

Rheological Characterization of Polymers in Presence of Supercritical CO₂: Applications in Polymer Processing and Modification

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Introduction

The viscosity of polymer melts plays a key role in processing operations like melt extrusion, where high viscosity leads to increased energy demand. As such, there is strong interest in lowering viscosity without the use of solvents, which often require additional removal steps.

Supercritical carbon dioxide (scCO₂) presents a promising alternative—it reduces melt viscosity without modifying the polymer structure and can also be used to generate foamed materials [1]. This makes the precise determination of viscosity under high-pressure conditions technically relevant for many applications.

The choice of pressurization gas significantly affects the outcome. This study examines how scCO₂ and N₂ influence the viscosity and solidification behavior of Polylactic Acid (PLA) and High-Density Polyethylene (HDPE) under elevated pressure.

Setup

An MCR xx2e in combination with a pressure cell was used (Fig. 1). The pressure cells, which operate up to 400 bar and 300 °C, are designed to simulate industrial conditions relevant to polymer processing, oil recovery, and food technology. The measuring geometries used were parallel-plates (PP) with diameters of 8 mm (HDPE) and 20 mm (PLA).

For comparison, additional measurements under ambient conditions (atmospheric pressure) were conducted using the same geometry (PP08) on an air-bearing setup to evaluate the influence of magnetic coupling/ball bearing on measurement accuracy.

