APPLICATION**NOTE**

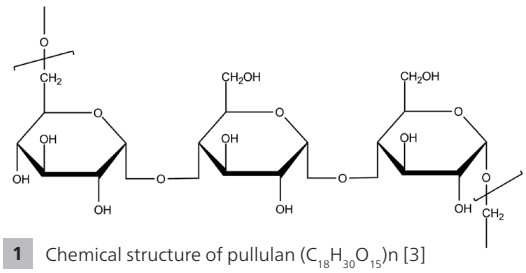
How Stable is Pullulan? TGA-FT-IR Provides Fast Answers.

Claire Strasser

Introduction

Pullulan is a linear polysaccharide polymer consisting of maltotriose units. It has applications in several industrial sectors such as the pharmaceutical, food and cosmetic industries. As an edible, mostly tasteless polymer, the main commercial use of pullulan is in the manufacture of edible films that are used in various breath freshener or oral hygiene products. As a food additive, it is known as E1204 (E stands for European license number). Pullulan is produced in a biotechnological process [1, 2].

In the following, the thermal stability of pullulan was investigated by means of TGA coupled to FT-IR.



1 Chemical structure of pullulan $(C_{18}H_{30}O_{15})n$ [3]

Measurement Conditions

Pullulan (9.42 mg) was prepared in an open alumina crucible and measured in the TG 209 ***F1*** *Libra*® thermobalance. The sample washeated to 600°C at a controlled heating rate of 10 K/min under a dynamic nitrogen atmosphere (40 ml/min). The gases evolved during heating were directly transferred into the FT-IR spectrometer by Bruker Optics GmbH. Use of the NETZSCH *PERSEUS* coupling allowed for a short gas transfer. This coupling interface does not require a separate transfer line as conventional coupling systems do. A heated tube connects the built-in heated gas cell directly to the gas outlet of the TGA furnace. The low volume of the short gas path guarantees fast response and minimizes the risk of condensation of the gases released.

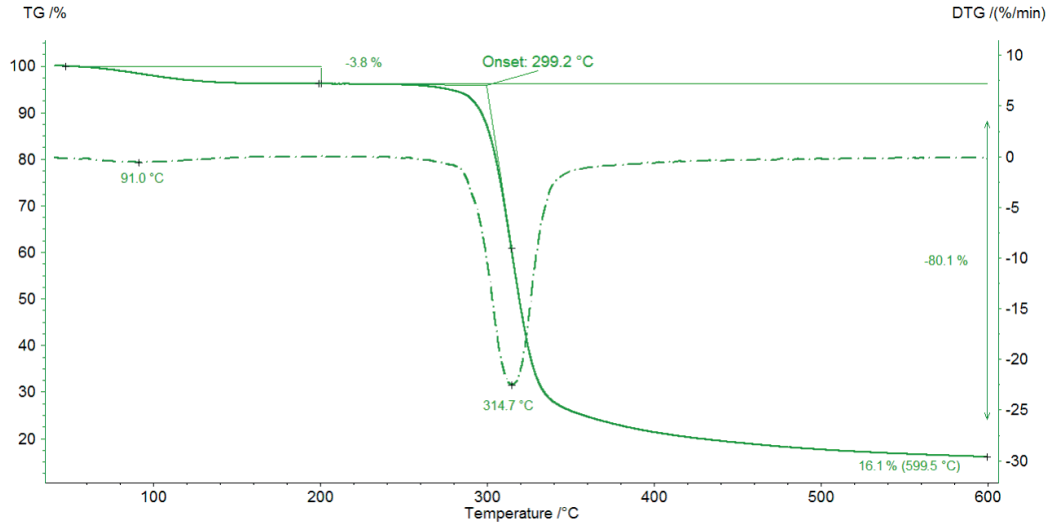
NGB · Application Note 124 · EN · 0418 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

