



# Dry. Humid. Wet. Polyamide and Water

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### Introduction

Polyamides are semi-crystalline polymers characterized by good mechanical resistance; this allows them to be used for various technical applications, such as cable protection in the automotive industry and robotics. Polyamide powder is also a popular material for SLS (Selective Laser Sintering), a 3-D printing method allowing for creating objects of any shape.

However, polyamides are also very sensitive to water. The molecular chains of polyamides contain polar amid groups that attract polar liquids such as water, so that this polymer absorbs the moisture present in the environment. The water molecules increase the free volume in the polyamide chain gaps, which results in polymer swelling and easier sliding of the molecular chains at mechanical load. This leads to lowering of the glass transition and is called water-induced plasticizing effect. [1, 2, 3]

Consequently, the water uptake drastically affects the mechanical, thermal and electrical properties of polyamides. In particular, increasing the water content leads to a decrease in stiffness and strength, while toughness increases. [3, 4, 5]

### DSC Investigates the Influence of Humidity on the Glass Transition of Polyamide

In the following, the influence of humidity on the glass transition of polyamide 6 (PA6) is investigated. To this end, DSC measurements were performed on samples containing different levels of water content between 0% and 4.9%.

Table 1 summarizes the measurement conditions. The glass transition of PA6 is usually overlapped with the endothermal peak due to water evaporation. This predestines it to perform temperature-modulated DSC measurements that separate the reversing (e.g., glass transition) from the non-reversing effects (e.g., evaporation of volatiles, curing) [6].

**Table 1** Measurement Conditions

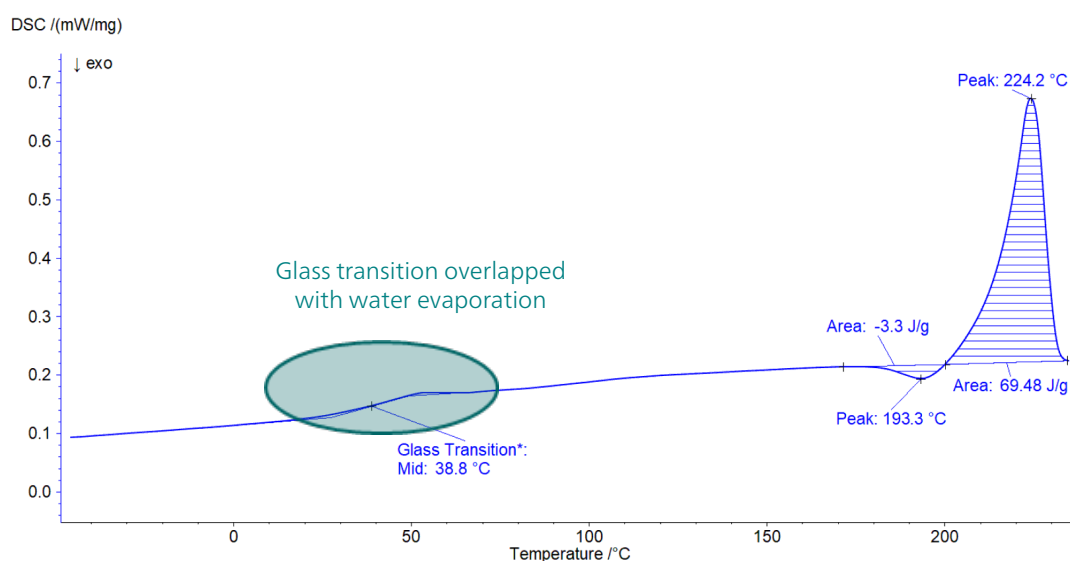
Device	DSC 300 Caliris®, H-Module			
Sample	Dried (0-% humidity)	1.2-% humidity	3.3-% humidity	4.9-% humidity
Sample mass	9.92 mg	10.04 mg	10.26 mg	10.44 mg
Crucible	Concavus® (aluminum) with pierced lid			
Temperature range	-60°C to 240°C			
Heating rate	5 K/min			
Period	60 s			
Amplitude	0.8 K			

