Miniaturized characterization of polymers: From synthesis to rheological and mechanical properties in 30 mg

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ABSTRACT

The determination of rheological and mechanical material properties becomes a challenge when the availability of material is limited to a few (milli)grams. This miniaturized testing is hampered by the contradicting requirements of small sample sizes (and thus surface areas) and sufficiently large generated torques and forces. In this paper we provide a feasible methodology to determine the relevant material parameters in terms of processing and mechanical performance starting from 30 mg of material, using micropillars with a diameter of 1 mm. Complex viscosity in small amplitude oscillatory shear as the relevant parameter for thermoconformation processes is determined by means of eccentric rheometry. Herein, the sample is placed off-centered, which results in an increase in the generated torque without the need for increasing the size of the sample. By combining experimental data and numerical simulations, we show that the choice of the pillar aspect ratio is essential to maintain a homogeneous sample deformation and thus to extract correct rheological parameters. Values obtained with eccentric rheometry collapse with those obtained from standard rheometry. The intrinsic mechanical behavior is evaluated at room temperature and the yielding kinetics is studied. The methodology developed here can be extended to other systems and testing conditions, allowing a full material characterization in the liquid as well as in the solid state with only 30 mg of material.

1. Introduction

Traditionally the characterization of newly synthetized materials has been severely hampered by their availability. As such the mechanical performance that ultimately defines their potential applications and the rheological characterization that provides relevant information about their processing remain rather unexplored.

The potential applications are based on the mechanical performance of the newly synthetized polymers. Often the characterization of the mechanical properties is limited to a few parameters determined from tensile tests conducted at room temperature and under one single loading condition. Although appropriate for a first comparison, a thorough analysis to prevent premature failure includes the determination of the yielding kinetics, i.e. the time and temperature dependence of yielding [1]. From a practical standpoint the yielding kinetics are evaluated from a set of tests covering a range of temperatures and imposed constant strain rates, \( \varepsilon \). From such analysis the time scale for ductile failure at any value of stress is predicted [2–4]. Moreover, the microstructure and thus the resulting mechanical properties of polymers largely depend on the processing conditions [5]. For instance, in semi-crystalline polymers the amount of crystallinity and crystal orientation depend on the flow type and intensity, temperature and pressure [6–8]. The rapid growth of 3D printing applications for polymers thus raises the need for mechanical testing procedures that are applicable on (often small-scale) 3D printed samples.

Secondly, the polymer needs to be processed into a component or device. Here, the relevant parameters are gathered from the rheological characterization. For instance, inside the nozzle of a fused deposition modelling (FDM) 3D printing device, the combination of stresses and temperature profiles that the polymer experiences during processing are fully described in terms of the temperature dependent and shear-rate dependent rheology, where the viscosity (\( \eta \)) is the relevant material parameter. Since \( \eta \) is a temperature and shear-rate dependent parameter, its determination must be performed through a range of

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temperatures and shear rates. Moreover, as long as thermorheological simplicity stands [9], which is in general the case for polymer melts [10], a master curve can be constructed by shifting the individual isothermal tests. Hence, all the information for processing can be gathered in one rheological function. From such analysis, phenomena like shear thinning or shear thickening can be screened and compensated for by tuning the processing conditions.

To allow performing the above mentioned thorough material characterization with minute sample quantities, miniaturized testing techniques are gaining importance. Miniaturization has been implemented in a variety of testing techniques resulting in nanotensile testing devices [11], nanobubble inflation measurements on thin-films [12,68], tensile testing of thin films [13] as well as compression experiments on micropillars [13,14]. When using micropillars, the intrinsic mechanical behavior can be characterized, both for small as well as large deformations far beyond the yield stress. Miniaturized compression tests, have widely been used for metals [14]. For polymeric materials, the limited studies available focus on size effects in mechanical properties when using micropillars with sizes on the order of 1-100 μm [13,15,16].

For the characterization of the material behavior in the liquid state (rheology), micro-rheology is the most well-known small-scale rheological characterization technique [17]. However, this technique is limited to systems with a low viscosity as generating motion of a probe in a high-viscous polymer requires a large force, which is not attainable with either thermal motion or standard external fields. Moreover, with this technique, the only local response of the sample is probed. In literature, several approaches have been presented that allow to characterize the bulk rheological response of materials at small scales [18]. The devices designed for this purpose such as microfluidic setups, micropillar sliding-plate rheometers and piezo vibrators have several disadvantages. They are often only suitable for materials with a low to medium viscosity, are not commercially available and are often optimized to characterize material properties on length scales that no longer represent the true macroscopic bulk behavior of the material. Of particular relevance for polymers is the multi-sample micro-slit rheometer developed by Migler and coworkers that allows characterization of the viscosity of polymer melts with only 20 μl of sample and for several samples simultaneously [19]. In conventional rotational rheometry, simply lowering the gap size and sample diameter would allow to reduce the sample size to the required value [20]. However, only lowering the gap size will introduce effects of misalignment and slip [21,22], whereas lowering the sample diameter will lead to torque and normal force values below the sensitivity of the device [20]. These restrictions can be alleviated by using eccentric rheometry, wherein a small sample is placed off-centered to increase the generated torque [23,24]. Although this approach has been used before to characterize the dynamic moduli of rat skeletal muscle and biopolymer gels, its accuracy and applicability to characterize the rheology of polymers has not yet been investigated.