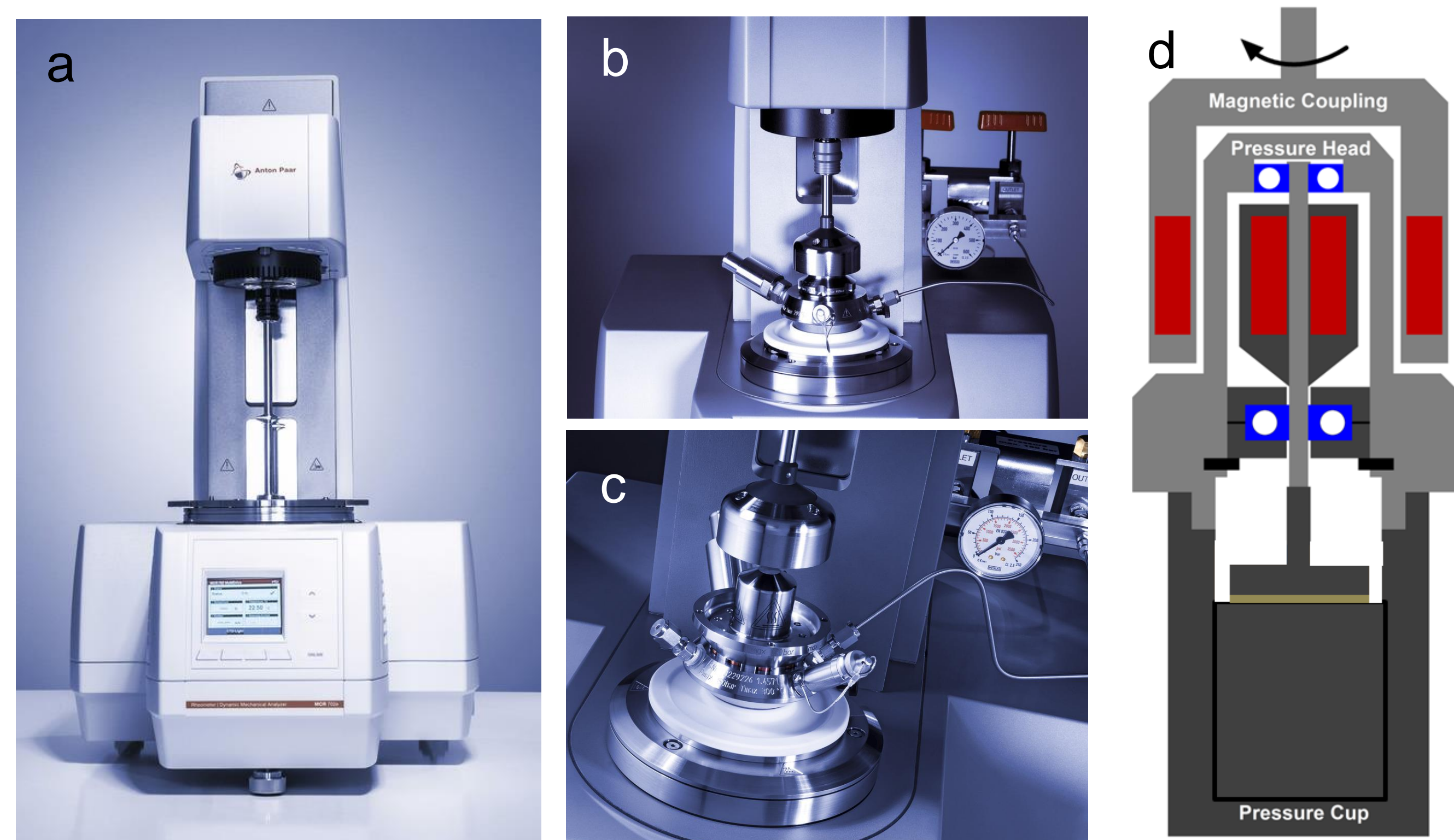


Fig. 1: Modular Compact Rheometer (MCR) with PP (a) and a pressure cell (b-c). Sketch of the pressure cell with parallel-plate (d).

Melting of PLA

The temperature ramp up to 165 °C was performed at a frequency of 2 Hz and a constant strain of 10% (Fig. 2). A distinct drop in the complex viscosity marked the onset of softening and melting. When CO₂ was used as the pressurizing gas, this transition began at around 140 °C, whereas under nitrogen, melting was only observed above 150 °C.

In addition, a notable reduction in the complex viscosity of the PLA melt was recorded in the presence of CO₂. This effect can be attributed to the function of CO₂ as a physical plasticizer, which enhances polymer chain mobility, thereby lowering both the viscosity and melting temperature of PLA [2].

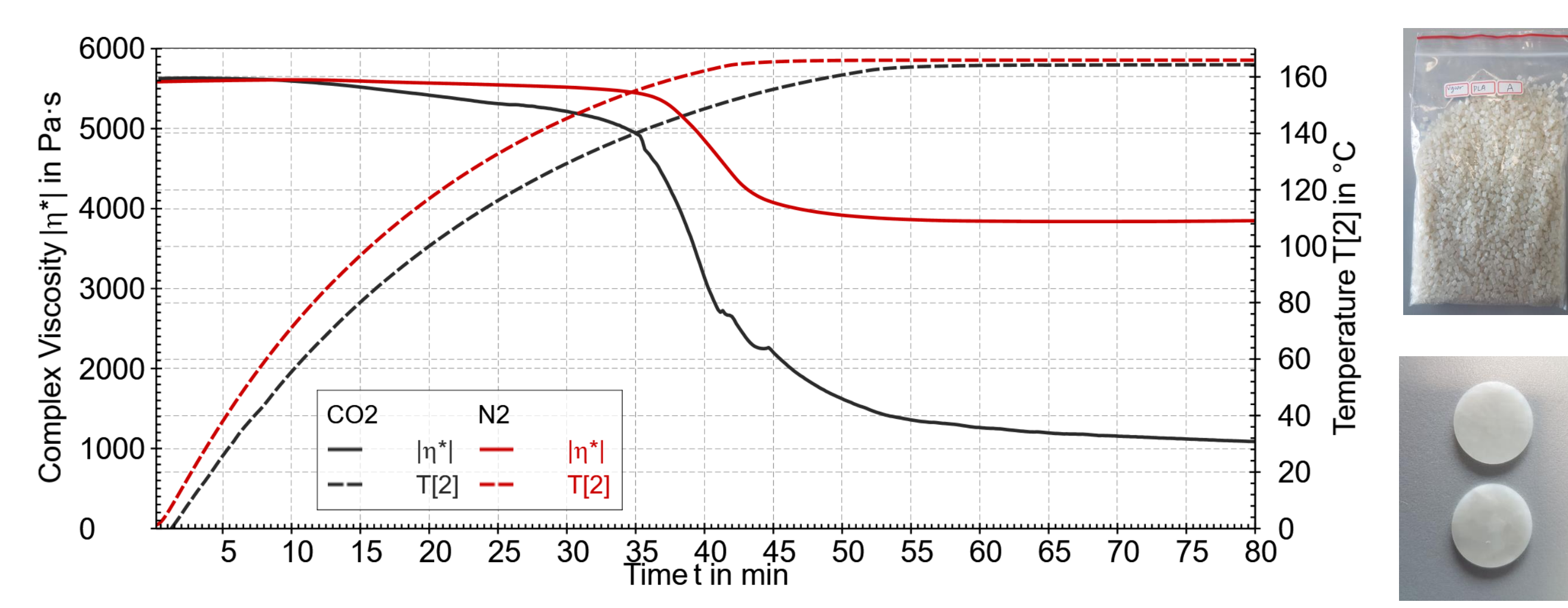


Fig. 2: Complex viscosity of PLA while increasing the temperature from 0 °C to 165 °C. With increasing temperature, the pressure reached up to 140 bar at 165 °. The gas applied was either CO₂ or N₂. On the right side pictures of PLA plates used for the measurement, as well as the raw material are shown.

