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Kraft lignin — Glass transition temperature by differential scanning calorimetry

Thiolignine — Température de transition vitreuse par analyse calorimétrique différentielle

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by CSA (as CSA W206:20) and drafted in accordance with its editorial rules. It was assigned to Technical Committee(s) ISO/TC 6, *Paper, board and pulps*, and adopted under the "fast-track procedure".

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Lignin exists naturally in plants and trees and is one of the main components in wood. Given its abundance and its aromatic structure, lignin has the potential to replace fossil-based starting materials in a range of products including polymeric materials and fine chemicals. It is currently being evaluated by companies around the world as an alternative to petroleum-based chemicals for products such as carbon fibres, flavour and pharmaceutical ingredients, resins, foams, rubber additives, and thermoplastics.

The majority of world commerce is governed by regulations-based product standards. An absence of standards for products and properties therefore limits market access. With international interest and ongoing work in developing and commercializing new products from lignin, a strong knowledge of the physicochemical properties of lignin including chemical structure, molecular weight (MW) distribution, and thermal properties is required.

The glass transition temperature (T_g) of an amorphous material including lignin is used to determine the softening point and to speculate on the level of crosslinking when processing these materials at elevated temperatures. It is of special relevance in the drying of lignin as well as in determining suitable processing conditions for lignin in a range of chemical and polymer industry processes.

The present method aims to provide a standardized method to measure the glass transition temperature of kraft lignins for various applications. It will provide lignin producers and manufacturers an advantage to improve access to the lignin and lignin derivatives marketplaces globally.

Kraft lignin — Glass transition temperature by differential scanning calorimetry

1 Scope

This document describes a method for the determination of the glass transition temperature (T_g) of kraft lignin. The procedure utilizes differential scanning calorimetry (DSC).

This procedure is applicable to solid lignins (e.g., powdered form) isolated using different isolation techniques (e.g., acidification with hydrochloric acid, sulfuric acid, etc., and carbonation using gaseous carbon dioxide) from the spent liquor (black liquor) generated from the kraft pulping process.

It does not apply to raw black liquor and lignin in the alkali form, (lignin that is separated from wood chips and dissolved in sodium sulfide and sodium hydroxide liquor such as that originating from black liquor).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4582:2017, *Plastics — Determination of changes in colour and variations in properties after exposure to glass-filtered solar radiation, natural weathering or laboratory radiation sources*

ISO/TS 24498:2022, *Paper, board and pulps — Estimation of uncertainty for test methods by interlaboratory comparisons.*

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
glass transition temperature, Tg
Temperature at which an amorphous material transitions from a glassy state to a rubbery state, determined as the point on the heat flow curve corresponding to half the heat flow difference between the onset and offset temperatures of the transition.

Note 1 to entry For an example on how to determine the Tg, see Figure 1.

