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

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Research question

How nanomechanics can help to understand macroscopic mechanical behavior of polymers/composites ?

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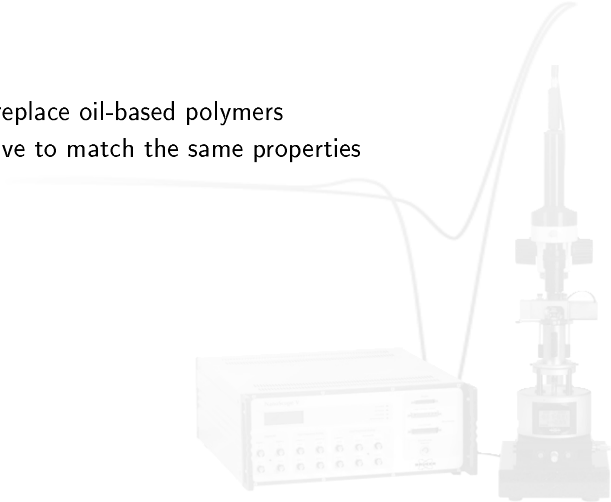
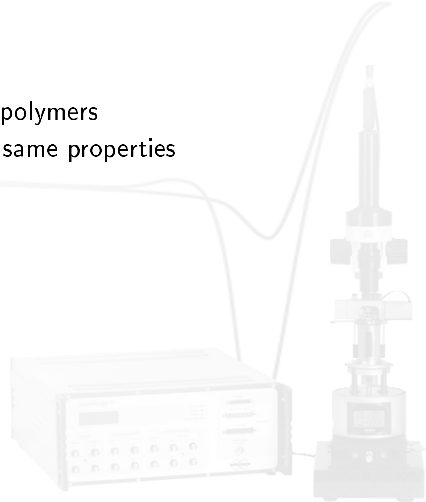
Context

- **Biopolymers** tend to replace oil-based polymers

  Problem : They have to match the same properties



Context



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  Problem : They have to match the same properties

  Solution : Biopolymer blends

Context

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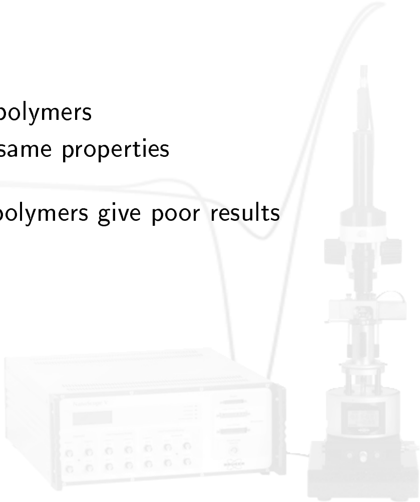
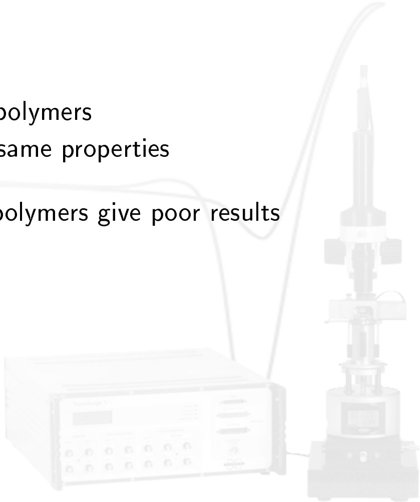
  Problem : Incompatibility of many polymers give poor results



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



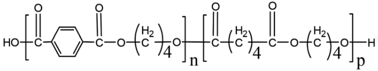
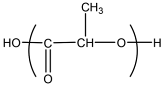
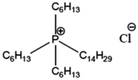
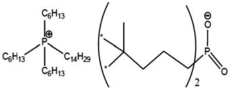
Context

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

What are the mechanisms beyond ionic liquids compatibilization ?

Materials

Polymer blends compatibilized with Ionic Liquids (ILs)

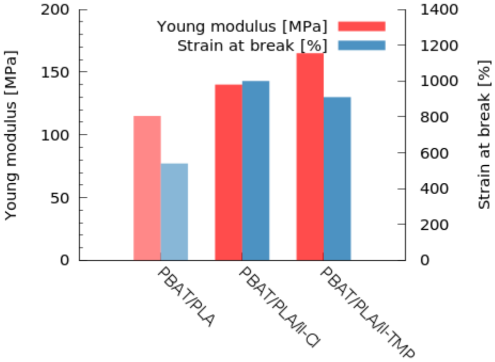
Designation	Chemical Structure
Polymers :	
PBAT	
PLA	
Ionic Liquids :	
il-Cl	
il-TMP	