### Glass Transition Temperature of PA6

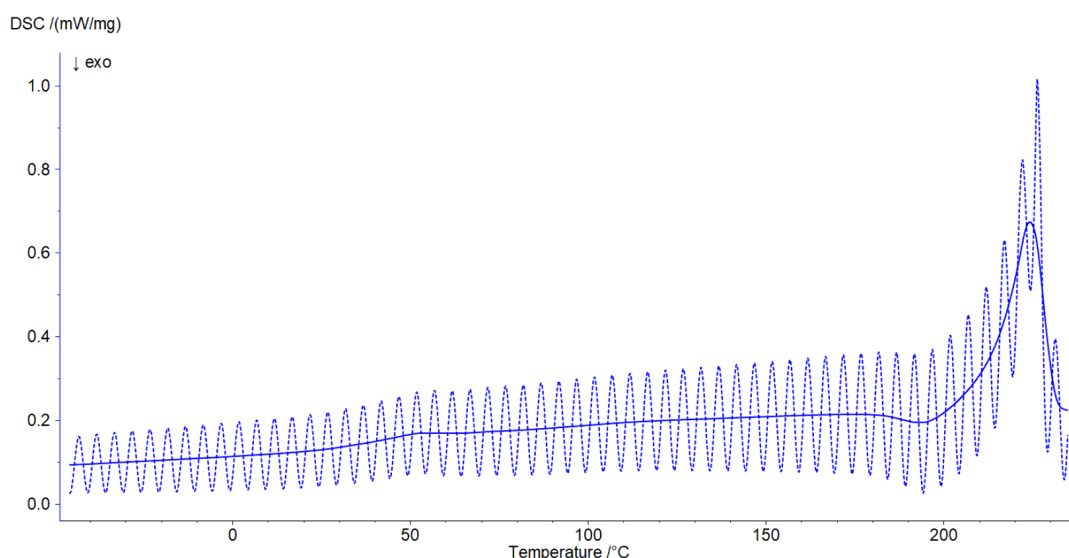
Figure 1 depicts the total heat flow of the sample with 1.2% humidity, which corresponds to a conventional DSC curve without modulation. The endothermic step at 38.8°C (midpoint) indicates the glass transition of polyamide 6. However, this evaluation is not accurate because the glass transition is overlapped with an endothermic peak, most probably due to the starting water release contained in the sample and from relaxation effects. Before melting takes place at 224.2°C (peak

temperature), the amorphous part of the PA6 crystallizes partly, explaining the exothermic peak at 193.3°C (peak temperature) in the DSC curve.

Figure 2 displays the total heat flow along with the raw DSC signal obtained during the temperature-modulated measurement. The total heat flow (continuous line) is equivalent to a standard DSC measurement, as described above. The raw signal (dashed line) shows how the material actually responds to temperature modulation.



1 PA6 with 1.2% humidity; DSC measurement (total heat flow)



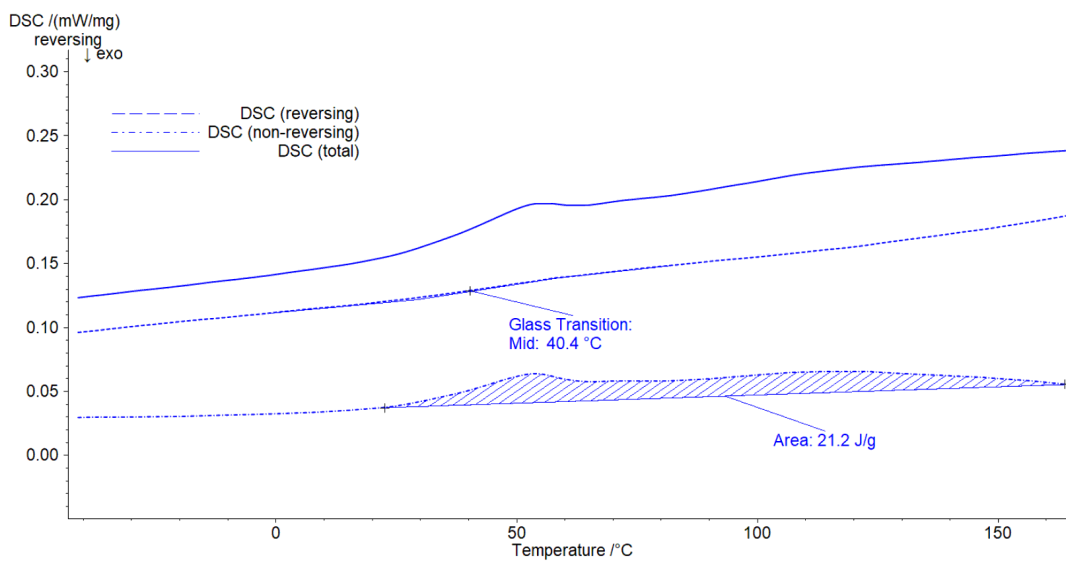
2 PA6 with 1.2% humidity; raw (dashed lines) and average (continuous) DSC signals during a temperature-modulated measurement

In figure 3, the total heat flow is separated into a reversing and a non-reversing part. This allows for separation of the glass transition and the evaporation peak. The glass transition is detected in the reversing part of the DSC signal and the evaporation effect in the non-reversing part.

