Lecturer

- Dónal Leech
- Room C205 (in Physical Chemistry)
- E-mail: donal.leech@nuigalway.ie
- Phone: 493563 (from outside), ext 3563 (internal phones)

Web-site:
http://www.nuigalway.ie/chemistry/staff/donal_leech/teaching.html

Lecture Resources

- Main Text:

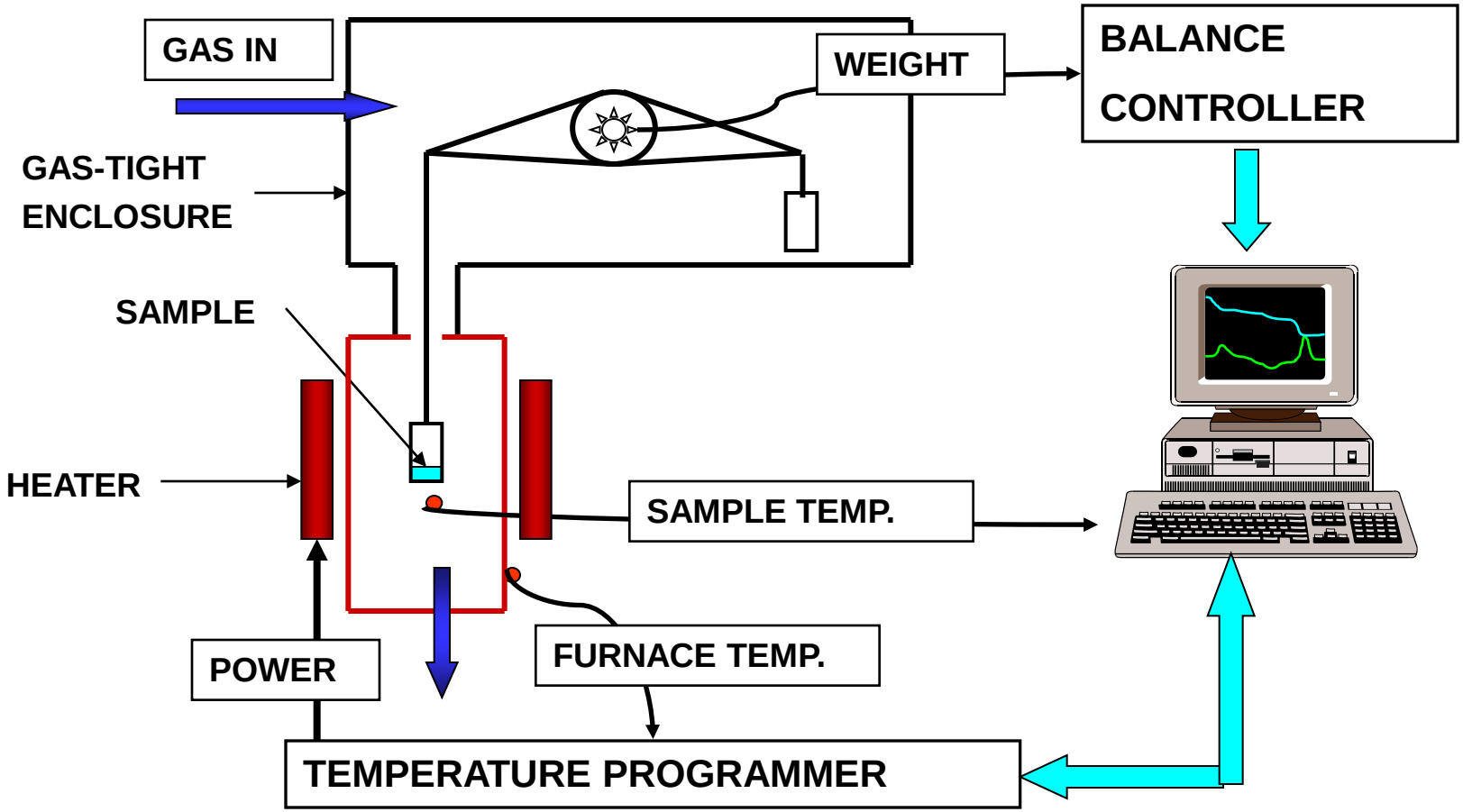
  "Thermal Methods of Analysis"

  Haines (Desk reserve)

Thermogravimetry (TG)

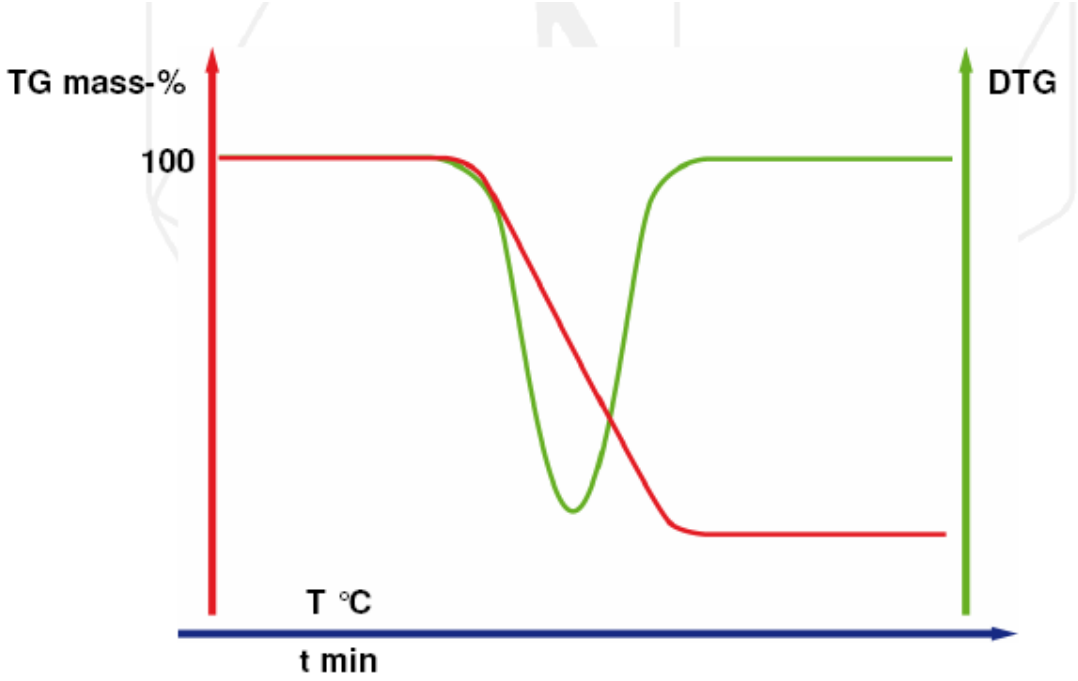
- Simplest
- Need precision balance, programmable furnace and signal output (chart recorder or PC).