This paper provides a proof of concept showing that all the relevant material parameters described above can be determined from 30 mg of material. The methodology is developed and validated for two semi-crystalline thermoplastic polymers, i.e. isotactic polypropylene, iPP, and polycaprolactone, PCL, and can be extended to other systems. The selection of these two model polymers is not arbitrary. On the one hand, iPP is one of the most characterized polymers in literature [6,25-32], therefore reported values can be used for comparison. On the other hand, PCL is one of the most promising biomaterials for biodegradable medical devices [33-38], but little is known about its mechanical performance [39]. Thus, the data generated from the mechanical characterization will serve to fill this gap.

2. Materials and methods

2.1. Materials

Polycaprolactone (PCL) with a number average molecular weight $M_n$ of 80,000 g/mol and a polydispersity index $M_w/M_n<2$ is purchased from Sigma-Aldrich and isotactic polypropylene (iPP) with a weight average molecular weight $M_w$ of 320,000 g/mol and $M_w/M_n=5.4$ is purchased from Sabic. PCL and iPP pellets are dried overnight at 30 °C and 100 °C respectively, in a vacuum oven prior to subsequent processing and characterization steps.

2.2. Sample preparation

2.2.1. Disks

For the standard rheological measurements disks with a diameter of 25 mm and a thickness of 1 mm are produced via compression molding at 100 °C and 15 kN compressive force for PCL and at 210 °C and 20 kN for iPP. Compressed samples are dried overnight at 30 °C and 100 °C respectively, in a vacuum oven and placed in a desiccator and kept under vacuum until further testing.

Further standardization of the micropillars to the required height and thus aspect ratio (diameter:height), is carried out by removing the excess sample in steps of 10 μm by means of a Biobots 3D printer from Allevi (USA) at 100 and 210 °C, respectively. Secondly, starting from the extruded rods, micropillars of 1 mm in diameter and 1.5 mm in height are produced using a heated mold (100 °C for PCL and 210 °C for iPP). A schematic representation of the setup is shown in Fig. 1. No external cooling was present and the cooling rate was monitored by means of a small calibrated thermocouple-data logger (Volkraft K202 + SE 305 software) embedded into one of the micropillars.

Further standardization of the micropillars to the required height and thus aspect ratio (diameter:height), is carried out by removing the excess sample in steps of 10 μm by means of a vibrating-blade micromot VT 1000S from Leica (Germany). The dimensions of the micropillars are determined for each pillar separately by using 3D digital images obtained with a confocal non-contact surface profilometer Sensofar (Spain). At least four measurements are averaged for each dimension. The surface roughness ($R_s$) of the bottom surface (in contact with the mold) and of the top surface (after microtoming) is determined from the Z-scan obtained from confocal images using an EPIx20 objective. The scanned area is 636.61 x 477.25 μm². Micropillars of PCL and iPP are dried overnight at 30 °C and 100 °C respectively, in a vacuum oven and placed in a desiccator and kept under vacuum until further testing.

2.2.2. Micropillars

Micropillars for eccentric rheometry and mechanical testing are produced by a two-step extrusion and molding process. First, PCL or iPP pellets are shaped into 0.6 mm diameter rods by means of a Biobots 3D printer from Allevi (USA) at 100 and 210 °C, respectively. Secondly, starting from the extruded rods, micropillars of 1 mm in diameter and 1.5 mm in height are produced using a heated mold (100 °C for PCL and 210 °C for iPP). The schematic representation of the setup is shown in Fig. 1. No external cooling was present and the cooling rate was monitored by means of a small calibrated thermocouple-data logger (Volkraft K202 + SE 305 software) embedded into one of the micropillars.

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2.3. Differential scanning calorimetry

Determination of the thermal transitions and the crystallinity fraction of the as-received pellets and of the micropillars is carried out by means of a differential scanning calorimeter Mettler-Toledo 823e/700 module with a Cryostat intra-cooler. Samples are heated from −70 °C to 120 °C for PCL or −30 °C-230 °C for iPP at a heating rate of 10 °C/min under constant flow of dry nitrogen (flow rate 50 mL/min). The crystalline fraction $X_c$ is determined from the ratio of the enthalpies of fusion of the measured melting peak and the heat of fusion of crystalline PCL (139.3 J/g [40]) and iPP (188.4 J/g [41]).

2.4. Rheometry

Small amplitude oscillatory shear (SAOS) tests are performed on a stress-controlled MCR 502 rheometer (Anton Paar, Graz, Austria) with a CTD 300/GL convection temperature device, which allows optical visualization of the sample during testing. In order to determine the linear strain amplitude ($\gamma_0$), a strain sweep is conducted at an angular
frequency ($\omega$) of 1 rad/s. From the strain sweeps, $\gamma_0$ is set to 10% for both polymers. Isothermal frequency sweeps (100–0.01 rad/s) are conducted in the 80–140 °C temperature range for PCL and in the 190–270 °C temperature range for iPP. A minimum of 4 measurements are conducted using a new sample each time.

