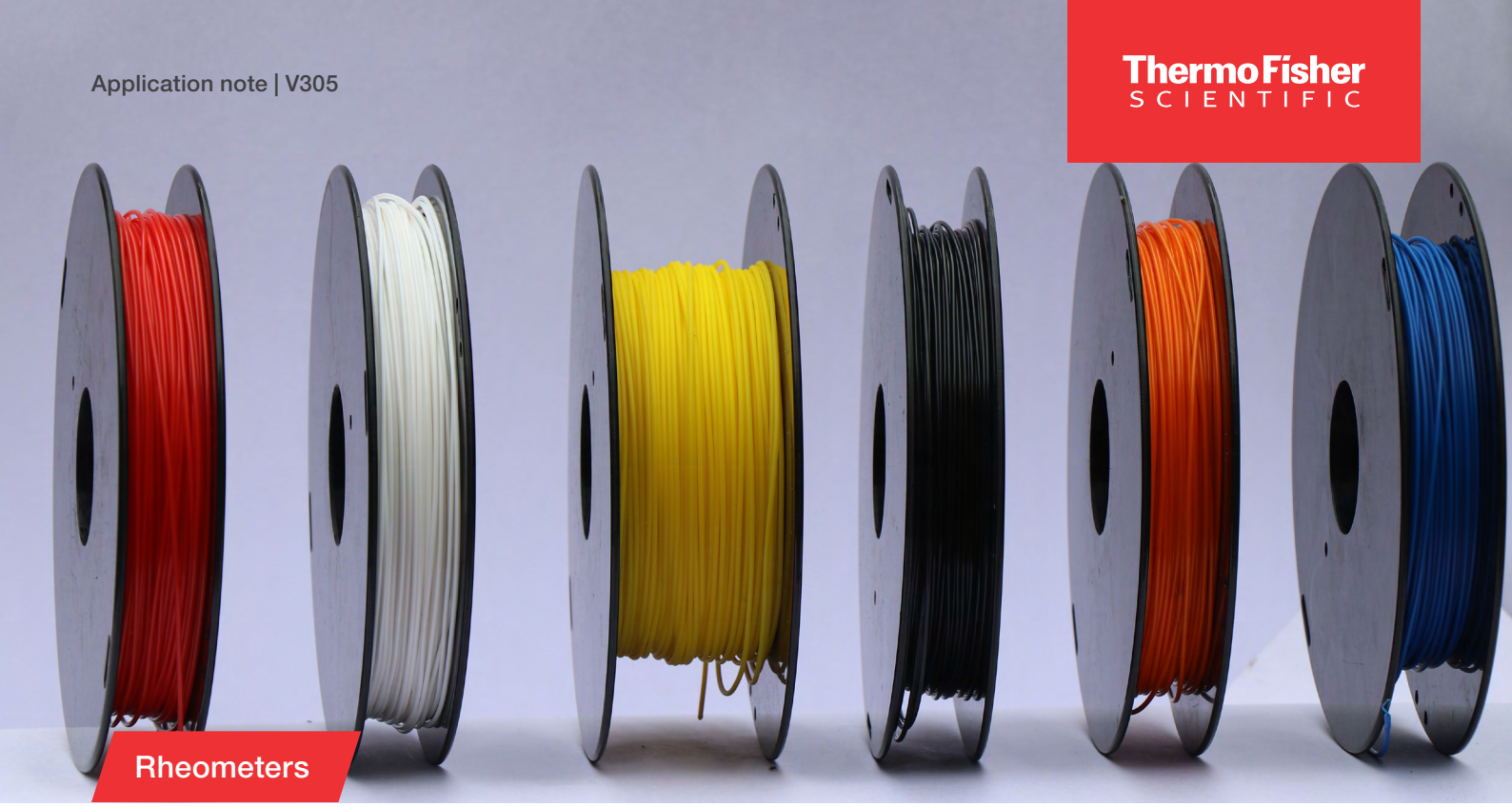

Rheometers

Uncovering the thermal history of a polylactic acid strand used for 3D printing applications with dynamic mechanical thermal analysis (DMTA)