Rheological characterization of a HDPE melt

Gap emptying depends not only on shear rate but also on measurement duration, and becomes more pronounced with increasing sample viscosity. This poses challenges for rotational rheology of highly viscous materials.

To address this limitation, oscillatory measurements can be employed, as they impose significantly less mechanical stress, minimizing gap emptying and enabling the analysis of high-viscosity samples.

Although oscillatory rheometry is somewhat limited in the pressure cell due to the ball bearing and magnetic coupling, the comparison in Fig. 3 demonstrates that it remains feasible and provides reliable relative results.

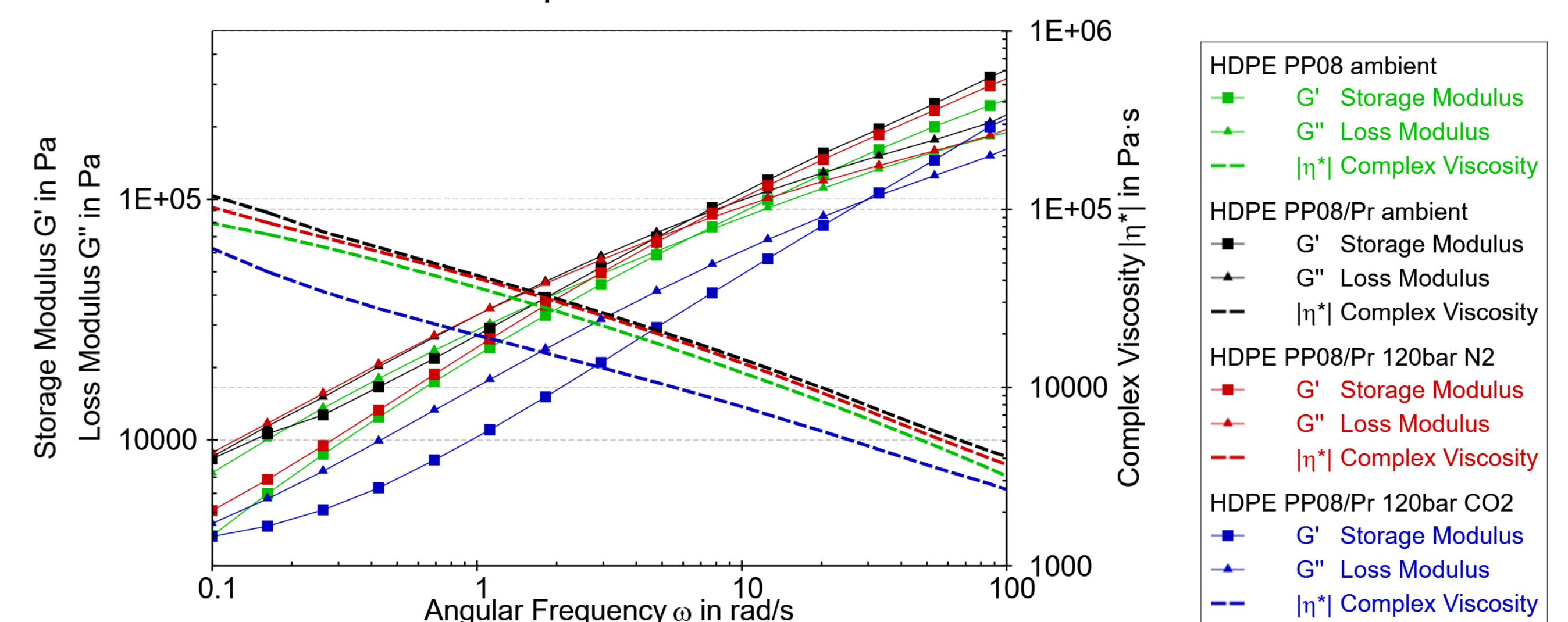


Fig. 3: Frequency sweeps at 160 °C. At ambient pressures, air bearing measurements (PP08) and pressure cell measurements (PP08/Pr) can be compared. Additionally, curves at 120 bar CO₂ respective N₂ are shown.

No significant differences in moduli or complex viscosity were observed between ambient pressure and 120 bar N₂. In contrast, measurements under scCO₂ showed a clear shift of the G'/G'' crossover to higher frequencies and a marked reduction in complex viscosity, highlighting its plasticizing effect.