2.4.1. Standard rheometry

For the standard rheometry, a parallel plate fixture of 25 mm diameter is used.

2.4.2. Eccentric rheometry

In eccentric rheometry, the sample is placed at an offset with respect to the center of the rheometer plates. Since the torque scales linearly with the lever arm, this increases the torque signal thus allowing the use of a small sample size [23]. A schematic of the eccentric configuration is shown in Fig. 2a. Here, instead of a standard parallel plate fixture, a custom-made parallel plates setup with pins is used. As shown in Fig. 2a, 1 mm diameter pins are machined at the edge of the plates, and the micropillar is located between these pins. This configuration allows to obtain a straight sample edge, in contrast to the ‘hour glass’ shape formed when a narrow pillar is mounted between ordinary flat plates, as can be seen in Fig. 2b and c. The role of the pins is twofold. On the one hand they allow complete filling of the gap, mimicking what happens in a standard parallel plate configuration. On the other hand, the fixed position of the pins eliminates sources of scatter in the measured torques between different samples associated to the positioning of the sample.

2.5. Simulations

The simulations are performed with the commercial non-linear finite element package MSC.Marc. The finite element mesh consists of 4336 linear brick elements. In order to describe the shear deformation accurately, 16 elements over the thickness of the disc are used. The bottom of the disc is fixed in all directions. A surface is added which represents the top part of the rheometer. This surface is, with a contact constraint, glued to the top part of the meshed disc. On this surface the required rotation is applied and the torque on the disc is measured.

2.6. Mechanical tests

2.6.1. Compression tests at constant strain rate

The intrinsic mechanical behavior of both polymers is evaluated from compression tests at room temperature using a DHR-3 rheometer from TA instruments. A custom-made 8 mm diameter parallel plate geometry is used. The exponential gap compression profile of the rheometer is used to apply a set of constant true strain rates, within the $10^{-4}$ - $10^{-2}$ s$^{-1}$ range. To ensure that all presented data are taken under conditions of constant strain rate, the raw data of the gap profile in the rheometer software is checked. To prevent barrelling of the sample due to friction between the sample and the plates, PTFE spray is applied to the surfaces in contact with the micropillars. During the tests, the sample geometry is tracked with a camera (The Imaging Source model DMK21AU04) to ensure that a homogeneous deformation is obtained.
resulting in a true stress-true strain response [42,43].

2.6.2. Creep compression tests

In order to evaluate the long-term behavior, creep compression tests are conducted at room temperature under a constant true stress by means of a Zwick/Roell Z5.0 universal tester equipped with a 100 N load cell. In creep tests the evolution of the strain under static load is recorded. The values of the static load are chosen from the non-linear visco-elastic region of the stress-strain behavior measured from compression tests.

2.7. X-ray characterisation

X-ray characterisation is used to determine the crystallinity and the lamellar thickness of the crystal, which were measured by wide- and small-angle X-ray diffraction and scattering (WAXD and SAXS) at the Dutch-Belgian beamline BM26 (DUBBLE) of the European Synchrotron Radiation Facility in Grenoble (France) using a Pilatus 300K and a Pilatus 1M detector, respectively. The pixel size of both detectors was 2.7. X-ray characterization was 2.74 μm. In the case of the WAXD experiments, the detector was placed at a distance of approximately 210 mm from the sample, whereas in the case of the SAXS experiments this distance was approximately 6470 mm. The wavelength of the X-ray beam was λ = 1.033 Å. The exposure time was 30 s. All WAXD and SAXS data were background subtracted and integrated with the software package Bubble. From integration of the observed peaks the weight percentage of crystallinity ($\rho_c$) was calculated. For the calculation of the volume percentage crystallinity ($\rho_v$) the values of the density of the crystal phase ($\rho_c$) and of the amorphous phase ($\rho_a$) are given in Table 1. The values for the magnitude of the scattering vector, corresponding to the maximum of the Lorentz corrected intensity ($q_{1 \text{max}}$), the long period ($\lambda_0$), the lamellar thickness ($l_c$) and amorphous layer thickness ($l_a$) are determined from the characteristic peaks in the SAXS data [6,7].

### 3. Results and discussion

#### 3.1. Sample preparation and conditioning

From the digital image analysis, the quality of the produced micro-pillars is evaluated in terms of the parallelism of the top and the bottom surfaces and the surface roughness. An example is shown in Fig. 3. From a set of preliminary compression tests, it is found that non-parallelism of the top and bottom surfaces (ΔH) > 10 μm, leads to 15% standard deviation in the yield stress. Therefore from the digital image analysis, only pillars with ΔH ≲ 10 μm are selected for mechanical testing. The surface roughness of the bottom (Ra,b) and top (Ra,t) surfaces is 0.34 ± 0.04 μm and 1.2 ± 0.5 μm respectively. The thus obtained pillars for rheological and mechanical characterization each contain approximately 1 mg of material and thereby their size is approximately 1/6th of that of a rice grain.