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Introduction

3D printing is a process that, compared to traditional manufacturing techniques, allows for a fast and efficient production of complex structures. When used as an industrial production technique, it is also referred to as additive manufacturing. Various types of 3D printing techniques are available nowadays. One of the most common is called fused deposition modeling (FDM®) or fused filament fabrication (FFF). FDM is an extrusion technique that builds a structure layer-by-layer out of a thermoplastic polymer. The process includes the melting of the plastic material that is fed as a strand into the 3D printer head.[1]

Typical thermoplastic materials that are used for 3D printing include polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), or polycarbonate (PC). Commercially utilized (especially for 3D printing applications) PLA is usually a semi-crystalline thermoplastic material that shows a glass transition as well as a melting point. However, depending on the processing condition of a PLA part, it can also exhibit an amorphous structure. A semi-crystalline structure is achieved by either adding a nucleating agent to the PLA melt or by a slow cooling (solidification) process.[2]

Rapid cooling and the avoidance of nucleation agents will cause a more amorphous structure of the final product. The type of structure will have a direct effect on the visual appearance of the PLA. An amorphous part will appear translucent (in the case no further color additives are included), while a semi-crystalline part will appear opaque. The degree of crystallinity does also affect a material's mechanical behavior below and above its glass transition temperature. Rheological testing has proven to be an excellent tool to analyze the mechanical properties of polymers in their different physical states.

To extend its range of testing methods into the field of dynamic mechanical thermal analysis (DMTA), modern rotational rheometers can be equipped with special clamping fixtures that allow for testing solid specimens. During DMTA testing, a material is exposed to an oscillatory mechanical excitation while the temperature is continuously changed. The obtained data is used to identify characteristic phase transitions, such as the glass transition or the occurrence of melting and / or crystallization within the polymer matrix. In addition, DMTA can be used to determine final product performance and to interrogate relevant application-based properties such as stiffness, brittleness, damping, or impact resistance.

Whether a PLA part was cooled down rapidly or slowly can also be revealed by performing DMTA tests. In this application report, the results of DMTA tests performed on a commercially available PLA filament for 3D printing are presented.

Materials and methods

All tests were performed with a Thermo Scientific™ HAAKE™ MARS™ iQ Air Rheometer, equipped with a solids clamping tool for performing DMTA with cylindrically shaped specimens. The solids clamping tool comprises an upper and a lower shaft. The end of each shaft consists of a collet chuck for clamping samples with a cylindrical cross-section. Collets with different internal (clamping) diameters are available for testing different size specimens. The temperature control for this setup was provided by a TM-CR-O450 temperature chamber. Figure 1 shows the rheometer setup with the solids clamping tool and a PLA filament attached.

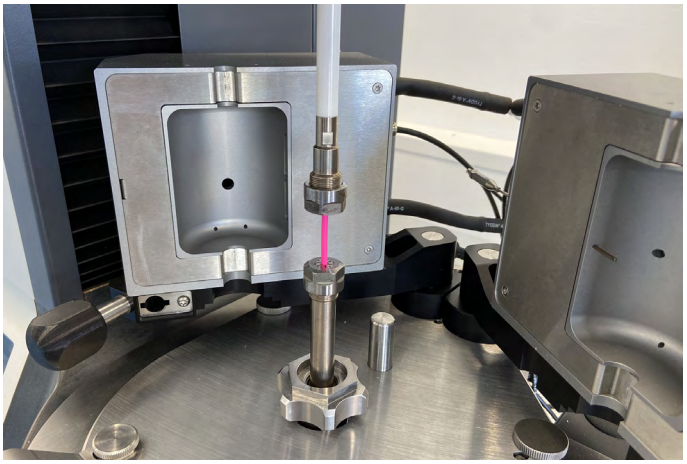

Figure 1: MARS iQ Air Rheometer with temperature chamber and solids clamping tool with PLA filament mounted.