Thermobalance



Method

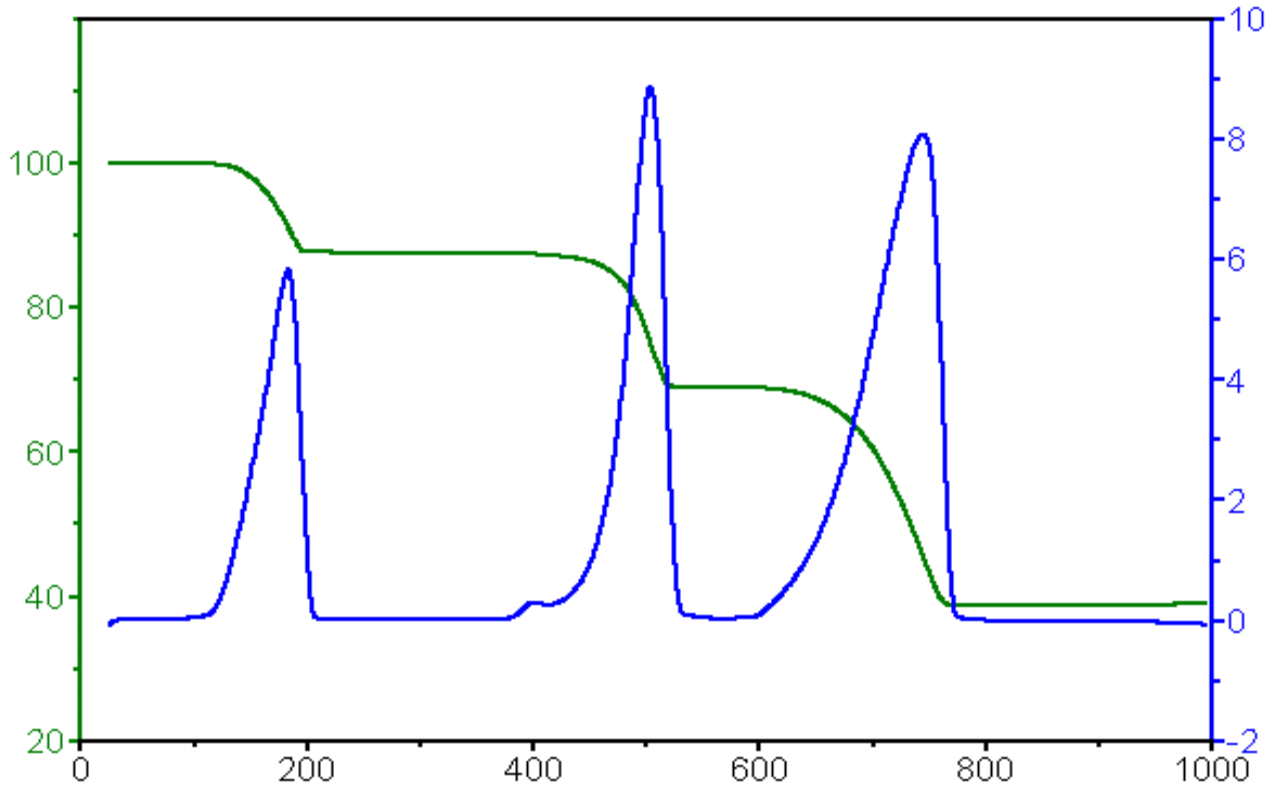
- Sample is heated in an oven with a specific heat rate and up to a defined temperature under a defined atmosphere
- Measured is the mass change of the sample during heating
- Simultaneously differential thermogram, DTG = d*m(T)*/d*t* (*or* d*T*) is recorded
- DT is plotted against temperature and/or time



Applications

- Stability and purity of standards
- Drying temperature selection
- Water of crystallisation determination
- Composition of binary mixtures
- Polymer degradation
  - Evolved gas analysis

Example curve

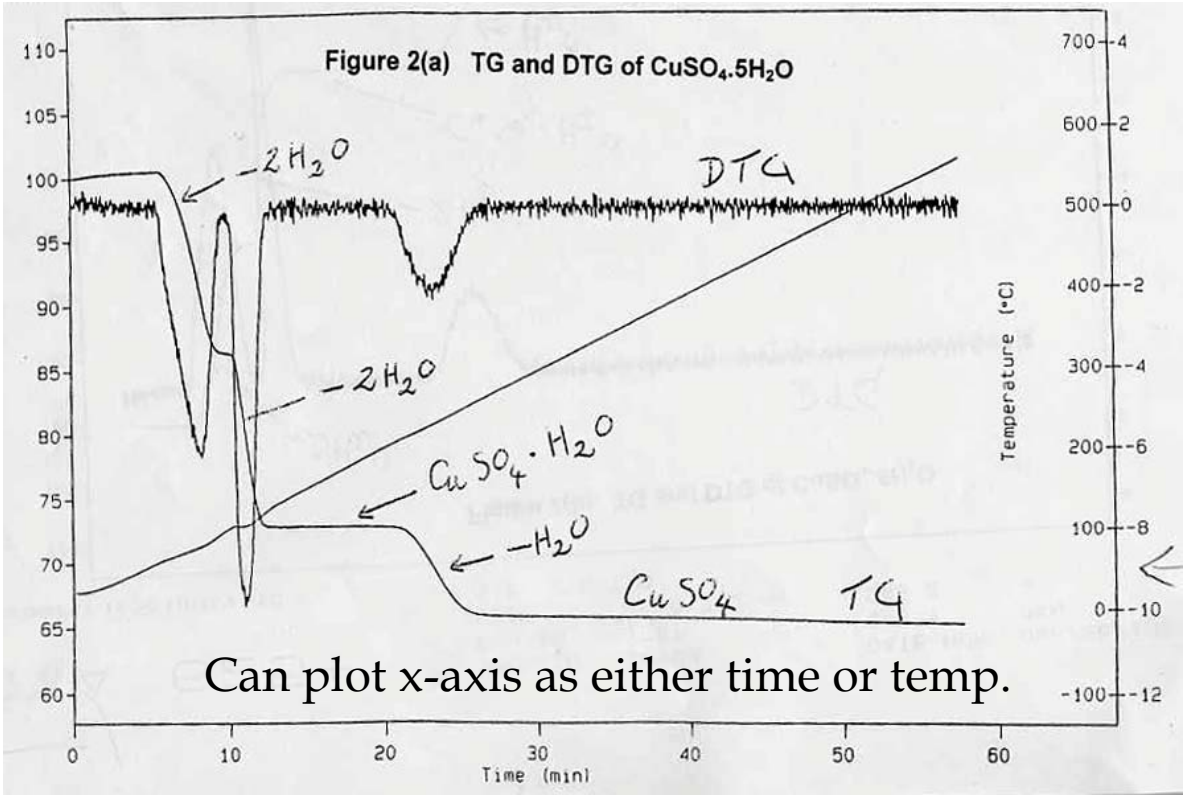


Mass (%) in green, rate of mass loss (%/°C) in blue.

