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Faculty of Exact Sciences
Department of Materials Science

Academic Year: 2025/2026
Level: 1st Year Master's in Materials Chemistry
Module: Thermal Analysis Methods

Exam (2h)

Full Name	Mark
....	....

Exercise 1– Choose the correct answer(s)

1. In thermogravimetric analysis (TGA), which of the following quantities is plotted directly as a function of temperature or time?

0,5

- [x] Sample mass or mass percentage
- [ ] Sample enthalpy change
- [ ] Temperature difference between sample and reference
- [ ] Sample dimensional change (length or volume)

2. A polymer shows a clear step change in baseline in a DSC heating curve without any associated peak. What process is most likely responsible?

- [ ] Melting
- [ ] Crystallization on heating
- [ ] Thermal decomposition with mass loss
- [x] Glass transition

0,5

3. During a TGA run in air, a carbon–filled polymer sample first shows a mass loss, then a later mass gain at higher temperatures. What is the most plausible explanation for the mass gain?

0,5

- [x] Adsorption or formation of oxides with higher molar mass
- [ ] Evaporation of residual moisture at high temperature
- [ ] Oxidation of residual carbon to gaseous CO_2
- [ ] Instrumental drift of the balance

4. In differential scanning calorimetry (DSC), which experimental setup best minimizes thermal lag when measuring a sharp first–order phase transition at high heating rates?

0,5

- [x] Using a small, shallow crucible with low thermal resistance and moderate sample mass
- [ ] Using a large, deep crucible and maximizing sample mass
- [ ] Increasing purge gas flow rate while keeping a very low sample mass in a large pan
- [ ] Using a hermetically sealed high–pressure pan filled to capacity

5. Which statement best distinguishes DSC from DTA in terms of what is actually measured?

- ☐ DSC measures dimensional change while DTA measures mass change
- ☐ Both DSC and DTA measure only the sample temperature
- ☐ DSC measures mass change while DTA measures heat flow
- 0,5 ☒ DSC measures heat flow, DTA measures temperature difference

6. In thermogravimetric analysis (TGA), which change in method most directly improves the resolution of overlapping mass–loss steps for a complex multi–component material?

- 0,5 ☒ Reducing the heating rate and using derivative thermogravimetry (DTG) analysis
- ☐ Increasing the heating rate from 10 K/min to 40 K/min
- ☐ Loading a larger sample mass to increase signal strength
- ☐ Switching from nitrogen to air as the purge gas at the same heating rate

7. Which of the following best describes the effect of a higher heating rate on a TGA curve?

- ☐ Shifts decomposition onset to lower temperature
- 0,5 ☒ Shifts decomposition onset to higher temperature
- ☐ Eliminates mass-loss steps
- ☐ Doubles all mass losses

8. A small mass loss below about 100 °C is most often related to:

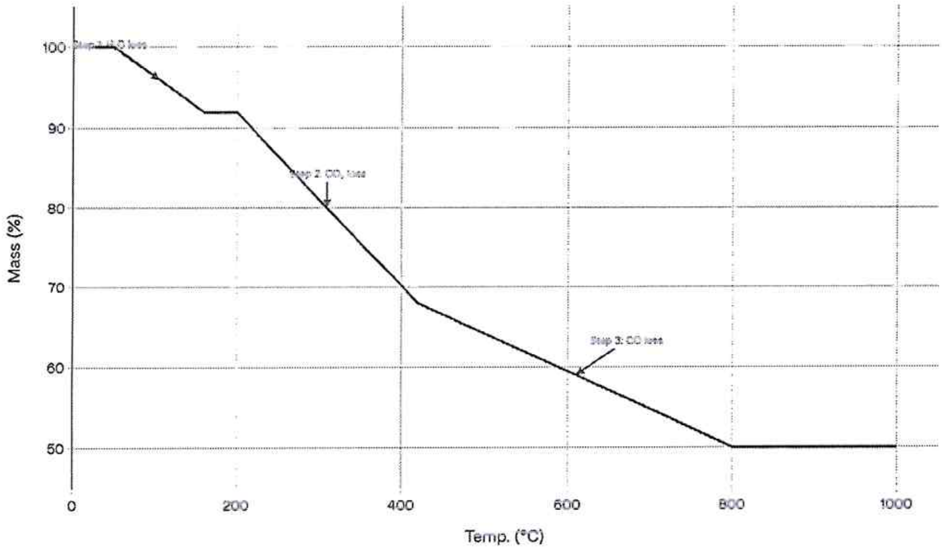
- ☐ Melting
- ☐ Glass transition
- ☐ Decomposition of the main matrix
- 0,5 ☒ Loss of moisture or residual solvent

