行政院及所屬各機關出國報告

（出國類別：考察）

高分子材料之電氣與燃燒性質分析

服務機關：標準檢驗局

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目次：

赴美考察「高分子材料之電氣與燃燒性質分析」

標準檢驗局第六組黃宗銘

壹、目的：

研習「高分子材料之電氣與燃燒性質分析」，並蒐集其他相關試驗資料。

貳、過程：

一、第一站至 MTS System Corporation 位於明尼蘇達州的總部。MTS 爲一專業儀器製造廠，擁有全世界一流的電子伺服油壓缸技術，該公司將此技術的極致的應用，設計出各種不同能量負荷的試驗儀器(萬噸-克)。總部設有一般高分子材料動態測試儀器部、橡膠高頻動態測試儀器部、結構工程測試部、地震模擬測試部、汽車測試部、度量衡校正試驗室等部門。分別與部門的經理 Pat Irwin, C. K. Lam, Craig L. Stanton, Randy Niesen, Steve Trout, John E. Swindeman, 討論目前橡塑膠材料試驗機的發展狀況以及該公司目前正執行的一些大型發展計劃，國內包括國家地震中心也正合作中。經由討論後可發現一材料力學試驗的現況：材料力學試驗現傾向於極小化及極大化之兩極發展。極小化是爲因應材料

設計之精密化，因爲當前材料科學發展極爲迅速，對材料的認知已由材料集體性能的表現發展至透過分子之設計去適應各種不同用途之需要；爲了方便此需要所以製造的儀器通常承受能量都不大，但試驗用之試片比以往精密。另極大化之意爲實物之測試，當由材料組合爲成品時基於結構力學等其它因素，現今試驗潮流則希望依使用方式做整體之試驗。但至目前爲止能統合該二種試驗模式之試驗室並不多。

二、第二站參觀 Photomechanics Inc.一台設置於紐約市的儀器，公司經理 B. Han 說明目前如何應用 Moire 技術測試微小平面之平整度。Moire 技術爲一種光干涉效應的應用；當光經過一間隔已設定之光柵後在一完全平整的平面上會顯現出完全規則性之干涉頻譜，但若顯示面非爲完全平整則光就會產生第二次干涉，造成不規則性干涉頻譜，將頻譜照相後經複雜數學計算後即可知道平面的狀況。該儀器本身並非極複雜，簡單分爲光柵、影像擷取設備及運算器等部分，而圖譜數學計算方式才是技術的重

點。

三、第三站參觀 Arkrometrix LLC.位於喬治亞州的總部。該公司同樣爲一家 Moire 技術應用廠商，但公司的技術督導 Patrick B. Hassell 說明該公司儀器利用新的影像拍攝技術，使得量測的面積比傳統上利用雷射量測方式要大得多，速度也更快，成本也更低。該項技術目前主要使用者大部分爲主機板製造商、晶片組製造商及系統製造商，用來量測機板由於多次加工產生之高溫導致的平面翹曲及接合處的不規則起伏。

四、第四站至 MTS System Corporation 位於田納西州的 Nano Instruments Innovation Center，該中心爲一微硬度試驗技術發展中心。分析服務部經理 Jennifer L. Hay 介紹：該試驗中心最新研發之儀器是以鑽石爲探頭，配合電子顯微鏡和拉力試驗機配件而組成之多功能試驗機。試驗時與一般硬度計相同採針入式，但因有精密電子顯微鏡的輔助，量測點可落在奈米之微小區域，另探針上端裝有一荷重元，施行硬度試驗的同時一併可得到各種物理量的數據。該

試驗方法具快速、無需製作大量的試驗用試片、精準等優點，並且一次試驗即可獲得多種材料性能包含硬度、強度、模數等數據於奈米的區域間。

五、第五站至波士頓的建築師事務所 Goody, Clancy & Associates，建築師 Ethan Y. Huang 說明美國建築師如何配合建築法規設計建築及火災和防火概念的一些演變。其中有不少概念極有特色，但可否適應於國內現有體系，卻是大有疑問。提出之意見將於心得中詳述，供大家參考。