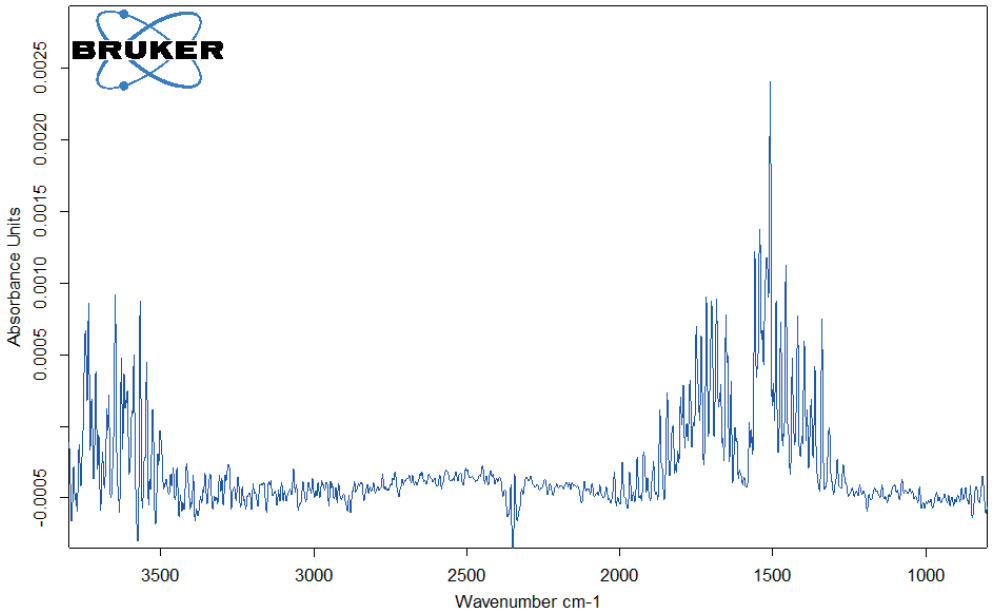
NETZSCH

Measurement Results

Figure 2 depicts the TGA curve of pullulan during heating to 600°C. The first mass loss amounts to 3.8% and is associated with the release of water, as confirmed by the FT-IR spectrum at 90°C (figure 3). The low temperature of this process indicates that it is surface water.



2 TGA curve (solid line) of pullulan: heating to 600°C and its first derivative, DTG (dash-dotted line)

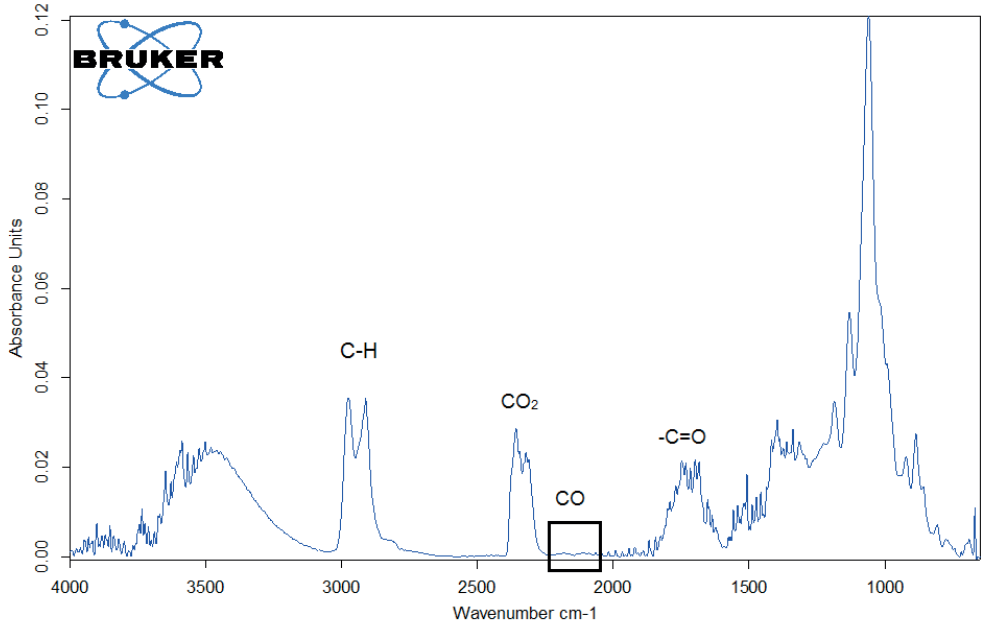


3 Characteristic FT-IR spectrum for water, detected at 90°C. The negative band at approximately 2300 cm^{-1} (CO_2) comes from the subtraction of the background spectrum.