Extruded/Injected

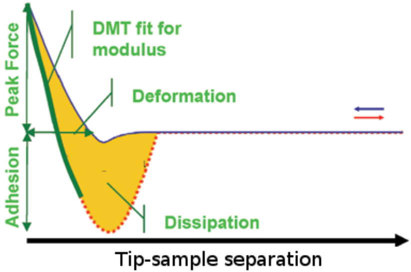
- PBAT/PLA (80/20 %wt)
- PBAT/PLA/il-Cl (80/20/1 %wt)
- PBAT/PLA/il-TMP (80/20/1 %wt)

Materials

- Macroscopic tensile tests show a sucessful compatibilization :

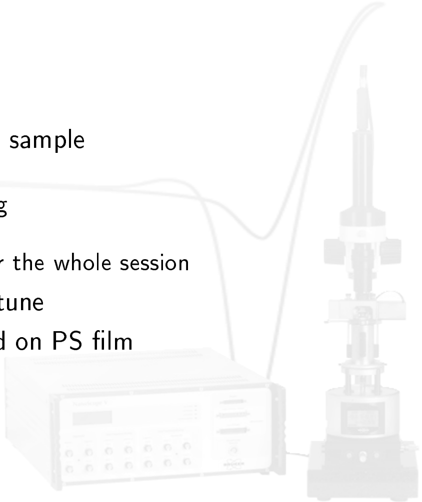


AFM setup



- **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 3.5μm scan rate ; 1 Hz for 1μm scan rate or less

Probe calibration



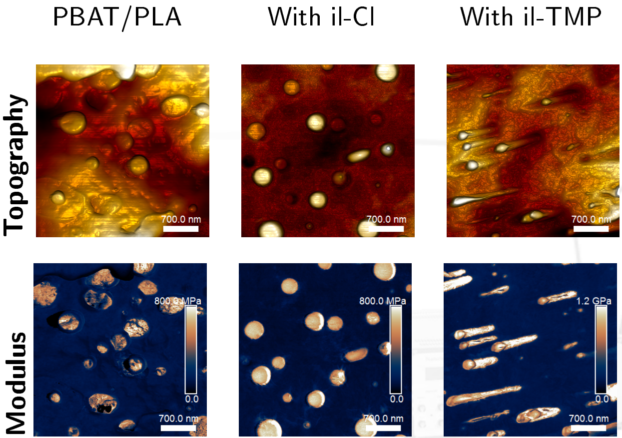
- **Deflection sensitivity** on hard sapphire sample
  - Single ramp calibration
  - **Drive3 Amplitude Sensitivity** adjusting
  - Calibration in scanning conditions
  - Setting the value of **Sync Distance** for the whole session
- **Spring constant** calibration : Thermal tune
- **Tip radius** calibration : Relative method on PS film

1. Materials / Methods
   - Materials, context
   - AFM setup

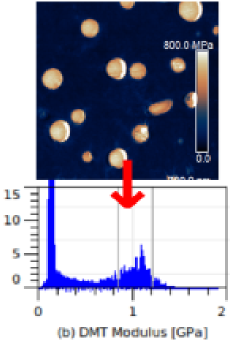
2. Results
   - Morphology
   - Nanoscale moduli
   - Interfaces
   - Modelization

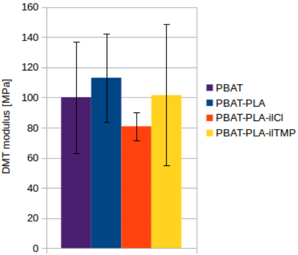
3. Conclusions / Further work

Blends morphology

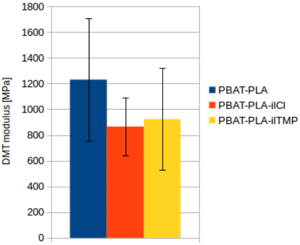


Modulus Quantification





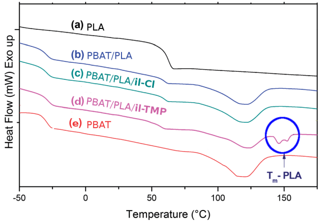
PBAT Phase



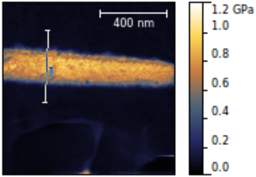
PLA Phase

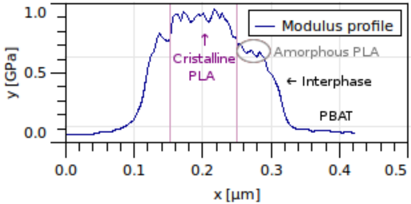
- Compatibilization achieved while each phase shows a modulus decrease
- ⇒ *Modification of the interface ?*

