Multi-scale characterization of the (visco)elastic properties of a semicrystalline polymer

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The mechanical response of polymeric materials strongly depends on the microstructure developed during process especially for semicrystalline polymers. With the idea to better understand the relationships between structure and mechanical properties it is becoming necessary to develop multi-scale mechanical characterizations for these heterogeneous materials and instrumented indentation proves to be the most appropriate tool. Regarding the study of viscoelastic properties by instrumented indentation, two complementary paths can be adopted: static nanoindentation (quite commonly used) and dynamic nanoindentation. The aim of this work is to compare the local mechanical properties of a polypropylene obtained by compression molding and injection. The latter is known to exhibit a skin-core morphology [1] with a non-spherulitic skin and a typically spherulitic core. Afterwards, the viscoelastic properties are investigated at different scales using both dynamic nanoindentation [2] and dynamic mechanical analysis (DMA).

Material

- **Polypropylene** : Block copolymer containing 14% of Ethylene Propylene Rubber (EPR)
- Thermal properties: T_g = 5°C, T_m = 170°C, $\chi_c \approx$ 30%

PP_{inj}: Injection molding

T_{inj} 190°C, 90 rpm

skin-core morphology

PP_{cm}: Compression molding

T 200°C, 40 bars, 10 min

mostly isotropic

ν = 0.43 (DIC)

Experimental characterizations

- Tensile tests

  $10^{-3}s^{-1} \leq \dot{\varepsilon}_0 \leq 10^{-1}s^{-1}$

  Extensometer

- DMA

  Strain sweep & Frequency sweep

  24°C ≤ T ≤ 120°C

  0.1 Hz ≤ f ≤ 100 Hz

- Indentation Hysitron TI980 (**BRUKER**)