$CuSO_4.5H_2O$ thermograms

- Copper sulphate pentahydrate
- No mass change in plateau regions of curves
- Curved portions represent mass loss
- TG is quantitative: can calculate stoichiometry

Can plot y-axis as either mass or %mass,

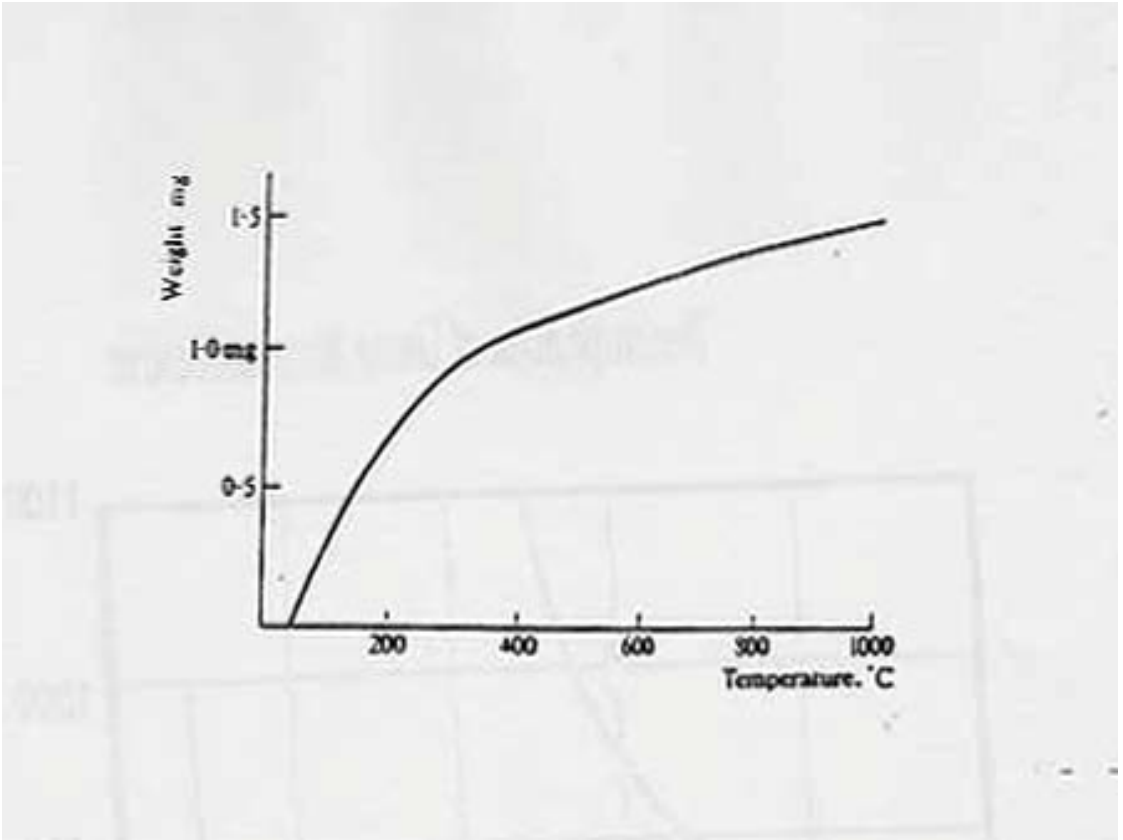


DTG y-axis can be rate of change of mass with either Temp. or time

Main advantage in DTG is resolution of closely spaced mass losses

TG Considerations

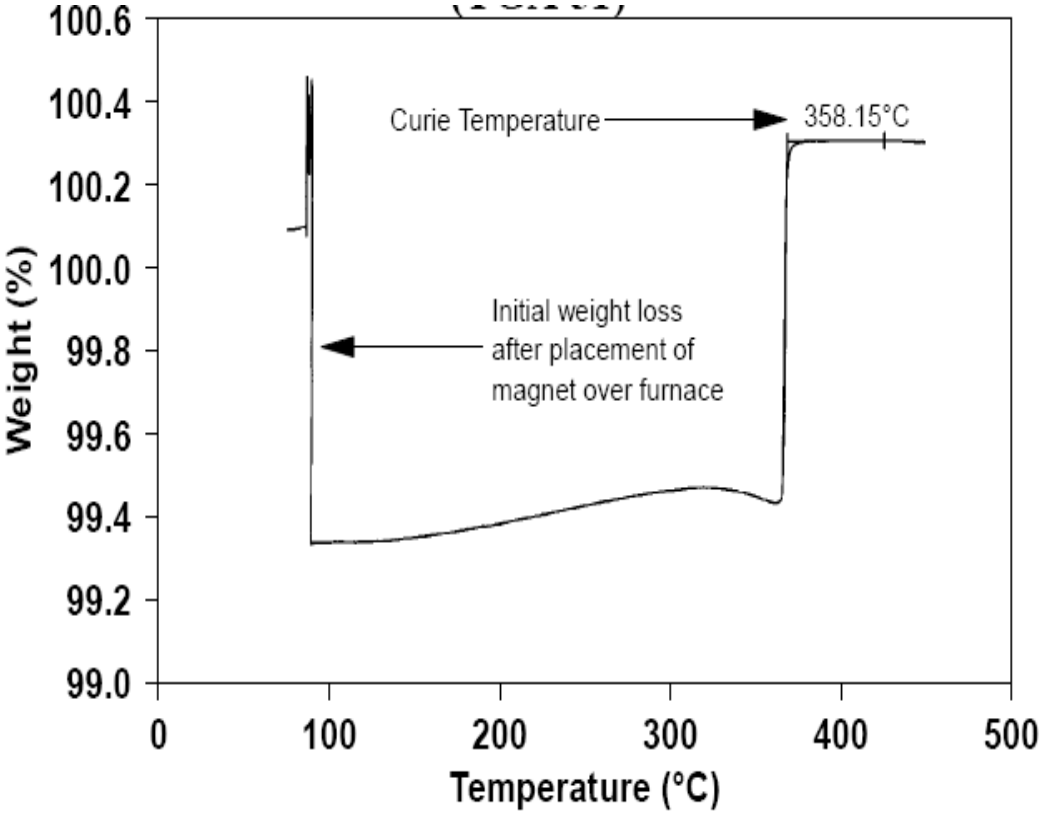
- Correction curves
  - Related to mass gain of the sample container (crucible, usually Pt – based….why?)
  - Correct using curves (old way) like that below
  - Correct automatically in instrument (use reference)



Calibration

- weight calibration using calibrated weights

- temperature calibration based on ferromagnetic transition of Curie point standards (e.g., Ni)
  - TGA temperature calibration is most commonly accomplished using melting point standards. However, a second calibration method exists which utilizes the magnetic transition of ferromagnetic materials.
  - In this procedure, a magnetic material is placed inside an empty, pan located near a strong magnet. The material is then heated. At the Curie Temperature, the magnetic properties disappear (i.e., the material goes from diamagnetic to paramagnetic) and thereduced attraction for the magnet results in a sharp apparent weight loss or gain