The tested PLA sample was a commercially available filament spooled for 3D printing with a filament diameter of 2.85 mm. A roughly 50 mm long strand was cut and mounted into the solids clamping tool to perform multiple DMTA tests. In all tests, a constant oscillatory deformation of 0.01 % was applied at a constant frequency of 1 Hz.

Results and discussion

Figure 2 shows the results of a DMTA test with a PLA filament performed over a temperature range from 30 °C – 160 °C. At low temperatures, the material was in its glassy state and showed high values for the storage modulus (G') and the loss modulus (G''). In this state, G' reached values of around 10^9 Pa and was about two orders of magnitude larger than G''. The resulting low values for tan δ of around 0.01 indicated that PLA is a rather brittle material at ambient conditions.

Up to a temperature of around 60 °C, G' remained nearly constant, while G'' was increasing continuously. At 62 °C, G'' reached a maximum which is considered a measure for the glass transition temperature in DMTA. With a further increasing temperature, both moduli dropped almost three orders of magnitude into a low rubber elastic plateau. At temperatures between 90 °C and 100 °C, the values for both moduli started to increase again rapidly before reaching another plateau region. At temperatures above 140 °C, the sample started to melt and both values were decreasing again. The increase in moduli between 90 °C and 100 °C can be attributed to a cold crystallization that occurred above the glass transition and below the melting point. Cold crystallization only occurs when the original specimen was processed in a way that included a rapid cool-down from melt into solid state. In those cases, the PLA chains do not have enough time to align and form crystalline domains before reaching the glass transition temperature. Below the glass transition temperature, the mobility of the molecules is reduced so much that no further crystallization will occur, and the PLA shows a dominantly amorphous structure. In the DMTA experiment shown in Figure 2, the amorphous PLA was heated with a slow rate of 2 °C / min that allowed the sample to align and form crystalline domains before reaching the melting temperature at around 150 °C.

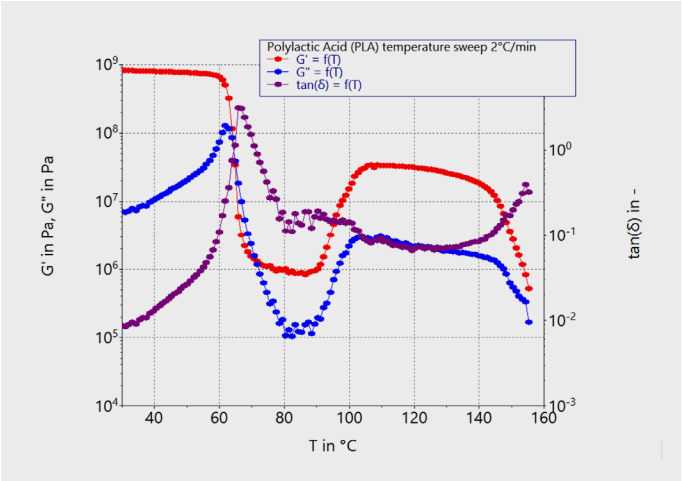

Figure 2: Storage modulus G', loss modulus G'' and tan δ as a function of temperature for a PLA. The test was performed with a heating rate of 2 °C / min.

Figure 3 shows the comparison of the data from Figure 2 with a DMTA test of a PLA filament with a different thermal history. Prior to the test, the specimen was heated to 130 °C (above cold crystallization temperature) and afterward cooled down below its glass transition temperature with a rate of -2 °C / min. It can be seen in this case that no cold crystallization occurred and the material showed the thermo-rheological behavior of a typical semi-crystalline thermoplastic material with a broad rubbery elastic plateau at temperatures above the glass transition and below the melting temperature.