Subsequently, the storage conditions in terms of humid environment exposure are considered for PCL. It is well established in literature that water absorption causes the plasticization of the amorphous fraction (preferentially) which results in a strong decrease of the mechanical properties and changes in the material morphology [45-48]. To determine the effect of moisture exposure on the rheological properties of PCL, four disks are exposed to a relative humidity of 75% in a desiccator containing a supersaturated salt (sodium chloride) solution. After 24 h the water uptake is quantified to be 0.3-0.5% by the increase in weight of the samples. Subsequently, the complex viscosity $\eta^*$ is measured from isothermal frequency sweeps at 100 °C. In parallel, four disks are stored in a desiccator under vacuum at room temperature and the complex viscosity is also measured. Comparison of the complex viscosities of humid PCL samples as compared to dry PCL samples shows a reduction of 4% in the value of $\eta^*$ and a higher variability of the values quantified by a standard deviation of 9% of the average value. Hence, samples are dried and stored under vacuum before all measurements.

#### 3.2. Differential scanning calorimetry

The thermal transitions of the as-received pellets and of the as-molded micropillars are investigated from the first heating scans of a DSC experiment, as shown in Fig. 4. These results reveal the resulting microstructure determined by the processing steps and storage conditions (thermal history). Accordingly, for PCL, the DSC heating scan of the as-received PCL pellet shows a single endothermic peak at $T_{\text{peak}} = 60.8 ^\circ$C, ascribed to the melting of the crystalline phase. From integration of the melting, the melting enthalpy $\Delta H_m = 75.28 \text{ J/g}$ is found, which compared to the melting enthalpy of the completely crystalline material (139.3 J/g [40]) yields $\chi_c = 54\%$. The DSC heating trace of the as-received IPP pellets is rather similar, featuring a double melting peak with corresponding centres at 121 and 165 °C. The occurrence of double melting peaks in thermoplastic materials has been explained in literature by the presence of two types of crystals which differ in perfection [40]. Accordingly, the lowest melting peak can be ascribed to melting of the less perfect or smaller crystals, whereas the highest melting peak can be associated with more perfect or bigger crystals. Here integration of the melting peak leads to a melting enthalpy $\Delta H_m = 98.93 \text{ J/g}$, and a crystalline fraction $\chi_c = 52.5\%$ when compared to the melting enthalpy of infinitely thick crystals (188.4 J/g [41]). Upon surpassing the melting peak, the previous thermal history is erased. From these scans, the corresponding processing temperatures are selected above the highest observed thermal transition, namely 100 °C for PCL and 210 °C for IPP. At these temperatures the polymers are in the molten state and can be easily processed by conventional thermoplastic processing techniques (molding, extrusion).

Regarding the heating traces of the as-molded micropillars, three thermal transitions are observed as follows. In the lower temperature region, a very subtle step in the base line, ascribed to the glass transition, is noted at $T = 26 ^\circ$C for IPP. The observed $T_g$ is in agreement with earlier studies on isotactic polypropylene [26]. Accordingly, as the heating scan proceeds, an exothermic peak associated to the cold crystallization of the amorphous phase is noted for IPP. Further heating results in the melting of the crystalline phase which includes the primary crystals formed during processing, and the secondary crystals formed during the dynamic crystallization. Since it is the size and distribution of the crystallites developed upon cooling from the melt that determine the final properties of materials [50], its fraction is calculated by subtracting the cold crystallization enthalpy from the total melting enthalpy. For the sake of clarity, the onset (CGonset) and the end (CGend) of the cold crystallization peak is indicated in Fig. 4. Thus, with a cold crystallization enthalpy of 6.44 J/g, and a melting enthalpy of 89.5 J/g, the primary crystalline fraction in the IPP micropillars is estimated to be 44.1%. This is substantially less as compared to that of the as-received pellets. Hence, for the latter the characteristic glass transition temperature of the amorphous phase cannot be observed in the DSC scans in Fig. 4. For PCL, the glass transition step and the cold crystallization peak are not observed, indicating that the amorphous phase is severely constrained by the crystalline phase so that the corresponding transitions are not observable. Hence, the crystalline fraction is determined solely from the melting enthalpy (64.43 J/g) yielding 46.3%.