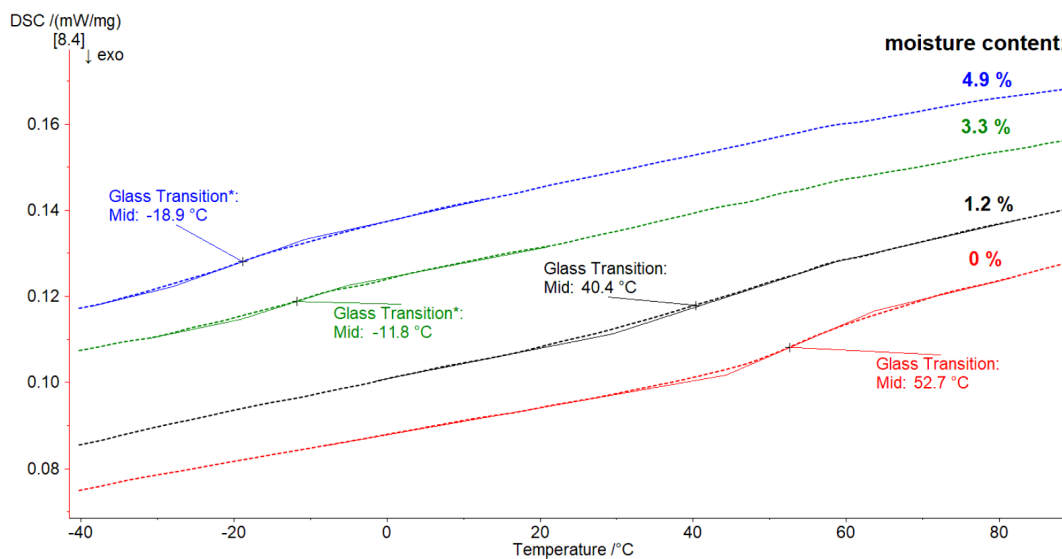
Subsequently, the glass transition is evaluated accurately (midpoint at 40.4°C). The non-reversing signal, however, highlights that the endothermic peak is much wider than initially assumed. This effect due to relaxation and evaporation is related to an enthalpy of 21.2 J/g.

### Influence of Humidity on the Glass Transition Temperature of PA6

Figure 4 shows the reversing signal of the different samples. The higher the moisture content, the lower the glass transition temperature. There is more than 70°C difference between the glass transition of the dry sample and the PA6 containing 4.9% water.



3 PA6 with 1.2% humidity; separation of the total heat flow into reversing and non-reversing signals



4 PA6 with differing degrees of humidity; reversing signals

## Conclusion

Due to their hygroscopic nature, polyamides absorb humidity from their environment. This, in turn, influences the properties and hence processing of the material. Even a small amount of water in PA6 will drastically decrease its glass transition. For this reason, the moisture content of the sample is an essential parameter to check and control.

A reliable and fast way to proceed is to perform temperature-modulated DSC measurements with the DSC 300 Caliris®.

## Sources

- [1] On the structure and properties of polyamides. XXVII. The mechanism of Water sorption in polyamides, R. Puffr, J. Šebenda, J. Polym. Sci. Part C: Polym. Symp., 16 (1967), pp. 79-93, 10.1002/polc.5070160109
- [2] Moisture absorption by various polyamides and their associated dimensional changes, L. Monson, M. Braunwarth, C. W. Extrand, Journal of Applied Polymer Science, Volume107, Issue1, 2007, Pages 355-363
- [3] Determination of moisture gradients in polyamide 6 using StepScan DSC, A. Sambale, M. Kurkowski, M. Stommel, Thermochimica Acta Volume 672, February 2019, Pages 150-156
- [4] Précis de matières plastiques, Alexandre Dobraczynski, Michel Piperaud, Jean-Pierre Trotignon, Jacques Verdu, Afnor-Nathan (2006)
- [5] Varun Venoor, Jay Hoon Park, David O. Kazmer & Margaret J. Sobkowicz (2021), Understanding the Effect of Water in Polyamides: A Review, Polymer Reviews, 61:3, 598-645, DOI: 10.1080/15583724.2020.1855196
- [6] ISO 19935-1:2018: Plastics – Temperature-modulated DSC, Part 1: General principles