the interphase

*Figure: Interface model deduced from AFM study*
Morphology
Nanoscale moduli
Interfaces
Modelization

PLA

il-Cl

PBAT

PLA

il-TMP

PBAT

London interactions

Dipole-dipole interactions

Dipole-dipole interactions

electrostatic interactions

London interactions
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Conclusions

- AFM nanomechanical study allowed to understand the compatibilization mechanism
  - Structuration
  - Localization of the ionic liquids
  - Effect on the interfaces
  - Localization of a crystalline phase

Further work:

- Deeper study of ILs/polymers interactions
- Extension of the method to composites
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Conclusions / Further work

Thank you!