#### Table 1

<table>
<thead>
<tr>
<th></th>
<th>$\rho_c$ (g/cm$^3$)</th>
<th>$\rho_a$ (g/cm$^3$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP</td>
<td>0.946</td>
<td>0.854</td>
<td>[26]</td>
</tr>
<tr>
<td>PCL</td>
<td>1.145</td>
<td>1.13</td>
<td>[44]</td>
</tr>
</tbody>
</table>
The range of achievable shear rates for the determination of the viscosity from rotational shear measurements is often limited by edge fracture. Accordingly, when the rotational speed of the parallel plate exceeds a critical value, the edges of the sample start to deform. If the fracture. Accordingly, when the rotational speed of the parallel plate fixture matches with the radius of the sample. Therefore, it can be seen that for a given minimum torque of the rheometer, the measurable stress value is a factor of the radius of the sample. Hence, it can be seen that for a given minimum torque value of 5 Nm, this is approximately a factor of 6 for eccentric rheometry as compared to standard rheometry. Hence, with \( R = 12.5 \text{ mm} \) and \( r = 0.5 \text{ mm} \), this is approximately a factor of 300 whereas it becomes a factor 1250 if \( R = 25 \text{ mm} \). In particular, the measured torques in eccentric rheometry for PCL range between \( 1.6 \times 10^{-6} \text{ N m} \) and \( 8.5 \times 10^{-4} \text{ N m} \), and for iPP between \( 9.5 \times 10^{-8} \text{ N m} \) and \( 1.3 \times 10^{-4} \text{ N m} \), for the range of experimental conditions studied here, which are above the minimum torque value of \( 5 \times 10^{-10} \text{ N m} \).

Initially, micropillars were placed off-centered in between standard parallel plates, as in prior work \([23]\). However, imaging at different stages of the isothermal frequency sweeps showed that as the temperature is increased, the micropillar does not remain cylindrical but spreads at the surfaces of the top and bottom plates thereby taking up a hour-glass shape, as shown in Fig. 2b. Since this effect increases the contact area with the plates, it will affect the measured torque values. For PCL and iPP, the error introduced by this spreading remained below 18%. However, depending on the wetting properties of the material, larger errors can be obtained. Hence, pins were machined on the bottom and top plate to fix the sample edge, whereby the initial cylindrical sample shape was retained, as shown in Fig. 2c.

As a reference case, rheological characterization of the PCL and iPP was performed with standard 25 mm disks. Fig. 5 shows a comparison between the complex viscosity obtained with the full disks and micropillars with different aspect ratios for a representative case of 80 °C and...
10 rad/s. When 1 mm thick micropillars (aspect ratio 1) are tested, the values of $\eta'$ are 18–23% lower as compared to the actual viscosity, as measured on the full disks. As the thickness of the micropillars is reduced, the measured viscosity value approaches the true value, with an error of less than 2% when the sample height is 0.4 mm (aspect ratio 2.5). If the thickness of the sample is further reduced, the values of the viscosity drop again. For standard rotational rheometry, it is well-established that for gap sizes below a few hundred $\mu$m, the measured viscosity value will be an underestimation of the true value due to two sources of error namely wall slip and misalignment [21]. Moreover, both effects can in general not be separated since they exhibit a similar dependency on the gap height [21]. When performing linear viscoelastic measurements on micropillars both slip and misalignment are expected to be modest due to respectively the low stress values and limited surface area. This is indeed confirmed by the data for a 300 $\mu$m thin full disk, which shows a much more pronounced underestimation of the viscosity as compared to the micropillars.

To better understand the optimum in the measurement accuracy with respect to gap height when performing eccentric rheometry, numerical simulations are performed for full disks as well as micropillars. Since wall slip and misalignment are absent here, the agreement between the full disk data and that of micropillars keeps improving when the aspect ratio of the pillars is reduced. The reason for the discrepancy at larger gaps can be understood from the plots of the strain field extracted for micropillars of 1 mm thickness in Fig. 6. From the side view image of the deformed pillar it can be seen that pillars with an aspect ratio of 1 do not undergo a homogeneous shear deformation. Rather, the pillar bends and exhibits zones with compressional and extensional strains. As a result, whereas the shear strain is constant across the sample cross-section for a thin sample (not shown), a large strain gradient, showing a factor 8 difference between the sample center and edge is clear from Fig. 6b for the 1 mm thick sample. This indicates that if the sample has a too large aspect ratio, it will not undergo a simple shear deformation but only the center will deform according to the applied shear strain whereas the edges deform less, thereby generating lower stress values. A similar reduction in the sample stiffness due to the presence of stress-free side walls has been analytically calculated for rectangular samples [52]. This effect appears to be more pronounced in the simulations as compared to the actual experiments. This may be caused by the fact that in the experimental results, surface tension and other components of the stress tensor may contribute to the force on the pins, which is not considered in the simulations. However, the simulations allow to clearly isolate the relevance of the sample geometry for the strain field in the sample. Based on the experimental results it can be concluded that sample thickness and aspect ratio are key factors that need to be considered when applying eccentric rheometry. For 1 mm diameter pillars, an optimum balance between small-gap errors and an inhomogeneous strain field for small sample aspect ratios can be reached with a sample thickness of 0.4 mm (aspect ratio 2.5). Overall, the simulations show that to obtain a homogeneous strain field, larger aspect ratios are better whereas the experimental data show that the sample thickness should remain large enough to avoid effects like wall slip and misalignment.