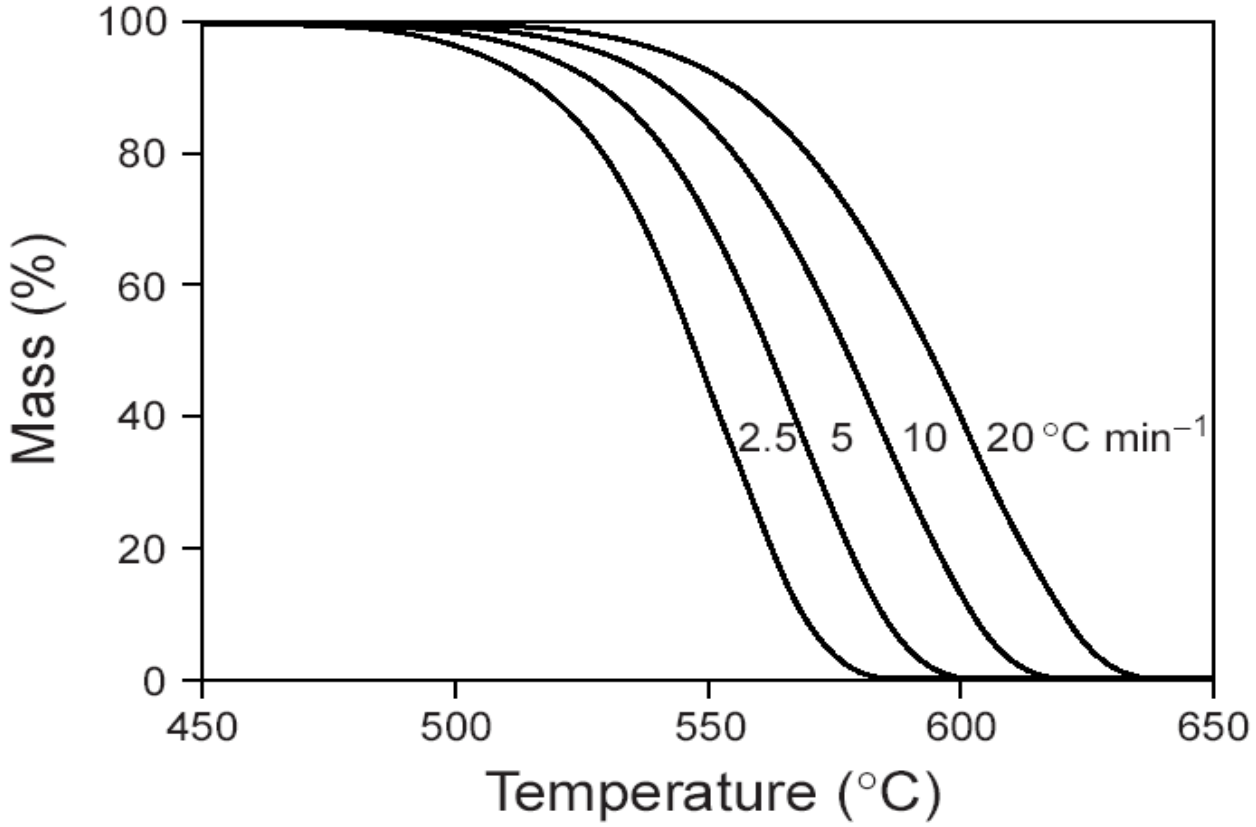


TG Considerations

- Heating rates
- Furnace atmosphere
- Crucible and furnace geometry

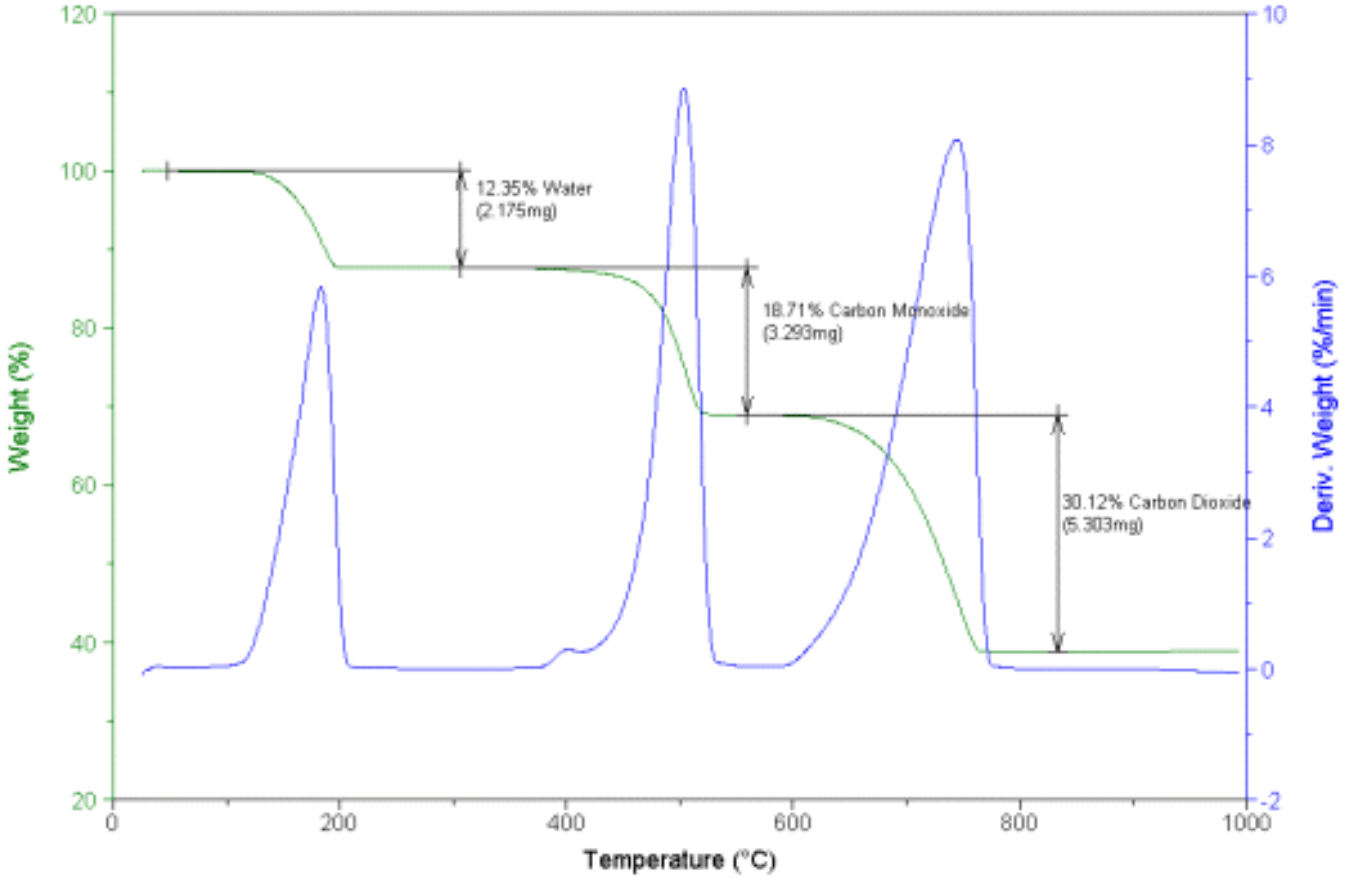
- Sample characteristics
  - Best to use small sample sizes (mg) and particle sizes (grinding)