Modulus quantification : Crystalline phase identification



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

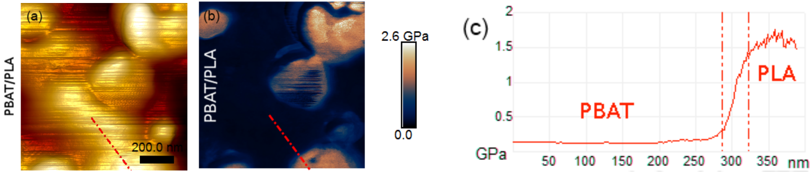




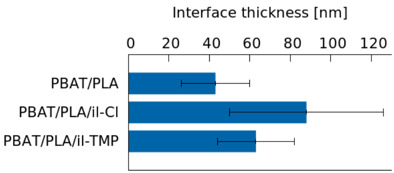
⇒ Crystalline phase localized in the center of the PLA fibril

Interfaces : Modulus evolution

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

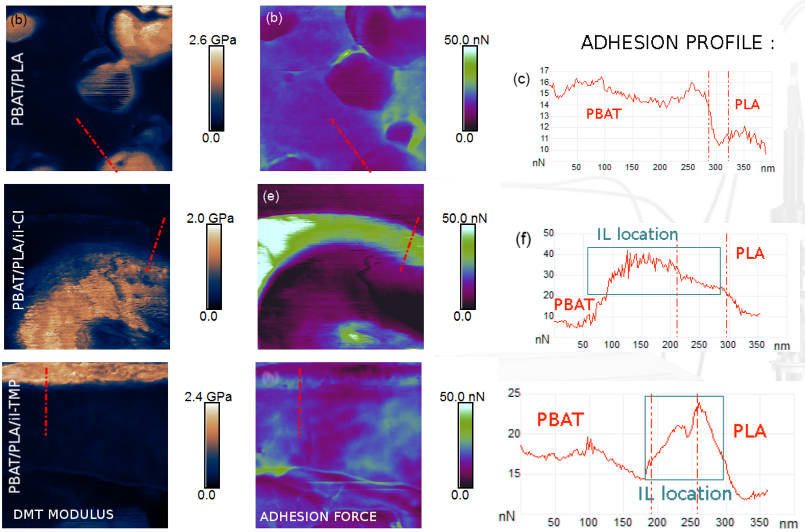


- Thickness of the interfaces :



$\Rightarrow$ With ILs the *interface* becomes an *interphase*

Interfaces : Adhesion of ionic liquids



Interfaces : Adhesion of ionic liquids

- Results :

Blend :	**Interfacial adheson evolution :**
PBAT/PLA	Adhesion step (PBAT-PLA transition)
PBAT/PLA/il-Cl	Large adhesion peak ! (more on PBAT side)
PBAT/PLA/il-TMP	Adhesion peak !

⇒ 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

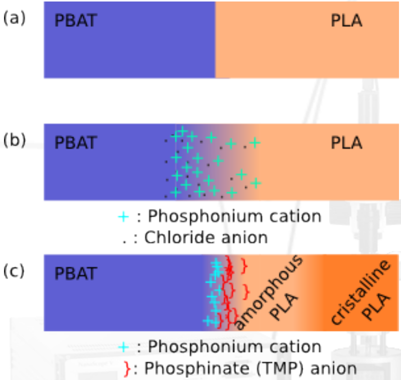
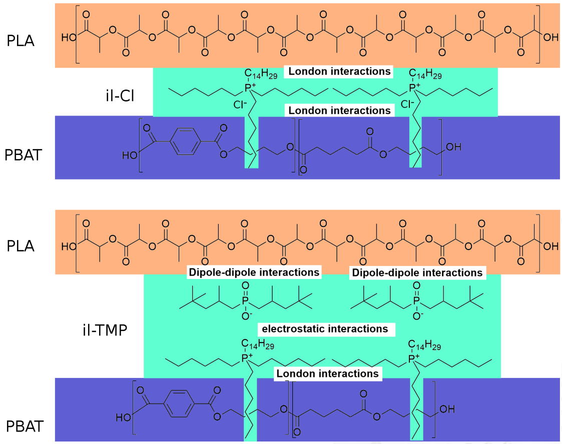


Figure : Interface model deduced from AFM study


PLA
il-Cl
PBAT
London interactions
London interactions
PLA
il-TMP
PBAT
Dipole-dipole interactions
Dipole-dipole interactions
electrostatic interactions
London interactions

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

Thank you !

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