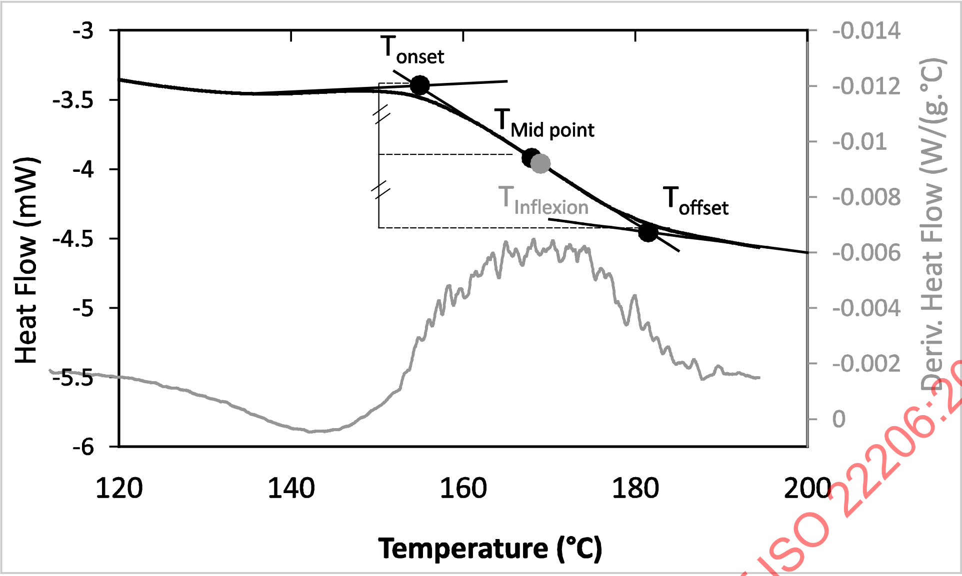

Figure 1 — Determination of glass transition temperature (Tg) see Clause 3.1.

3.2
heat capacity change
The difference between the heat capacity of the sample at the onset and offset temperatures.

3.3
kraft lignin
Depolymerized and chemically modified lignin isolated from a kraft pulping process, such as that originating from kraft black liquor laboratory sample.

3.4
laboratory sample
Total quantity of a type of material from a unique batch, available for testing and evaluation [prepared from a specific source using a specific procedure (e.g., a hardwood kraft lignin)]. It must be representative of the batch.

3.5
lignin
Class of complex, organic molecules, containing aromatic subunits that play a key role in the formation of cell walls in wood and bark, conferring mechanical strength and rigidity to the cell walls and to plants as a whole. Lignin is the main non-carbohydrate constituent of wood.

3.6
onset and offset temperatures (T_{onset}, T_{offset} respectively)
Temperatures corresponding to the intersection of the maximum slope tangent of the transition curve with the extrapolated baselines before and after the transition, respectively. The extrapolation is done from the beginning to the end of the relatively flat regions of the heat flow vs temperature curves as indicated by the derivative of the heat flow vs temperature curves. The temperature increment that is used is determined by the heating and cooling rates as mentioned in section 9.2.3 core cycle.

3.7
replicate specimens
Identical pieces of test material being evaluated which are all exposed, conditioned, and tested at the same time.

3.8
test sample
Portion of material taken from the laboratory sample after, for example, homogenizing, which is then prepared for testing or evaluation.

3.9
test specimen
Specific portion of the material upon which testing is being performed.

4 Principle

The DSC method is used to measure the glass transition of a lignin sample by annealing the material in a first cycle, and then by increasing the temperature at a constant rate to record the difference in heat flow of the sample compared to that of the reference (e.g., an empty pan). At the onset of the glass transition, the test material begins to absorb energy to mobilize the molecules in the material and the change in the heat flow curve is visible on the DSC graph. The T_g, represented by the inflection point and/or the mid-point, is calculated by the instrument software.

5 Apparatus

The following apparatus shall be used for this protocol:

5.1 Differential scanning calorimeter

A differential scanning calorimeter or combined DSC/TGA instrument.

5.2 Pans and lids (pierced lids) inert to the test sample

Example is aluminum crucibles.

NOTE If the lid does not have a pinhole (i.e., the pan is a hermetic one), one must be pierced when the lid is placed on the pan.

5.3 Pressing tool

A pressing tool for the pan and lid.

5.4 Analytical balance

Analytical balance accurate to 0,01 mg.

5.5 Drying oven

Drying oven with temperature control of (105 ± 2) °C.

5.6 Desiccator

Desiccator using Drierite™ or equivalent desiccant.

5.7 Inert purge gas

Gas such as helium, nitrogen or other inert purge gas, with an oxygen content of 0.001% (v/v) or less and a water content of less than 0,001% (w/w).

6 Sampling and test sample preparation

All samples and specimens shall be stored in a room-temperature desiccator at all times when not in use.

The test sample (1 g to 3 g) shall be representative of the whole sample material.

The operator shall:

a) Air-dry the lignin at ambient conditions until it reaches sufficient dryness to allow grinding if the initial lignin moisture content is too high for it to be ground;

b) Gently grind the laboratory sample with a mortar and pestle to homogenize the sample to a uniform powder;

c) Sieve the powder through a 200-mesh screen to ensure homogeneity;

d) Dry the test sample [1 g to 3 g of 200-mesh (P200) lignin powder] to constant mass at 105 °C; and

e) Cool to room temperature in a desiccator.