六、第六站至 Materials Characterization Center of Western Kentucky University，中心爲一專業的熱分析試驗室，試驗室包含 DSC、Modulated DSC、TGA、TGA-FTIR、TGA-MS、TMA、DMA、DEA、Micro-TA 等相關儀器。該中心現爲 ASTM 之合作試驗室，相關之熱分析方法欲制定爲標準前均需於該試驗室模擬。中心之主持人 Dr. Pan 爲北美熱分析學會之會長，他認爲地處偏僻的學校試驗室能有此等發展，最先進而完整的設備最是重要；因此該試驗室長期與全世界最大的專業熱分析儀器製造

商訂有合作關係，故該試驗室之儀器均爲同級試驗室之首。

七、第七站參加於 Washington D.C.舉辦的一熱分析研討會，研討會爲北美熱分析協會舉辦之一中型研討會，以 DSC、DMA 爲主，針對使用該類儀器之博、碩士班研究生所辦理。該研討會雖非極尖端之研討會，但可促進同儕間之相互砥礪，另也證明美國學術活動之發達。另由於該等儀器主要使用於研究領域，在一般之學術機構不易有足夠的修習人數可供開課，藉由短期研討會聘請在該領域的大師授與精闢之課程，不但個別學生可得到最權威的知識，且個別學校也可省下大筆的開課經費。(摘錄重要內容於附錄)

八、第八站至 TA Instruments 位於德拉瓦州的總部，並參加該公司舉辦爲期一週的熱分析訓練，由於該公司爲全世界最大之單一種類儀器製造商，所以辦理之訓練也爲目前可找到最專業之熱分析訓練。訓練的重點爲原理解說，儀器操作的部份較少提及。該訓練爲從事該類試驗者必須參加之訓練。訓練內容

簡述如下：週一、熱示差掃描儀之原理說明，含傳統式及動態調幅式。週二、熱重分析儀之原理說明，含傳統式及動態調幅式。週三、熱機械分析儀之原理說明。週四、流變儀之發展現況。週五、動態機械分析儀之原理說明。從該訓練可發現，該公司專業人員的專業養成速度非常快。從新進人員到從業專家大概只可有一年的時間。而熱分析之所以在現今研發試驗室占有重要之地位以下將以幾個例子說明之：1. 液晶(LC; liquid crystal)，液晶爲一物質之一種物理狀態，顧名思意其狀態就介於液體與固體之間，其分子排列不似固體的井然有序，但又非如液態之雜亂無章，因此只要可找到適合的外力如電場，就可以操縱該物質之分子排列或分子運動。以相變化的角度分析，固-液相之相轉移的能量就遠大於固-液晶相、液晶-液相。所以目前在量測物質是否存在液晶相及液晶相存在的範圍，最理想的工具即是用熱分析儀器家族的熱示差掃描儀(DSC)，因爲至目前精密儀器中只有 DSC 這種儀器可記錄物質內能與溫度之函數關係。再者，若該物

質存在液晶相時，通常會使用熱分析儀器家族的另一儀器介電分析儀(DEA)量測該物質在電場效應下的分子運動狀況。其實目前熱門的產品「液晶顯示器」，即是運用電場控制液晶物質的運動，使液晶物質產生光柵的效應而顯像。而目前本領域的研究，熱分析儀器是最基本的工具。2.一般化工廠最擔心的工安問題爲鍋爐或反應槽的爆炸。以往工廠建造設計公司通常以增加安全係數的方式，來提高設備的安全性。但此種方法漸遭淘汰，因爲若無合理的模擬試驗時，過高的安全係數會影響工廠建造成本，但安全係數不足時又會把工廠建造成一不定時炸彈。目前工廠建造設計公司或工安單位多以高壓熱示差掃描儀(PDSC)來做反應槽的模擬試驗。該儀器爲熱分析儀器家族的新成員，提供壓力-溫度曲線、反應熱-壓力曲線等相關資料，將該些微量測試的結果依適當的模擬公式按比例放大後加入適當的安全係數，即可做爲工廠建造設計公司或工安單位對於高危險性行業的一個設計與管制之依據。