<u>Berkovich tip</u>

<u>Loading protocol:</u>

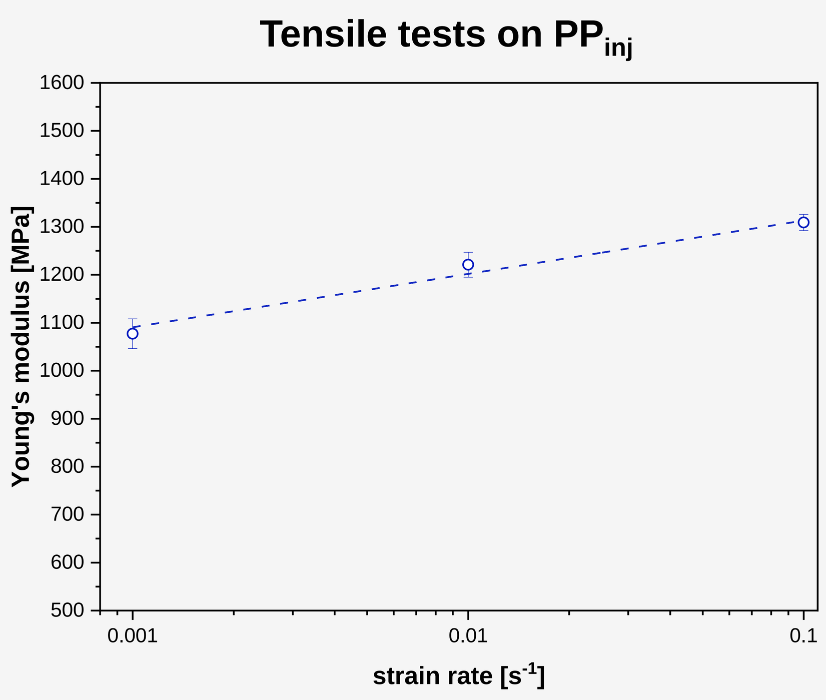
1. Loading-creep-unloading
2. Nano-DMA

   24°C ≤ T ≤ 120°C

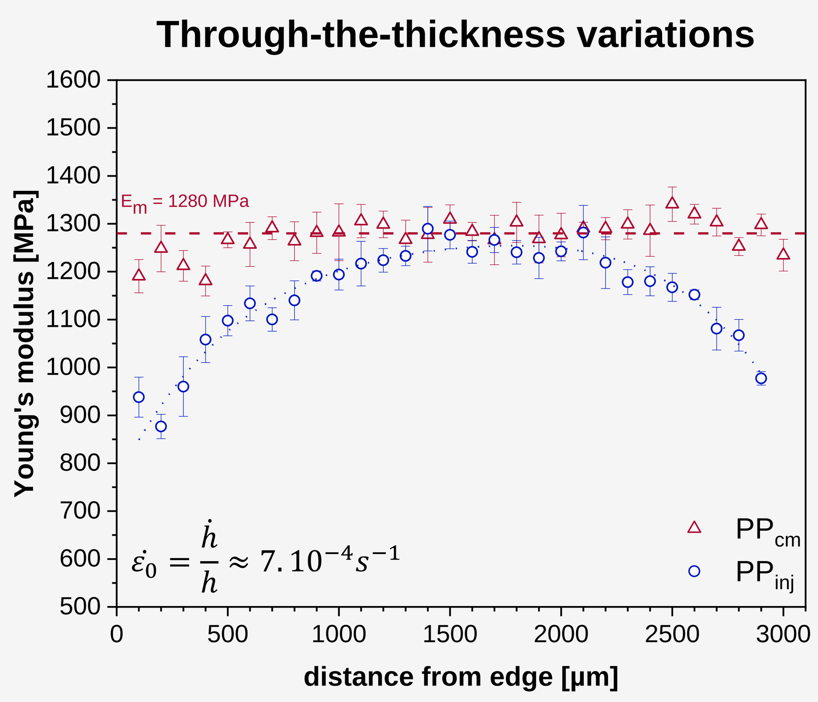
   0.3 Hz ≤ f ≤ 100 Hz

Elastic properties

3mm-thick samples



Indentation – Loading protocol 1



$$\dot{\varepsilon}_0 = \frac{\dot{h}}{h} \approx 7.10^{-4}s^{-1}$$