Effect of heating rate



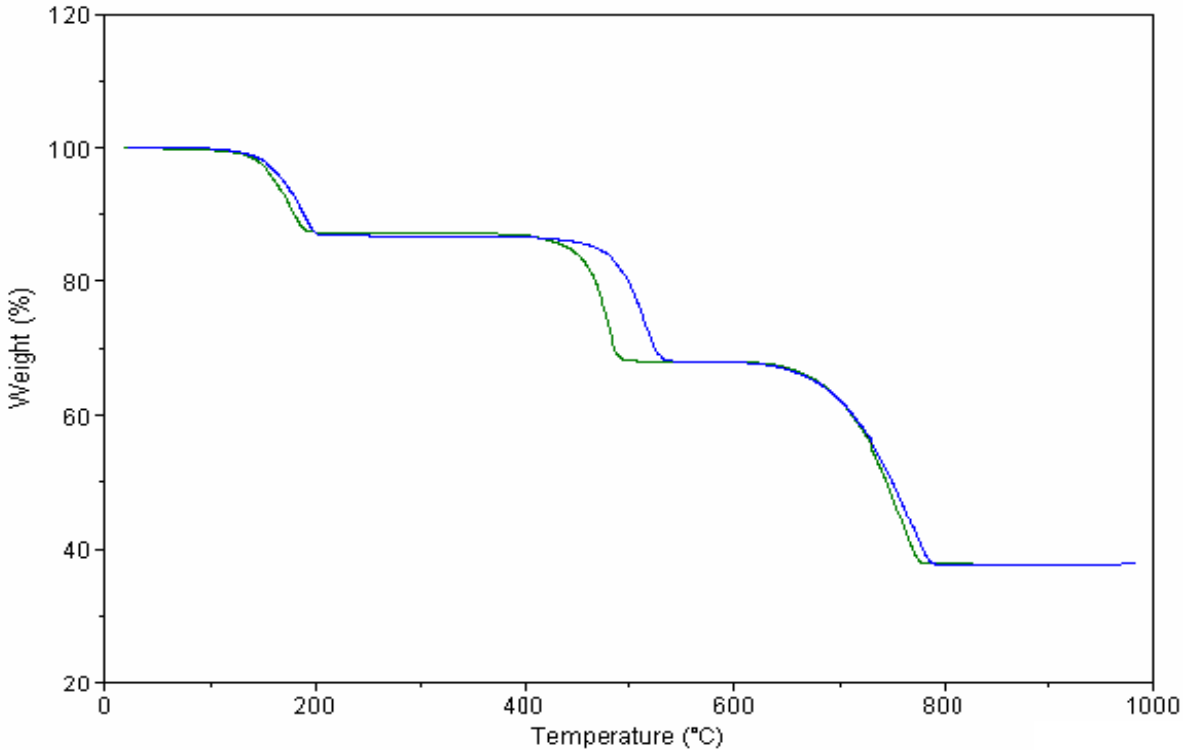
10 mg samples of PTFE, heated at 2.5, 5, 10 and 20 °C/min in nitrogen

Example of TGA. Calcium oxalate monohydrate



RMM 146: Theoretical loss of water: 18/146 = 12.3%
Theoretical loss of CO: 28/146 = 19.2%
Theoretical loss of CO_2: 44/146 = 30.1%