參、心得：

本次出國考察研習之心得可分爲以下三點:：

一、到底該如何定位一政府機構之試驗室？就參觀一些儀器公司及試驗室後發覺：當設定的目標、擁有的資源與負責的任務不同時會形成不一樣的試驗室。欲驗證一試驗室之程度，通常至現場參觀試驗的工作者如何操作儀器與操作何種儀器，便可了然於胸。由於科技的發展一日數變，同類型的儀器翻新的速度甚是驚人，若無強大財力做後盾，在試驗室能力的競賽中往往居於劣勢。故要維持試驗室的水準，慎選試驗室發展方向爲有限經費試驗室首要任務，發展方向確定試驗室才有成長空間。

二、在 Goody, Clancy & Associates 建築師事務所的建築師對防火的看法整理如下：

若大家親訪過美國即可發現：大多數的美國住家使用木材爲其建物之結構體材料，且內裝材料上木頭及紡織品的用量也不在少數，但何以就火災發生的比例而言並不算高？一般說來美國的的防火政策有以下幾大主軸。第一、改質材料的使用。大多數

的建材均需依各種不同的方式提高其難燃程度後，方可使用。故，在美國防火試驗規範之完備與防火測試試驗室之規模均屬世界之首位，如此也造就美國爲全世界擁有最先進材料改質技術的國家。第二、審慎的都市規畫。依研究顯示，不同行業造成火災的比例會不同。若將都市依使用方式畫分成各種不同之區域，較易發生火災之行業集中於特定區域，並提高其相關設施之防火要求，如此當可在不大幅提高總體防火支出下，降低火災之發生率及嚴重性，美國新的都市計畫其實是逐漸朝此方向演變中。

三、英語爲一重要之溝通平台，幾乎所有重要的資訊均會有英文表示。於各種專業資料中新出現之物品，若無親眼所見，其實常常會發生想像物與實體存在嚴重差距的情況發生。台灣在國際化的過程中尤其新技術的取得，以往靠廣大的留學生族群爲界面，今後在留學生族群尤其是理工類科人數逐年下降的情況下，如何保有技術資訊之溝通無礙將是未來之重要課題。

肆、建議：

一、為因應本局無可避免的國際化及業務升級，本局應設法與世界其它重要的測試試驗室訂定長期合作關係，定期派遣人員至該試驗室熟悉相關運作模式，使局務運作更符合國際走向，並且藉該機會增加專業之外語能力。

二、選擇在台灣具競爭力之產業，全力發展該產業之試驗能力，除可解決廠商之問題外，尚可建立試驗室在世界的領導地位。

Fundamentals of Thermal Analysis

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Thermal Analysis

A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere is programmed.

Thermal Analysis

The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these.

Thermal methods

Technique	Abbrev.	Property	Uses
Thermogravimetry (Thermogravimetric analysis)	TG (TGA)	Mass	Decompositions Dehydrations Oxidation Kinetics
Differential thermal analysis	DTA	Temperature difference	Phase changes Reactions Kinetics
Differential scanning calorimetry	DSC	Power differences	Heat capacity Phase changes Reactions Calorimetry Kinetics
Thermomechanical analysis	TMA	Deformations	Mechanical changes Expansions

Thermal methods (cont'd)

Technique	Abbrev.	Property	Uses
Dynamic mechanical analysis	DMA	Moduli	Phase changes Polymer cure
Dielectric thermal analysis	DETA	Permittivity	Phase changes Polymer changes
Evolved gas analysis	EGA	Mass IR absorbance Absorption	Decompositions Catalyst and surface reactions
Simultaneous thermal analysis (eg. Simultaneous TG-DTA)	STA (eg. SDT)	Two or more techniques used on the same sample at the same time.	
Controlled-rate thermal analysis	CRTA	The rate of change of the property is held constant.	