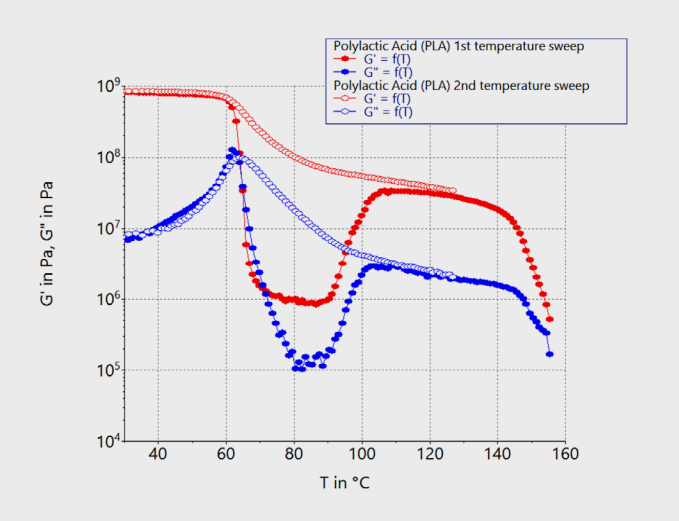

Figure 3: Comparison of storage modulus G', loss modulus G'', and tan δ as a function of temperature for data in Fig. 2 with a PLA sample that was heated up above the cold crystallization temperature and cooled down slowly afterward.

The occurrence of cold crystallization can be suppressed or at least reduced when performing DMTA test at significantly faster heating rates than 2 °C / min. Figure 4 shows the comparison of DMTA tests performed with the original PLA filament and a heating rate of 2 and 20 °C / min. With the faster heating rate, the recrystallization of the sample above the glass transition was significantly reduced. After passing the glass transition, the moduli data went into a broad and low rubber-elastic plateau before increasing again slightly at temperatures above 130 °C. Due to the faster heating rate, all phase transitions occurred at higher temperatures compared to the sample that was tested with the lower heating rate.

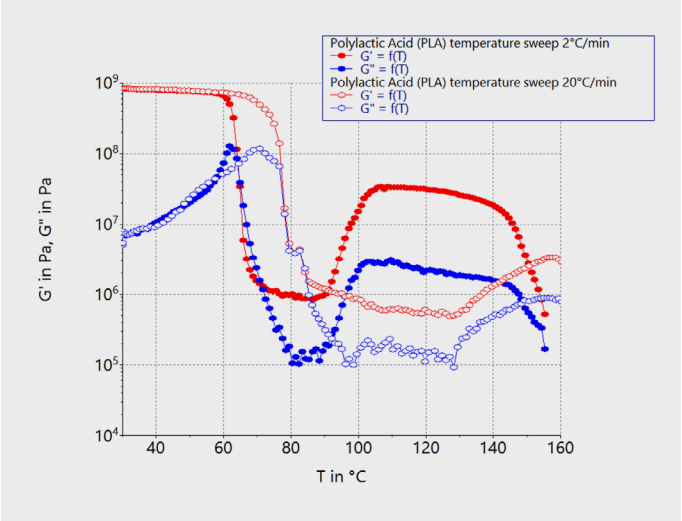

Figure 4: Comparison of storage modulus G', loss modulus G'' and tan δ as a function of temperature for PLA samples tested with different heating rates.

Conclusions

DMTA was performed with a rotational rheometer equipped with a solids clamping tool to investigate the thermo-rheological behavior of PLA filaments used for 3D printing applications. The presented results not only allowed the identification of the general mechanical properties of the material over a wide temperature range, but also revealed its thermal history and demonstrated the influence of the cooling and heating rates on the occurrence of cold crystallization. Cold crystallization is a phenomenon that becomes visible when a PLA sample is heated up at low rates. The degree of crystallinity has a direct impact on the optical and mechanical properties of a thermoplastic polymer.

References

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