NOTE If a non-convection oven is used, make sure that the sample temperature is at 105 °C when it is in the oven.

7 Test specimen preparation

The operator shall:

a) Weigh an empty pan with a lid, record the mass, and tare the balance;

b) Add 3 mg to 10 mg of test sample (the test specimen) to the pan ensuring that the minimum amount of material needed to completely cover the bottom of the pan is used [do not fill up to the top, an excess amount of sample reduces heat transfer]

c) Record the mass of the test specimen; and Push the lid onto the test specimen to seal it in order to limit contamination in the DSC chamber.

d) Ensure that the outer surface of the pan is clean and not contaminated with material; and

e) Use a clean pressing tool to push the lid into the pan and seal.

8 Calibration

The operator shall calibrate the DSC instrument according to the manufacturer's instructions.

NOTE Indium is the preferred reference material.

9 Procedure

9.1 Cleaning Cycle

The operator shall run a cleaning cycle of the DSC instrument before starting a new batch of lignin samples to avoid contamination from previous samples.

9.2 Analysis method

9.2.1 General

The entire procedure shall be carried out on at least three replicate test specimens.

9.2.2 Pre-Cycle

The following heating and cooling steps shall be conducted as a pre-cycle under inert pure N_2 gas medium:

a) Heat to [Td2% - 5°C]120 °C at 10 °C/min; and

b) Cool to 25 °C at 10 °C/min and then hold for 10 min.

9.2.3 Core Cycle

The following shall be conducted for core cycle under inert pure N_2 gas medium:

a) The measurement is performed by heating the test specimen under an inert atmosphere (N_2) from room temperature to [Td2% - 5°C]200 °C at 10 °C/min; and

b) If the T_g of the test sample is higher than 180 °C, the end temperature of the final temperature ramp is increased to T_g + 40 °C and repeated with a new test specimen.

10 Evaluation

The following evaluation shall be conducted:

a) The T_g is the inflection point provided by the instrument. If the instrument does not provide the inflection point, the mid-point shall be considered as the T_g.

b) If more than one inflection point appears on the curve, the highest temperature inflection point shall be reported.

c) The average value and standard deviation of three determinations shall be calculated for each sample. Temperatures are reported to the nearest integer.

11 Test Report

The test report shall include the following information:

a) A reference to the test method specified in this document, i.e. ISO 22206:2024;

b) The date and place of testing;

c) The mass of the sample tested;

d) A description of the instrument used for the test (DSC 25, TA instruments);

e) A brief description of the instrument calibration procedure;

f) Identification of the sample material tested;

g) The T_g value in °C and the standard deviation in °C; and

h) Information regarding any deviation from the standard procedures described in this test method and/or any other circumstances that might have affected the result.

Annex A
(informative)

Precision – Results of the round robin study

NOTE This Annex is not a mandatory part of this document.

In 2019, a round robin test was performed. Three samples, two softwood lignins and one hardwood lignin isolated from kraft black liquor, were used to determine the repeatability and reproducibility of this test method. Results from eight national and international laboratories are given in Table A.1.

The calculations were made according to ISO/TS 24498.

The repeatability and reproducibility limits reported are estimates of the maximum difference which would be expected in 19 of 20 instances, when comparing test results for material similar to those described under similar test conditions. These estimates may not be valid for different materials or different test conditions.

NOTE Repeatability and reproducibility limits are calculated by multiplying the repeatability and reproducibility standard deviations by 2.77, where $2.77 = 1.96\sqrt{2}$.

Table A.1 — Determination of glass transition temperature (Tg)

Sample	**Number of laboratories**	**Grand mean value (°C)**	**Repeatability standard deviation, *Sr* (°C)**	**Repeatability limit, *r* (°C)**	**Reproducibility standard deviation, *SR* (°C)**	**Reproducibility limit, *R* (°C)**
SW-1	8	168	4.0	11.1	12.5	34.6
SW-2	8	152	2.3	6.4	4.9	13.6
HW-1	8	150	2.9	8.0	9.7	26.9