Instrumental factors affecting thermal curves

- Heating rate
- Atmosphere
- Furnace size and shape
- Sample holder material and geometry
- Thermocouple location
- Wire and bead size of thermocouple junction

Sample characteristics affecting thermal curves

- Sample mass and particle size
- Sample packing
- Thermal conductivity
- Heat of reaction
- Heat capacity
- Effect of diluent
- Solubility of evolved gases in sample

Effect of atmosphere

- Inert/reactive
- Thermal conductivity
- Flow rate
- Pressure

Optimum operating conditions

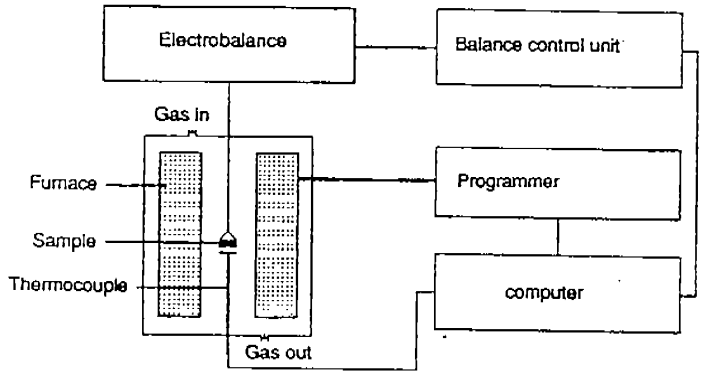
- Small amount of sample (eg. few mg)
- Thin layer of sample
- Shallow inert container (eg. platinum)
- Inert purge gas (eg. dry N_2)
  (except for oxidation studies)
- Slow heating rate (eg. 5-10 °C min^{-1})

Thermogravimetry (TG)

Thermogravimetry (TG)

A technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

TG – Schematic diagram



TG – Measured signals

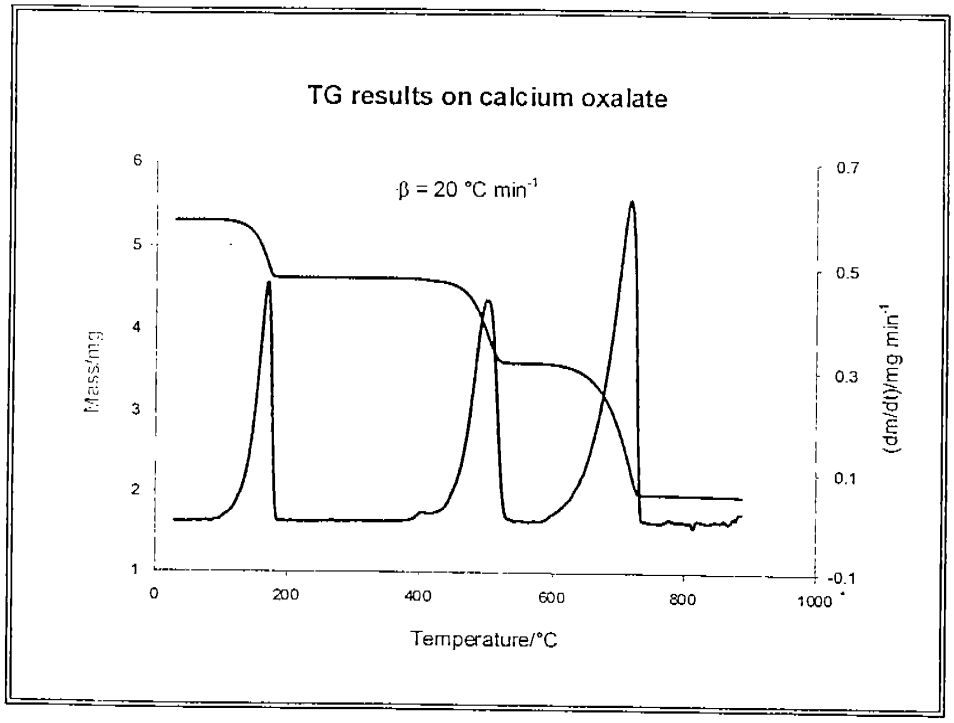
- Mass
- Rate of mass change
  > Differential thermogravimetry
- Temperature
- Time

Differential Thermogravimetry (DTG)

A method of expressing the TG results by giving the first derivative curve as a function of temperature, or time.