With the optimum sample dimensions and plate geometry for eccentric rheometry being set, a comparison between data obtained with full disks and with micropillars can be performed. The results of
isothermal frequency sweep tests for a range of temperatures are presented in Fig. 7 for both PCL and iPP. Although eccentric rheometry was used before in literature for muscle tissue and biopolymer gels [23, 24], accurate comparison with reference measurements is lacking. From Fig. 7 it is clear that good agreement between standard rheometry and eccentric rheometry is obtained. Hence, the validity of the eccentric rheometry technique is demonstrated. It should be noted that it was verified that the sample shape remained unaltered over the complete temperature range e.g. gravitational sagging was negligible, which is a prerequisite to maintain data accuracy.

Based on the data in Fig. 7, using the time-temperature superposition principle allows to collapse the viscosity values on a master curve. As long as thermorheological simplicity stands any parameter can be used for the master curve construction. Accordingly, together with \( \eta^* \), \( \delta \) is also chosen in Fig. 8 because it is a primary reading from the rheometer software and it is not dependent on the dimensions of the sample, therefore it is an unbiased reference parameter for the validation of the methodology. Reference temperatures of 140 °C and 270 °C were chosen for PCL and iPP respectively. Both for the phase angle \( \delta \) and the complex viscosity \( \eta^* \), a good quality of the shifting is noted since all the values collapse onto one master curve where the angular frequency range is extended to 600 rad/s. The vertical shift factor \( b \), taking into account density and temperature effects directly [10] was found to be not required. From the representation of the complex viscosities, both polymers show a small amplitude oscillatory (SAOS) behavior featured by a decrease of the viscosity with increasing angular frequency. The Newtonian complex viscosities \( \eta_{0, \text{ref}} \) at the reference temperatures for both polymers are given in Table 2.

From the shifting of \( \delta \) or \( \eta^* \), the respective horizontal shift factors \( \alpha_T \) and \( \alpha_r^* \) are determined. For temperatures of more than 100 °C from the glass transition temperature, the shift factors generally follow an Arrhenius dependency [53]:

\[
\ln(\alpha_T) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)
\]

Where \( \alpha_T \) is the horizontal shift factor (\( \alpha_T \) and \( \alpha_r^* \)), \( R \) is the universal gas constant \( = 8.31 \text{ J/Kmol} \), \( T \) is the measurement temperature, and \( T_{\text{ref}} \) is the reference temperature and \( E_a \) is the activation energy for flow. The activation energy \( E_a \) for flow is determined from the slope of the graphical representation of \( \ln(\alpha_T) \) versus the inverse of the absolute temperature (Fig. 9). The values obtained for PCL and iPP are given in Table 2. In both cases, the values of \( E_a \) obtained from \( \delta \) and from \( \eta^* \) master curve constructions are similar, and they are in good agreement with previously reported values in literature for PCL [54] and iPP [25, 32]. This once more confirms the validity of the eccentric rheometry technique.

### 3.4. Mechanical characterization

Compression tests are used to characterize the intrinsic mechanical behavior of iPP and PCL at room temperature. Since the forces and displacements at play during compression tests of small micropillars are in the range of Newtons and micrometers, a device with a high sensitivity and sufficient accuracy in the range of interest is required. Therefore, a stress controlled rotational rheometer is used for the mechanical characterization.

Since the typical stiffness of rotational rheometers in the axial direction is significantly lower than that of tensile testing devices, it may be needed to correct for the rheometer compliance. Thereto, the axial machine stiffness of the rheometer is determined at room temperature. From the slope of the normal force (N) –axial displacement (\( \mu \)m) curve (Fig. S2 in the supporting information) the stiffness is quantified to be \( 2.2 \times 10^6 \text{ N/m} \), which corresponds to a compliance of 0.45 \( \mu \text{m/N} \). This value is in agreement with axial compliance values reported in literature for other types of rotational rheometers [55]. This rheometer stiffness needs to be compared with the sample stiffness \( k \):
and $h$ is the sample height at any time, $t$. However, it turned out that deviations from the theoretical exponential profile were occurring at the end of the programmed gap profile (Fig. S3 in Supporting information).

Since only the data generated from a constant strain rate can be used for the determination of the intrinsic behavior, the implementation of the strain rate was monitored by taking the derivative of the true strain (true strain rate) with time. This condition is realized for all the loading conditions at least until the yield point. Data failing this condition were discarded. Moreover, there was always a small discrepancy between the applied and the measured strain rate (Fig. S3). Taking this into account and with a displacement resolution of the linear motor of 10 nm, strain rates in the range of $10^{-4}$ s$^{-1}$ to $10^{-2}$ s$^{-1}$ can be accurately applied.

With such considerations, the mechanical characterization at room temperature of iPP and PCL is evaluated from compression tests at constant strain rate and creep tests. Examples of these tests are shown in Figs. 10 and 11. The yield stress is defined either by the maximum of the curve (iPP) or by the intersection between the tangents of the initial (elastic) and final (plastic) part (PCL) of the stress-strain curve [56]. The insertions of Fig. 10 correspond to photographs taken at regular intervals during the compression tests, where the uniformity of the strain and negligible barrelizing effects are demonstrated (see also Fig. S4 in supporting information).