Exercise 2 – TGA of a Hydrated Salt

A hydrated salt $MX \cdot yH_2O$ is analyzed by TGA from room temperature to 1000 °C in nitrogen at 10 °C/min. The TG curve shows three mass–loss steps:

- Step 1: 8.0% between 50–160 °C.
- Step 2: 24.0% between 200–420 °C.
- Step 3: 18.0% between 420–800 °C.
- Final residue at 1000 °C: 50.0% of the initial mass.

Given: M(MX) (anhydrous) = 200 g·mol⁻¹. Assume the successive losses correspond to: first water H_2O, then CO_2, then CO.



1. Determine the hydration number y of $MX \cdot yH_2O$ using the first step and justify your calculation.

$M(MX.yH_2O) = 200 + 18y$

$(MXyH_2O)\ 200 + 18y \longrightarrow 100\%$ | $1800y = 1600 + 144y$

$(H_2O)\ 18y \longrightarrow 8\%$ | $y = 1{,}035 \simeq 1$

the hydration number is $\boxed{y = 1}$ (1)

$MX.H_2O$

2. Calculate the theoretical mass percentage corresponding to the loss of 1 mole of H_2O, 1 mole of CO_2, and 1 mole of CO for this compound, and compare with experimental data.

$M_{tot} = 200 + 18 = 218\ g/mol$

1 mol H_2O : $\%m(H_2O) = \frac{18}{218} \times 100 = \boxed{8{,}26\%}$ (0,5)

1 mol CO_2 : $\%m(CO_2) = \frac{44}{218} \times 100 = \boxed{20{,}18\%}$ (0,5)

1 mol CO : $\%m(CO) = \frac{28}{218} \times 100 = \boxed{12{,}84\%}$ (0,5)

1. Explain, using the concepts of inert vs oxidizing atmosphere, why the degradation profile is simpler in N_2 than in air.

0,5 . In N_2 (inert atmosphere): the polymer decomposes primarily by pyrolysis in a single major step, then form a stable char (20% residue)

0,5 . In air (oxiding atmosphere): in addition to pyrolysis, there is oxidation of the fragments and that char residue generating several degradation steps and almost no final residue

2. For the experiment in air, suggest possible assignments for the three mass–loss steps (e.g. degradation of different polymer fractions, oxidation of char).

0,5 1st step: (~250°C) decomposition of the most unstable parts (side groups, plasticizers, ...)

0,5 2nd step: (~380°C): main degradation of the polymer chain formation of char.

0,5 3rd step (~480°C) oxidation of the residual carbon char to CO/CO_2, leading to the near complete disappearance of the residue

3. Discuss how DTG curves could help distinguish the three steps more clearly and indicate at least one advantage of DTG representation.

0,5 DTG curve shows peaks at maximum mass loss rates, wich better separates the overlapping stages on TG curve.

Avantage:

0,5 - Allows for precise identification of peak temperatu and the start/end ~~the~~ temperature of each stage

. the comparaison of similar degradation processes and the evaluation of Kenetic effect.

4. The same polymer is now tested at 5 °C/min in air. Predict qualitatively how the onset temperatures of the main mass–loss steps will change and explain why, with reference to heating–rate effects.

By decreasing the heating (from 10 to 5°C/min), the starting temperature of the stages shift to lower values. the system has more time to react to each temperature change so, decomposition begins earlier, reducing lag and improving stage resolution

0,5

Exercise 4 – Dilatometry and Glass Transition

A polymer specimen (initial length $L_0 = 20.000$ mm at 25 °C) is analyzed by push–rod dilatometry from 25 °C to 150 °C. The following data are obtained:

Temperature (°C)	Length (mm)	ΔL	$\Delta L/L_0$
25	20.000	0,000	0,000
50	20.015	0,015	$0,75 \times 10^{-3}$
75	20.028	0,028	$1,40 \times 10^{-3}$
90	20.036	0,036	$1,80 \times 10^{-3}$
100	20.052	0,052	$2,60 \times 10^{-3}$
125	20.084	0,084	$4,20 \times 10^{-3}$
150	20.106	0,106	$5,30 \times 10^{-3}$

0,25 x 14

= 3,5

From previous DSC measurements, T_g is expected near 90 °C.