DTG – Applications

- "Fingerprinting" materials
- Separation of overlapping reactions
- Calculation of mass changes in overlapping reactions
- Quantitative analysis by peak height measurement
- Determination of the maximum temperature at greatest rate of change

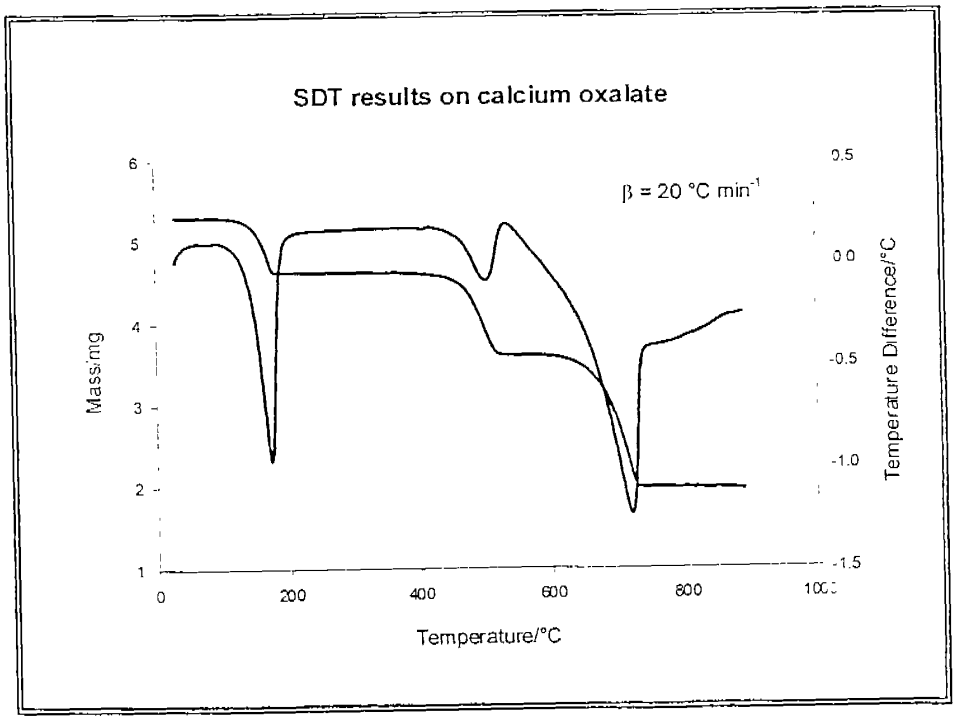


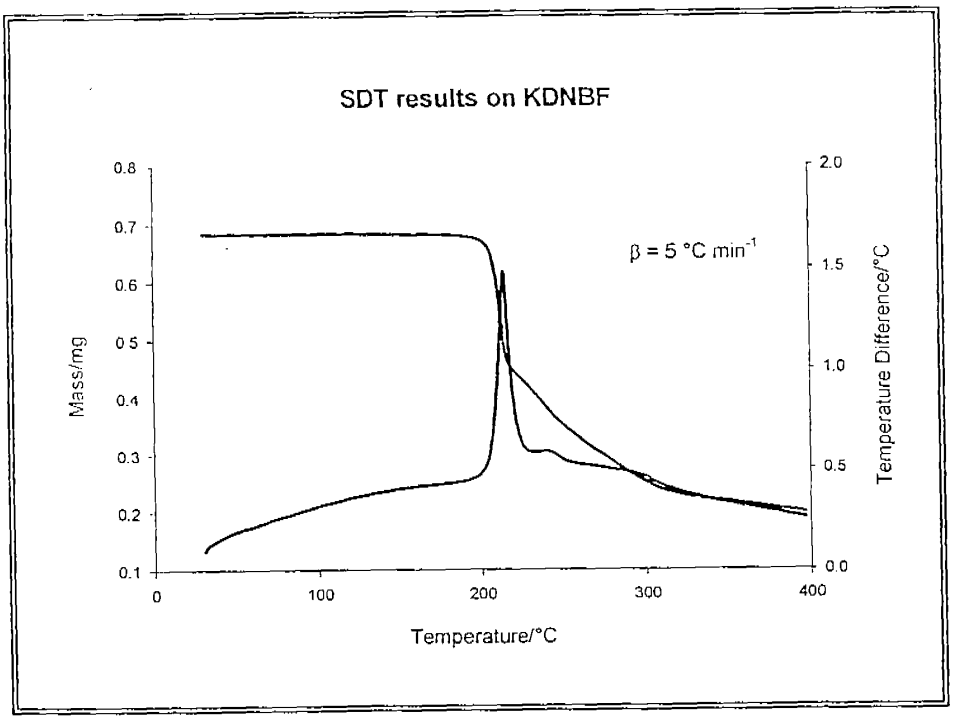
Simultaneous TG-DTA (SDT)

A technique which measures both differential temperature and mass changes in a material as a function of temperature or time in a controlled atmosphere.