The stress-strain behavior is based on stress-enhanced mobility leading to different regions in the stress strain response. The first region is featured by a non-linear viscoelastic regime. As the strain is further increased, the stress reaches a maximum value ascribed to the yielding behavior. Here the plastic strain rate exactly matches the experimentally applied strain rate. For both polymers lowering the strain rate results in a decrease of the observed yield stress. Vice versa, when applying a constant stress, i.e. a creep experiment, a constant plastic strain rate results [57]. Plotting the yield stress versus the logarithm of applied strain rate a line with constant slope is observed which can be described with Eyring’s flow theory [58], suggesting thermorheologically simple

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**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>$E_{a,\delta}$</th>
<th>$E_{a,\eta^*}$</th>
<th>$\eta_0$, TRef</th>
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<tr>
<td></td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>Pa·s</td>
</tr>
<tr>
<td>PCL TRef = 140 °C</td>
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<td></td>
</tr>
<tr>
<td>Full disks</td>
<td>34.8 ± 1.0</td>
<td>31.2 ± 1.8</td>
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<tr>
<td>Micropillars</td>
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<td>34.0 ± 0.6</td>
<td>6567</td>
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<tr>
<td>iPP TRef = 270 °C</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>40.0 ± 0.2</td>
<td>1452</td>
</tr>
<tr>
<td>Micropillars</td>
<td>39.5 ± 0.4</td>
<td>38.8 ± 0.6</td>
<td>1369</td>
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</table>

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**Fig. 8.** Master curves of a) the phase angle ($\delta$) and b) the complex viscosity ($\eta^*$) at reference temperature 140 °C for PCL and 270 °C for iPP.

**Fig. 9.** Arrhenius dependence of the horizontal shift factors ($a_T$) on the reciprocal of the absolute temperature. Full symbols represent the shift factors for the standard geometry and empty symbols those for eccentric rheometry.

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**Fig. 10.** True stress-true strain response, as measured in compression of PCL and iPP at $\dot{\varepsilon} = 10^{-2}$ s$^{-1}$ and room temperature with photographs taken at $\varepsilon = 0$; $\varepsilon = 0.1$ and $\varepsilon = 0.5$. 

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behavior, see Fig. 12. The experimental window in the lower strain rate region is extended by means of compressive creep tests. A typical response of such a test is shown in Fig. 11. Here a constant true stress is applied to the micropillars, whereby the final value is reached within a very short time (10 s), as compared to the duration of the test, and the evolution of the strain with time is monitored. The initial region of high strain rate in the creep test, i.e. the stage where the stress is applied, is the primary creep region. Subsequently, during secondary creep, a constant strain rate is measured, which spans until a gradual increase of the strain rate is noted until failure occurs, i.e. tertiary creep. In agreement with previous findings [59-62], the same linear correlation as for the yielding kinetics of iPP from the compression tests was found. The curve of PCL in Fig. 11 shows that a constant plastic strain rate is not reached. The most probable cause is micro texture development, since we are measuring close to the melting temperature. Quantification, however, goes beyond the scope of this manuscript and therefore the data is omitted in Fig. 12.

For the mechanical characterization part, a direct comparison with data obtained from tests conducted on bigger samples is not straightforward. This is due to the fact that the mechanical properties in the solid state depend on the structure, which is in turn determined by the thermal history [63]. Accordingly, for the validation of this part, reference values from bigger samples are not generated, but data from literature are presented and discussed.

For iPP, the yield stress values obtained from compression molded cylindrical samples of 4 mm diameter and 4 mm height, tested at 23 °C in the $10^{-2}$–$10^{-3}$ s$^{-1}$ constant strain rate range [7] are included in Fig. 12. For PCL, to the best of the authors’ knowledge, the available data are limited to the work of Eshragi et al. [39] where cylindrical samples of 12.7 mm diameter and 25.4 mm height with a porosity of 0.05 obtained by selective laser sintering (SLS) were compression tested at a rate of 1 mm/min. From the reported values for the engineering yield stress ($\sigma_{y,e}$) and strain ($\varepsilon_{y,e}$), the true stress value ($\sigma_y$) was estimated assuming the conservation of volume upon deformation (which is not necessarily true for porous samples) and the compression rate was translated into strain rate units. With such considerations, the obtained value is included in Fig. 12.

Yielding is a stress activated process which for semicrystalline polymers involves intralamellar (process I) and interlamellar (process II) deformations [64,65]. Within a sufficiently large strain-rate experimental range both processes are observed featuring what is called thermorheologically complex behavior, described by the Ree–Eyring theory [66]:

$$\sigma_y(\dot{\varepsilon}, T) = \sum_i \frac{kT}{V_i} \sinh^{-1} \left[ \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \exp \left( \frac{\Delta U_i}{RT} \right) \right], \quad (8)$$

where $i$ corresponds to independent molecular processes whose stresses are additive. For the set of constant strain rates studied in this paper a simple correlation between $\sigma_y$ and $\dot{\varepsilon}$ is found indicating thermorheologically simple behaviour, which can be described by the simplified version of Equation (11) as follows:

$$\sigma_y(\dot{\varepsilon}, T) = \frac{kT}{V} \sinh^{-1} \left[ \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \exp \left( \frac{\Delta U}{RT} \right) \right]. \quad (9)$$