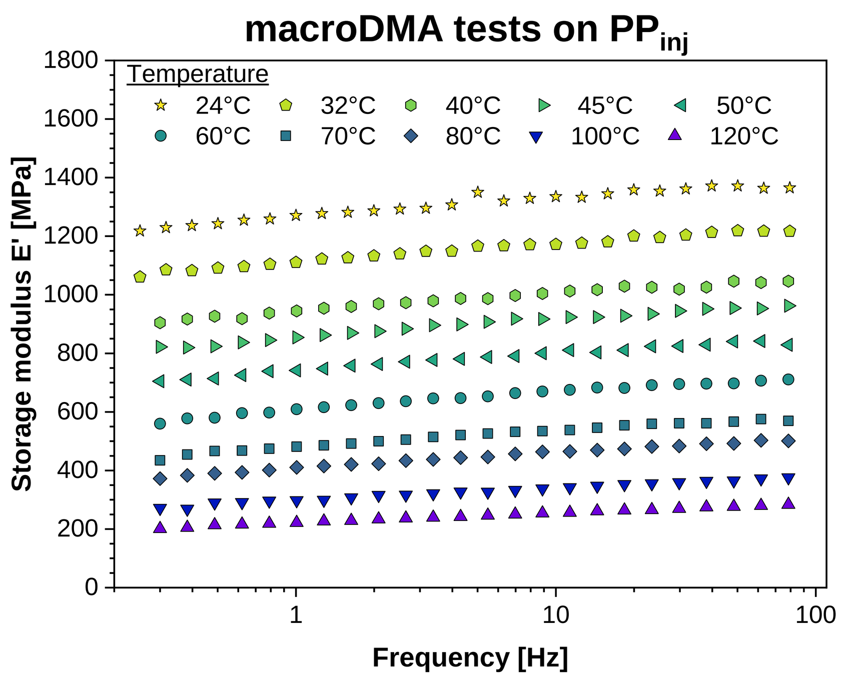
PP_{cm}

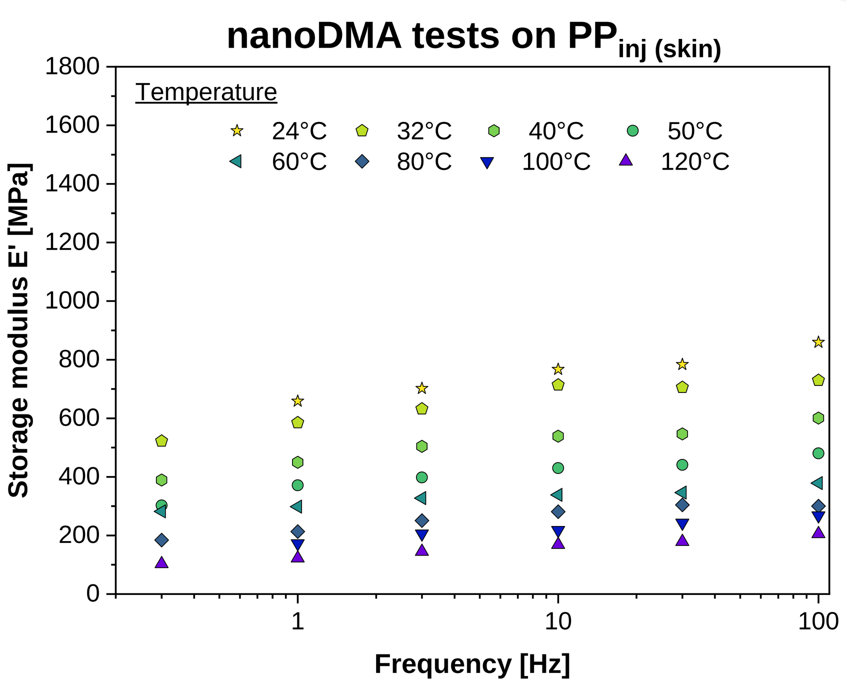
- **Homogeneous** properties through the thickness (E = 1280 ± 12 MPa)

PP_{inj}

- **Heterogeneous** properties through the thickness
- Skin layer softer than the core
- Confirms, from a mechanical point of view, the morphology heterogeneities

Viscoelastic properties (frequency sweep)