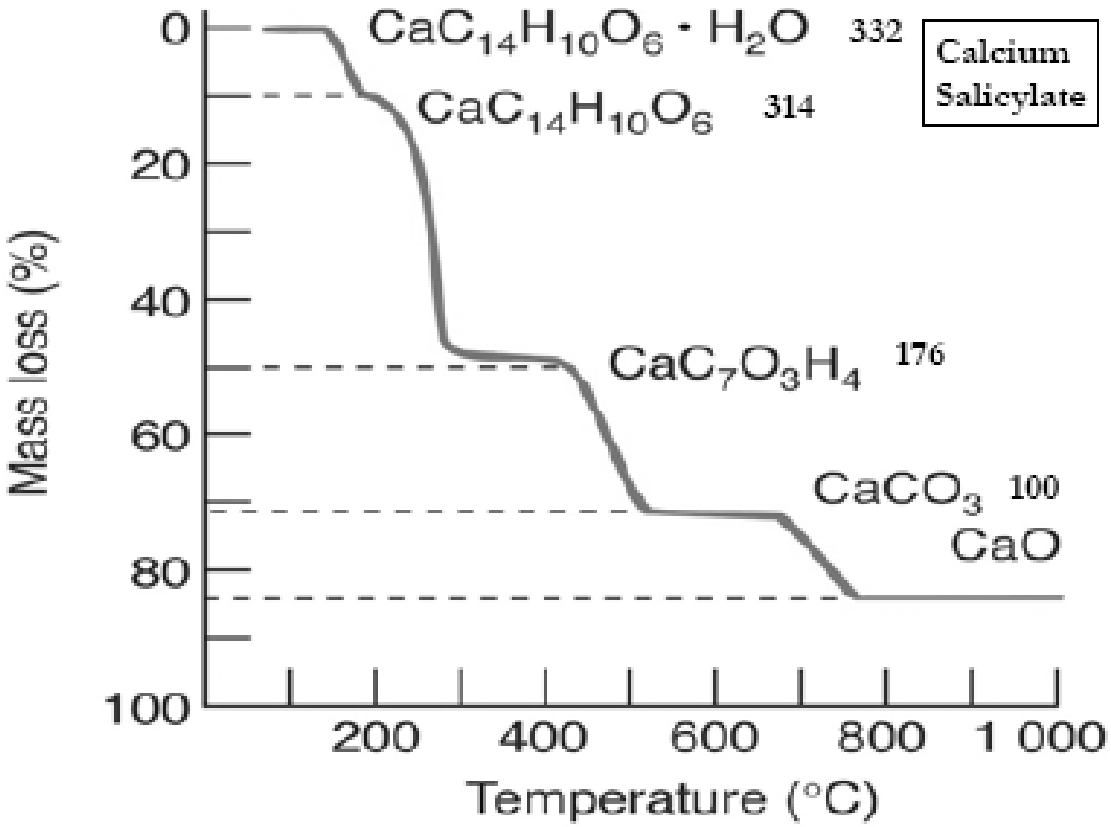
effect of atmosphere



$CaC_2CO_4.H_2O$ in air and nitrogen

CO transformation to CO_2 in air exothermic

Degradation of calcium salicylate



$CaC_{14}H_{10}O_6 \cdot H_2O$

↓

$CaC_{14}H_{10}O_6$

↓

$CaC_7H_4O_3$

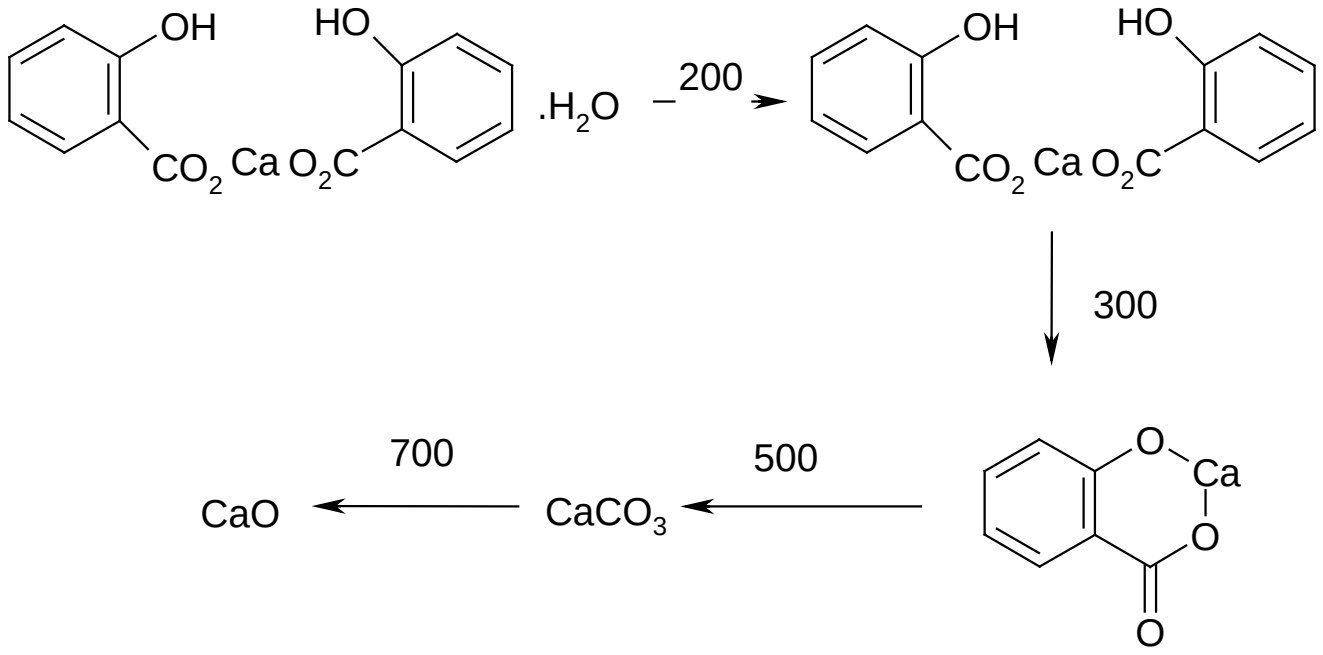
↓

$CaCO_3$

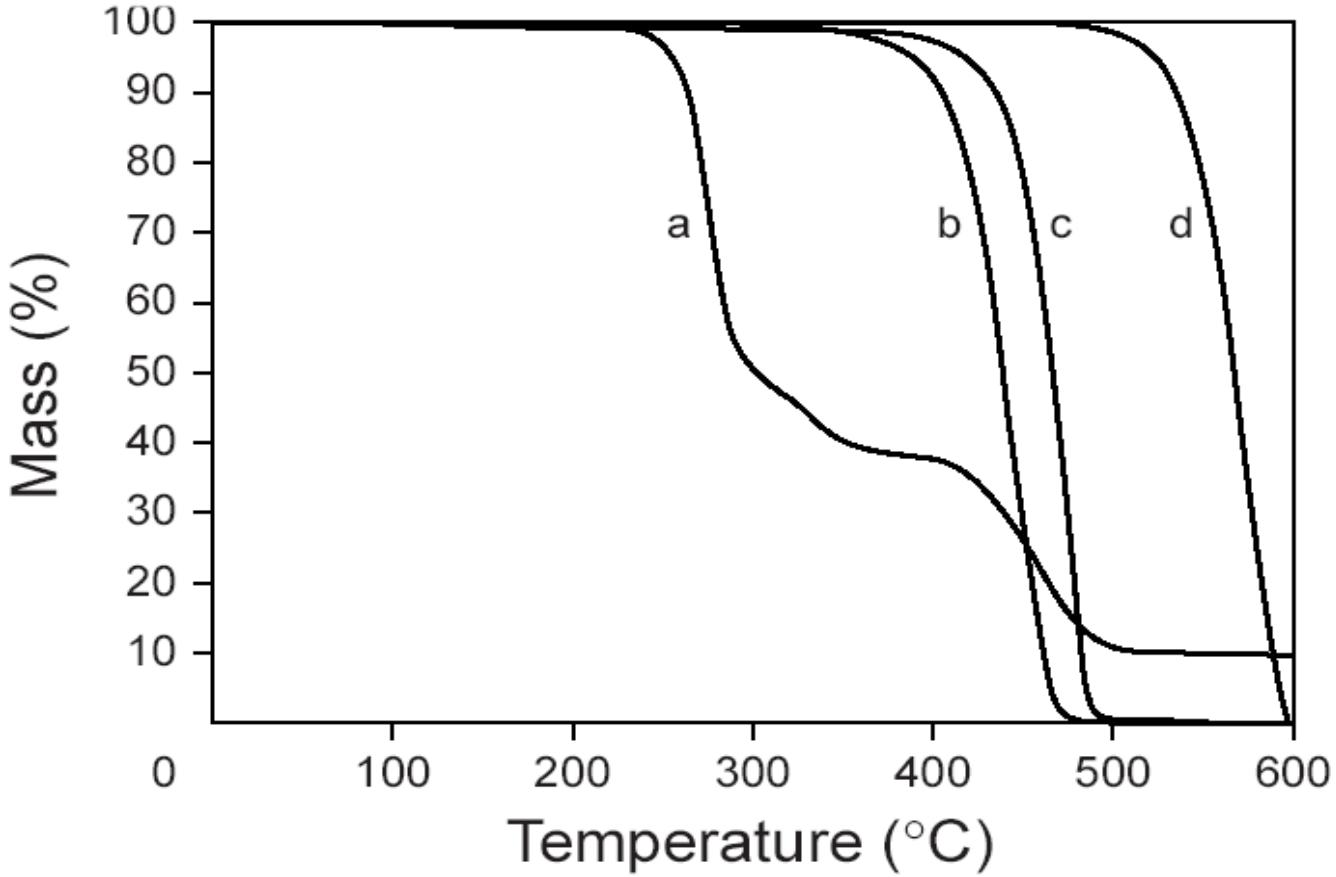
↓

CaO

Mechanism


OH
HO
CO2 Ca O2C
.H2O
– 200
OH