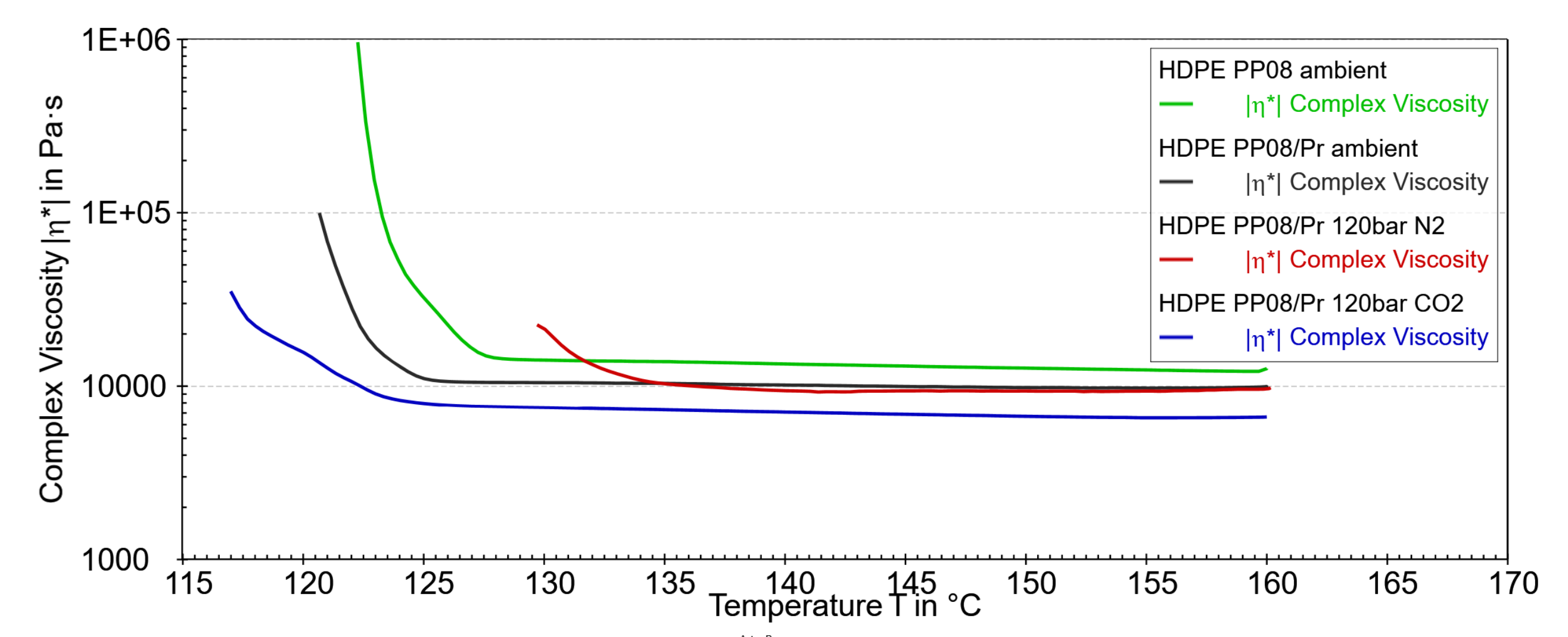


Fig. 4: Temperature ramps of HDPE starting at 160 °C. At ambient pressures, air bearing measurements (PP08) and pressure cell measurements (PP08/Pr) can be compared. Additionally, curves at 120 bar CO₂ respective N₂ are shown.

Temperature ramps were carried out at a strain of 1% and an angular frequency of 10 rad/s, with the temperature decreased from 160 °C to 80 °C at a cooling rate of 2 K/min (see Fig. 4).

A comparison between the air-bearing setup and the pressure cell revealed noticeable differences in absolute viscosity values and solidification temperatures. These discrepancies may be attributed to slight variations in the gap and temperature lag in the pressure cell, indicating a need for slower ramp rates. Nevertheless, the data remains valid for relative comparisons.

The results clearly show that the solidification behavior of HDPE is affected by the type of pressurizing gas: N₂ raises the solidification temperature, CO₂ lowers it.

Conclusions

The results provide insight into the rheological behavior of PLA and HDPE under N₂ and scCO₂. The results demonstrate that a pressure of 120 bar using N₂ has no significant effect on the melt viscosity but raises the solidification temperature. In contrast, applying 120 bar of scCO₂ leads to a notable decrease in melt viscosity and a slight reduction in solidification temperature.

References

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