SDT – Advantages

- Direct comparison and simplified interpretation of results
- Cost effectiveness and productivity
- Easier method for temperature calibration

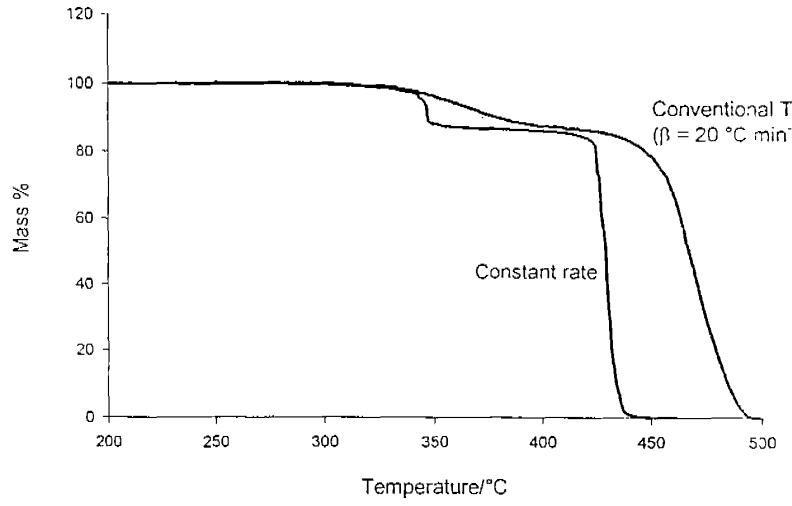




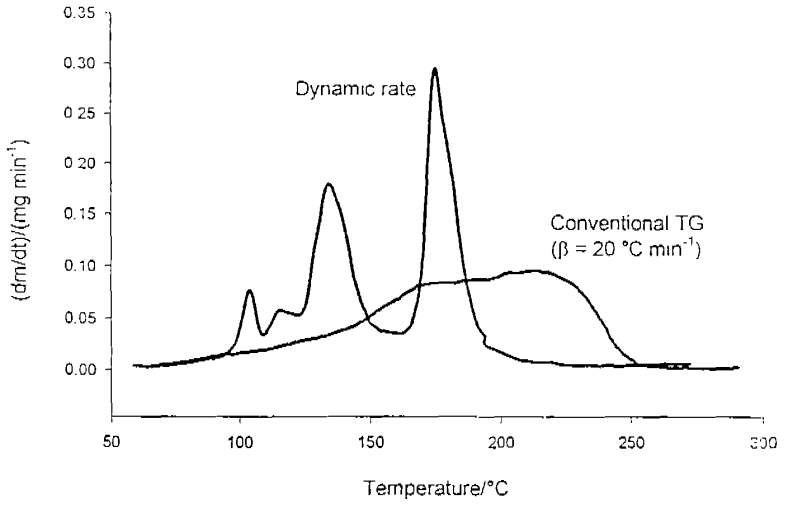
TG – Modes

- Dynamic
- Isothermal
- Step isothermal
- Constant rate (CRTA)
- Dynamic rate

Comparison of constant rate and conventional TG
Example: ethylene-vinyl acetate blends



Comparison of dynamic rate and conventional TG
Example: polymer derivative fuel additive