HO
CO2 Ca O2C
300
O
Ca
O
O
500
CaCO3
700
CaO

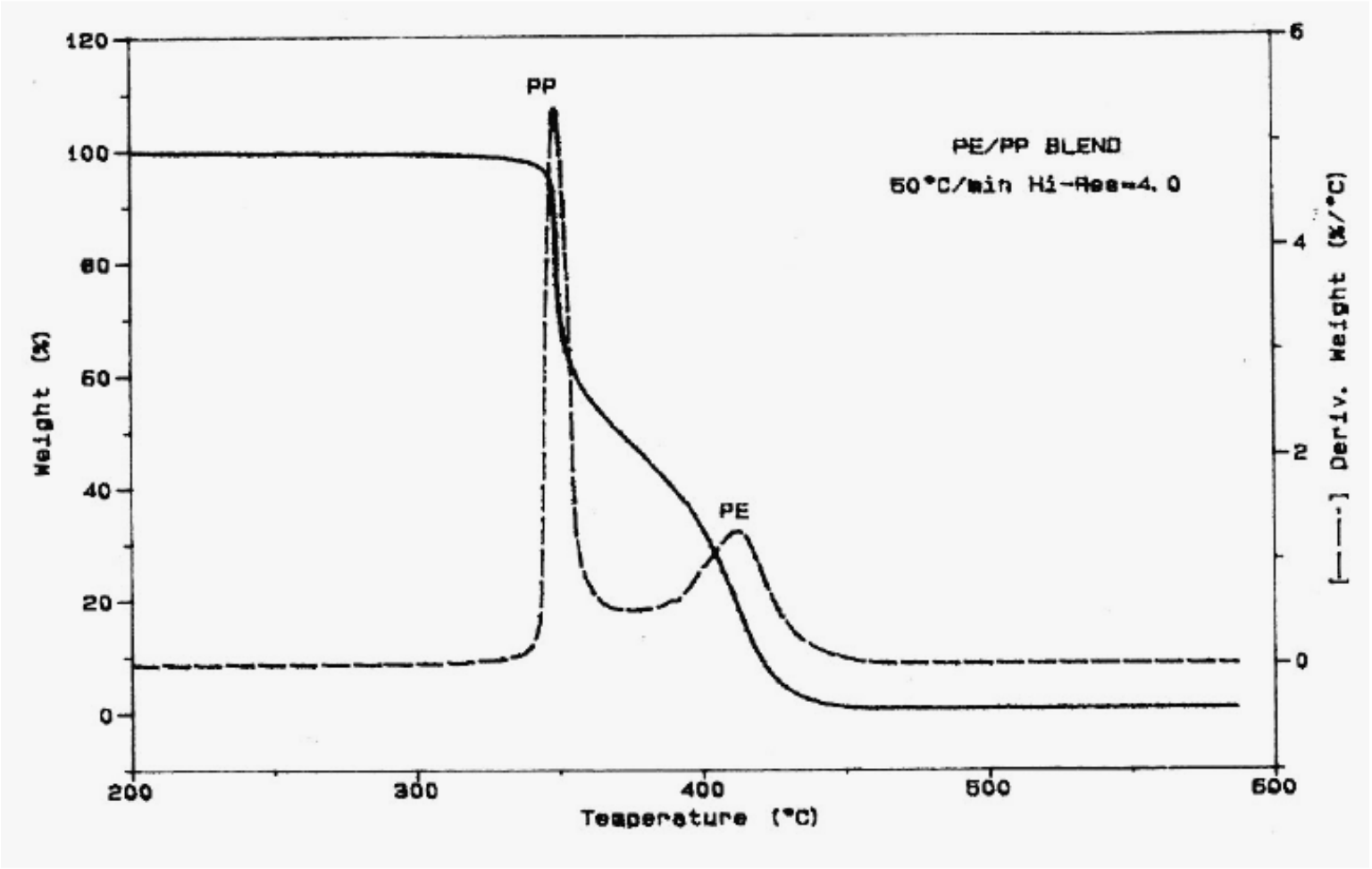
polymer stability/identity studies



a = PVC, b= nylon-6, c = LDPE, d= PTFE

TGA-EGA can help identify gases evolved

Polymer identity



Compositional analysis of filled rubber

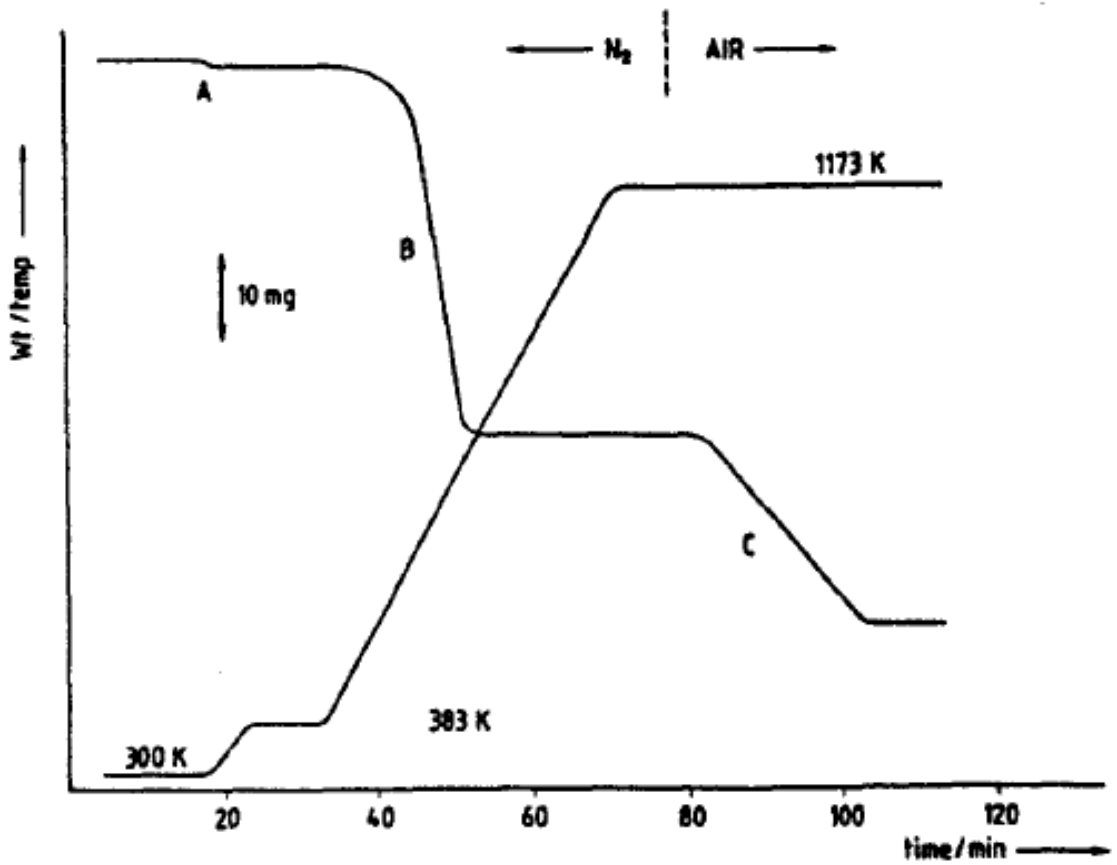
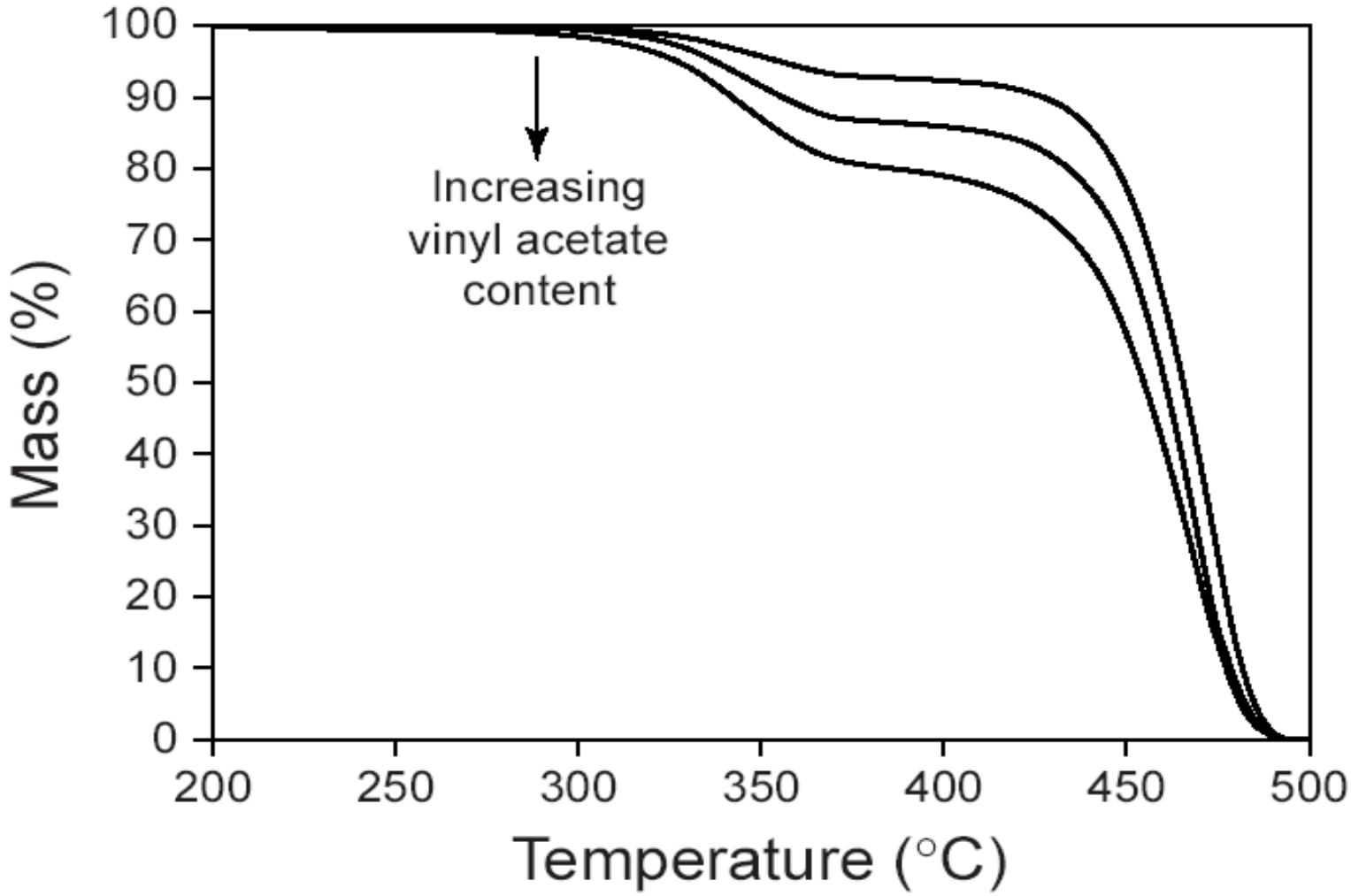
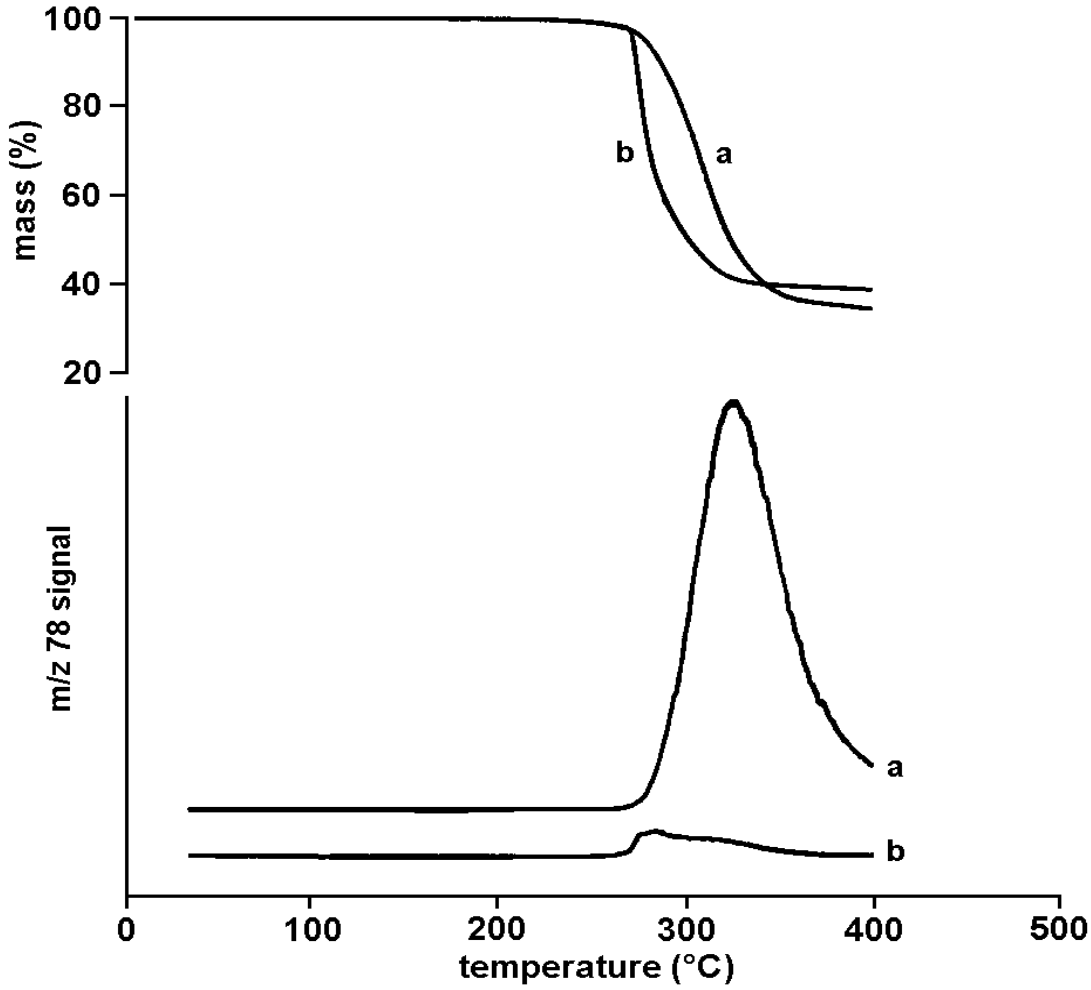


Fig. 3 Proximate analysis by TG of 73.3 mg rubber (Dunlop tire). Program: N_2, 20 K min^{-1}, 300 → 383 K; iso at 383 K for 20 min; heating at 20 K min^{-1}, 383 → 1173 K; iso at 1173 K. Change of N_2 into air at 1173 K. Mass changes: A=0.1 mg (water), B=46.3 mg (rubber) and C=23.7 mg (carbon)

composition of PVAc



TGA-MS of PVC


100
80
60
40
20
mass (%)
b
a
m/z 78 signal
a
b
0
100
200
300
400
500
temperature (°C)