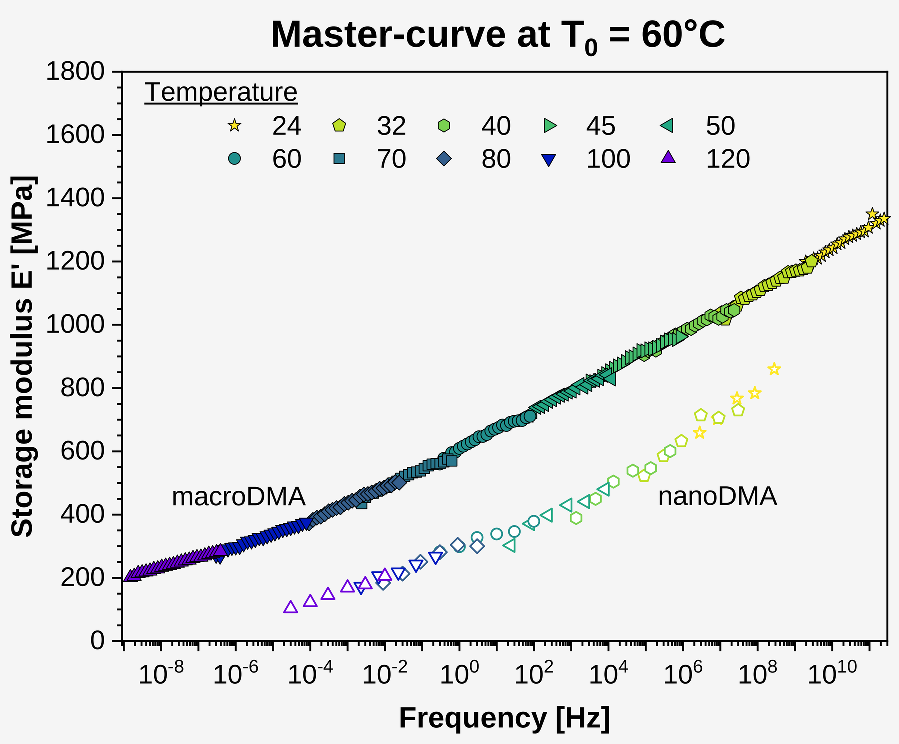


Indentation – Loading protocol 2

T_α : glass transition of the amorphous phase ≈ 5°C (DMTA-1Hz)

$T_{\alpha'}$: interlamellar shear + intralamellar motions of tie molecules ≈ 80°C (DMTA-1Hz) [3]

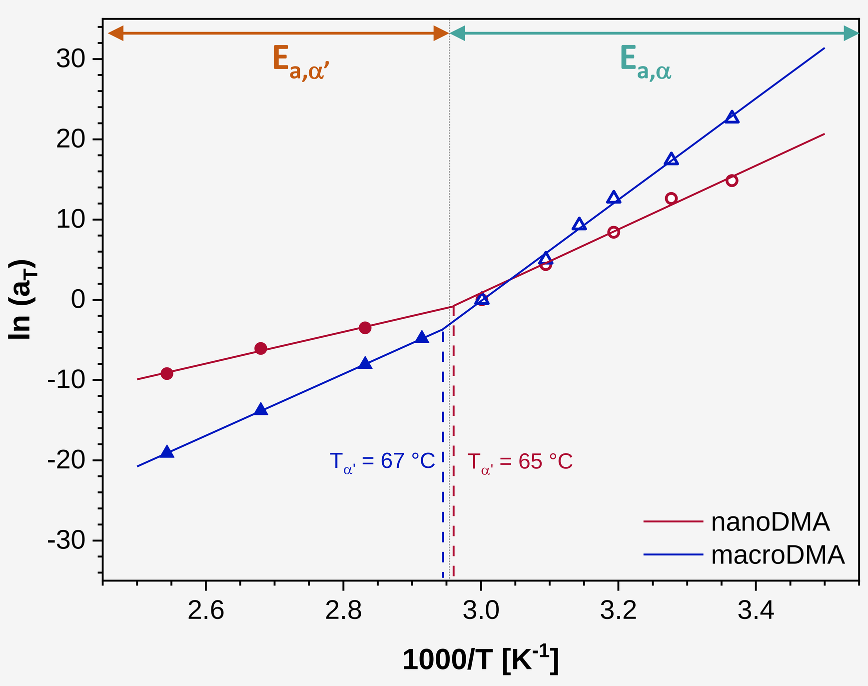
Time-Temperature Superposition principle (TTS)



Arrhenius law

$$a_T = \exp\left(\frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right)$$

R: universal gas constant



nanoDMA:

$E_{a,\alpha}$ = 330 kJ.mol^{-1}

$E_{a,\alpha'}$ = 164 kJ.mol^{-1}

- Pronounced decrease in Young's modulus with T which follows the Arrhenius law.
- Possibility to build a master-curve at different scales.
- Trends are similar but not the values which can be explain by the morphology heterogeneities in PP_{inj}.
- Evolution of the shift factors with T allows to determine $T_{\alpha'}$ (non-monotonic dependence).
- E_a determined by **nanoDMA** are consistent with literature [4].

Indentation allows to characterize the morphology gradient of injected semicrystalline polymers from a mechanical point of view. Nano-DMA is a promising tool to investigate the local response of polymers which are viscous by nature. Nonetheless, protocols need to be developed. First results on PP show a good agreement between DMA and nano DMA. The difference in storage modulus can be explained by the fact that nano-DMA focused on the skin of the injected sample which is softer than the core. Moreover, it is possible to determine the crystalline relaxation temperature by both methods. Future works will be devoted to characterize the viscoelastic properties of PP_{cm} and the core of PP_{inj}.

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