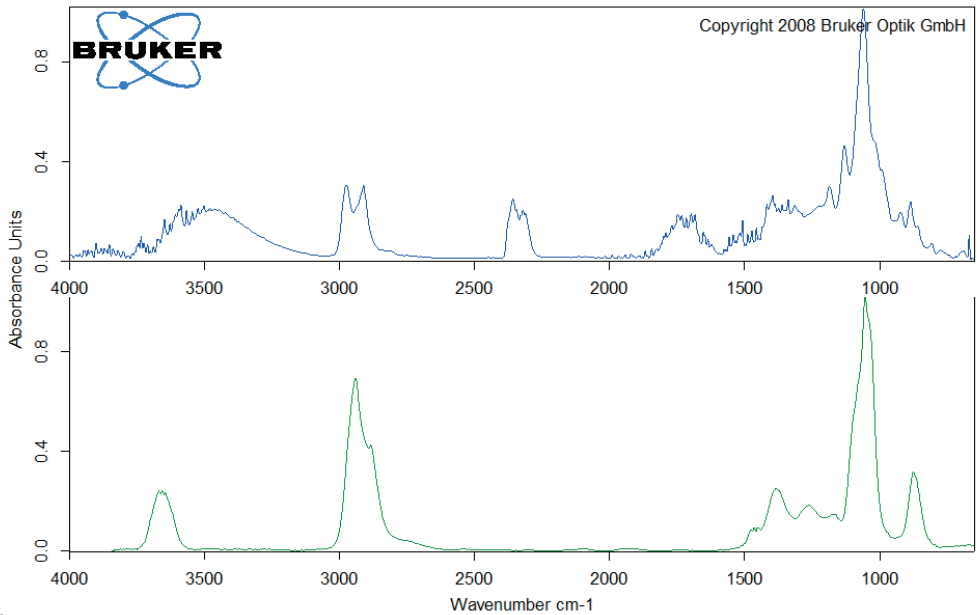
NGB · Application Note 124 · EN · 0418 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

Decomposition of the sample begins at 299°C (extrapolated onset of the TGA curve) and yields a one-step mass loss of 80% between 200°C and 600°C. Figure 4 shows the FT-IR spectrum of the products released at 315°C. The double bands between 2300 cm^{-1} and 2500 cm^{-1} and between 2100 cm^{-1} and 2300 cm^{-1} indicate the presence in the gas phase of carbon dioxide and carbon monoxide, respectively. The bands detected below 3000 cm^{-1} and above 1000 cm^{-1} are typical for C-H bonds and C-O bonds, respectively. These peaks correspond to those of 1,2-ethanediol (see comparison spectrum in figure 5). This is a clear sign that the rings are breaking open and decomposition is taking place.



4 FT-IR spectrum of the products released at 315°C during heating of pullulan



5 FT-IR spectrum of the products released at 315°C (blue, top) in comparison with the EPA-NIST spectrum of 1,2-ethanediol (green, bottom)

NGB · Application Note 124 · EN · 0418 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

Conclusion

The TGA-FT-IR measurement of pullulan allows for determination of the thermostability: In an inert atmosphere, the substance starts decomposing at 299°C after the evaporation of its surface water. The decomposition is associated with the break-up of the rings, leading to the release of ethanediol.

Literature

[1] https://www.interesjournals.org/articles/pullulan-production-and-usage-in-food-ndustry.pdf → LINK
[2] https://en.wikipedia.org/wiki/Pullulan
[3] https://en.wikiedia.org/wiki/Pullulan#media/File:Pullulan.png

NGB · Application Note 124 · EN · 0418 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com