1. Calculate ΔL and $\Delta L/L_0$ at each temperature and tabulate the values. (In table)
2. Using the numerical data, estimate the average CTE below T_g (25–75 °C) and above T_g (100–150 °C) using $\alpha = \frac{\Delta L}{L_0 \Delta T}$.

below Tg (25-75°C) $\Delta T = 75 - 25 = 50$°C

$\Delta L = 20,028 - 20,000 = 0,028$ mm $\alpha_{below} = \frac{0,028}{20 \times 50} = \boxed{2,8 \times 10^{-4}\ °C^{-1}}$ 0,5

Above Tg (100 – 150) : $\Delta T = 150 - 100 = 50$°C

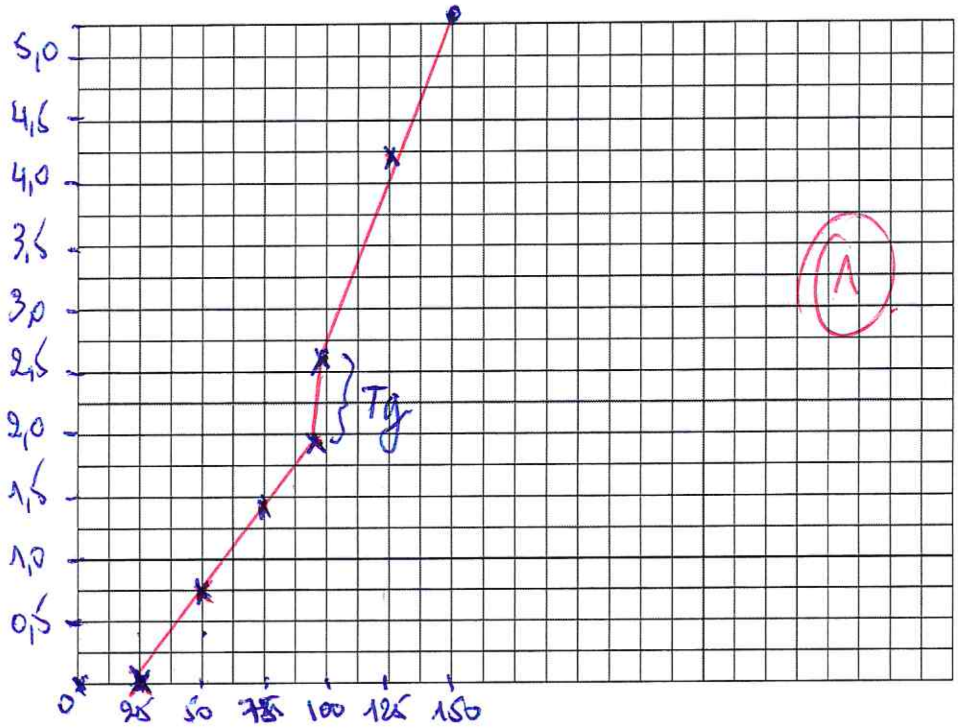
$\Delta L = 20,106 - 20,052 = 0,054$ mm

$\alpha = \frac{0,054}{20 \times 50} = \boxed{5,4 \times 10^{-4}\ °C^{-1}}$ 0,5

the CTE is approximately doubled above Tg

3. Identify the approximate glass transition temperature from the change of slope in the $\Delta L/L_0$ vs T plot and compare it to the DSC value.

the marKed change in slope around 90°C 0,5
in good areement with the value obtained by DSC.



4. Briefly explain, in terms of polymer microstructure and molecular mobility, why the CTE is different below and above T_g.

BelowTg = the polymer chains are fixed, in glassy state with very limited segmental mobility, the free volume is small, therefore the thermal expansion coefficient (CTE) remains relatively Low.
0,5

Above Tg = the chain segments gain mobility, the polymer transitions to a rubbery / viscoelastic rubbery state, and the free volume increase more rapidly with temperature, CTE is higher, as the chains can reorganize and spread further apart upon heating
0,5