With V the activation volume, $U$ the activation energy and $\dot{\varepsilon}_0$ the rate constant. After the work of [6] with isotactic polypropylene, it is known that whereas $V$ and $U$ are material parameters, i.e. independent of the structure, the pre-exponential factor $\dot{\varepsilon}_0$, captures the thermal history through the lamellar thickness, $l_c$:

$$\log(\dot{\varepsilon}_0) = -Al_c + B \quad (10)$$

From the dependence of $\sigma_y$ on the reciprocal of the rate constant ($\dot{\varepsilon}_0$) (Equation (9)) it follows that a decrease of the rate constants shifts processes I and II horizontally along the strain-rate axis in Fig. 12 towards lower rates. In terms of lamellar thickness ($l_c$), thinner crystals result in a lower overall stress response.

A characterization of the microstructure of the bulk samples and

![Graph showing creep compression behavior of PCL and iPP at room temperature and a constant stress of 15 MPa for PCL and 20 MPa for iPP.](Image 40x87 to 287x297)

![Graph showing dependence of the yield stress on the applied strain rate.](Image 40x540 to 287x738)

**Table 3**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>IPP</th>
<th>iPP literature</th>
<th>PCL</th>
<th>PCL literature</th>
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<tr>
<td>Average cooling rate</td>
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<td>3.4</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Temperature range</td>
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<td>210-22</td>
<td>100-22</td>
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<td>$X_c$ (DSC)</td>
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<td>–</td>
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<tr>
<td>$X_c$ (WAXD)</td>
<td>%</td>
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<td>54</td>
<td>48</td>
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<tr>
<td>$\theta_{c,\text{max}}$</td>
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<td>$l_c$</td>
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<td>$l_p$</td>
<td>nm</td>
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<td>$l_t$</td>
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<td>6.8</td>
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micropillars is provided in Table 3. It should be noted that there is a difference between the crystallinity for iPP as measured via DSC (44%) or X-ray techniques (54%), which is attributed to the presence of an intermediate connecting phase in between the amorphous and crystalline phase that has sufficient order to contribute to the X-ray diffraction [28,67].

To infer the dependence of the microstructure upon the cooling rate only the crystalline parameters derived from the X-ray analysis are considered. The semicrystalline microstructure obtained by Caelers et al. [7] after an average cooling rate of 0.83 °C/s, consists of 60% crystalline fraction with a lamellar thickness (L) of 8.2 nm. Instead, the significantly faster average cooling rate applied on the micropillars (3.4 °C/s) led to a lower crystallinity (52%) featured by thinner lamellae (7.2 nm) and a thicker amorphous layer (lₐ = 6.8 nm). In this type of crystals interlamellar and intralamellar deformations are more easily activated and the yield behavior is shifted to the right (high strain-rate region) as compared to the observed kinetics for thicker crystals. From Fig. 12 two main conclusions can be extracted. First, the material dependent parameters in the yield kinetics that determine the slope of the yield stress versus strain rate behavior are obtained correctly from the micropillars. Second, the horizontal shift in the data originates directly from the difference in crystallinity due to the different cooling rates. Thereby, it is established that miniaturized mechanical testing can be performed accurately, whereby identical cooling is essential if it is desired to consider the microstructure-dependent behavior.

For PCL, the 29% lower yield stress value for pillars obtained from SLS as compared to molded micropillars is attributed to the manufacturing-induced porosity which results from the incomplete coalescence of polymer particles during sintering, melting and resolidification. Moreover, it is argued that these pores may enhance the absorption and diffusion of moisture from the ambient environment, leading to the plasticization of the amorphous fraction [47], resulting in the reduction of the observed σ₀. With the developed methodology, it will be possible to investigate the effects of different processing-induced microstructures or to include effects of humidity and temperature during mechanical testing.

4. Conclusions

In this work a rheological and mechanical characterization of PCL and iPP polymers was performed on millimeter sized samples. To overcome the limitation of too low torque values in standard rotational rheometry of small samples, eccentric rheometry was used. It was found that selecting an optimal aspect ratio of 2.5 is essential to strike a balance between a non-homogeneous sample deformation at large aspect ratios and errors due to wall slip and plate misalignment at low aspect ratios. With the optimal aspect ratio of 2.5 for both polymer melts, the complex viscosities and the Arrhenius fitting parameters for micropillars equalled the values obtained in standard rheometry with full disks of 25 mm diameter. From compression experiments on small pillars, a full mechanical characterization of the yielding kinetics was performed. Comparison with data obtained from bigger samples revealed the effect of the microstructure resulting from different cooling rates. With the developed methodology for processing of small polymer pillars and the miniaturized mechanical and rheological tests, only 30 mg of each material was used for the complete characterization. Therefore, it can be concluded that the methodology developed here provides a feasible way to characterize polymers that are only available in limited amounts and will benefit material screening with variations in material recipes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.121918.

References