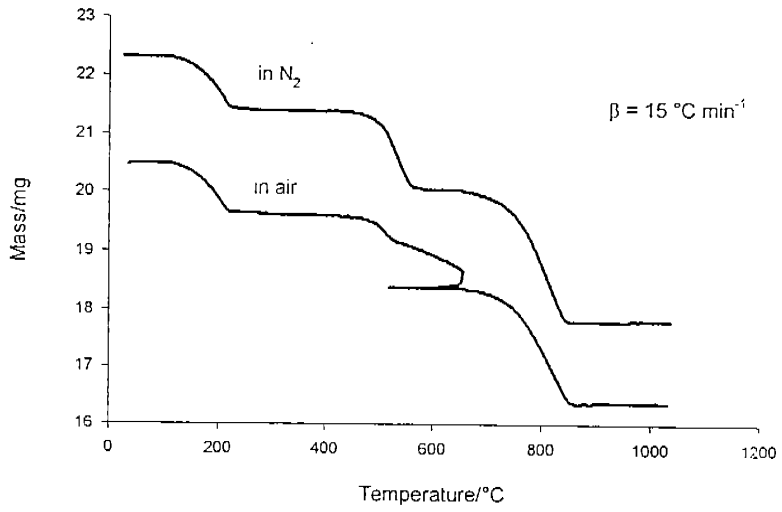
TG – Source of error

- Sample container air buoyancy
- Furnace convection currents and turbulence
- Furnace induction effects
- Random fluctuation in the recording mechanism and balance
- Electrostatic effects on balance mechanism
- Environment of the thermobalance

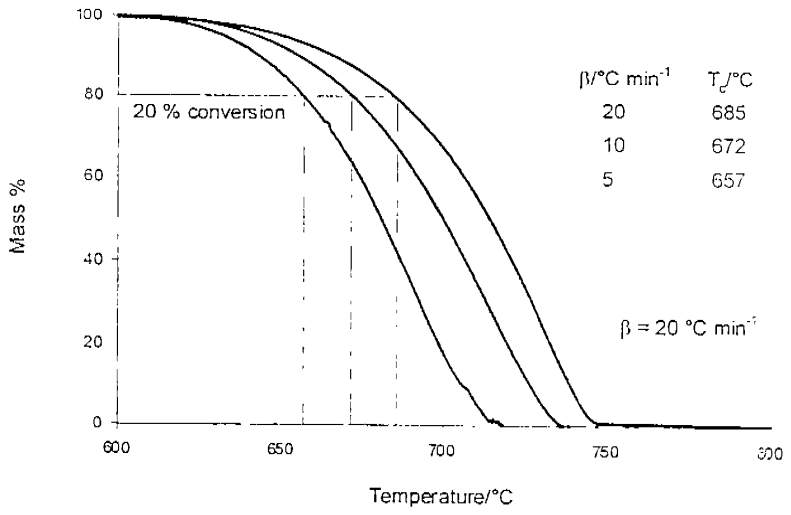
TG – Source of error (cont'd)

- Condensation on balance suspension
- Reaction between sample and container
- Mass measurement and calibration
- Temperature measurement and calibration
- Temperature fluctuations

Effect of atmosphere on the TG curves
Example: calcium oxalate



Effect of heating rates on the TG curves
Example: $CaCO_3$ in N_2



TG – Temperature calibration

Variables:

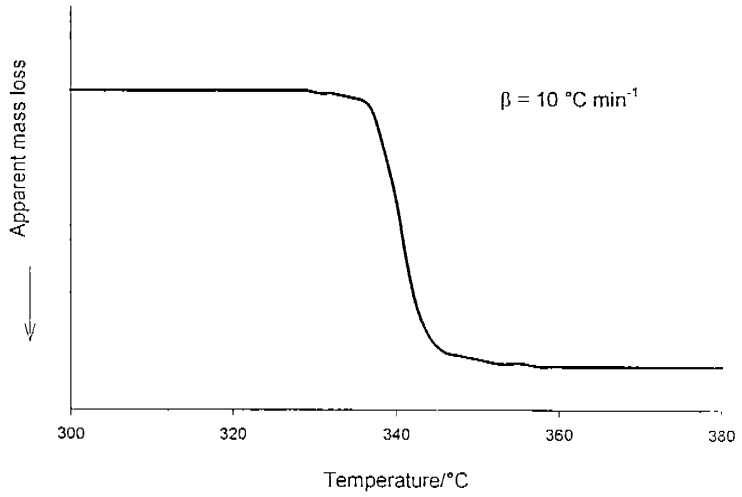
- Heating rate
- Pan type
- Purge gas type and flow rate
- Thermocouple position

TG – Temperature calibration

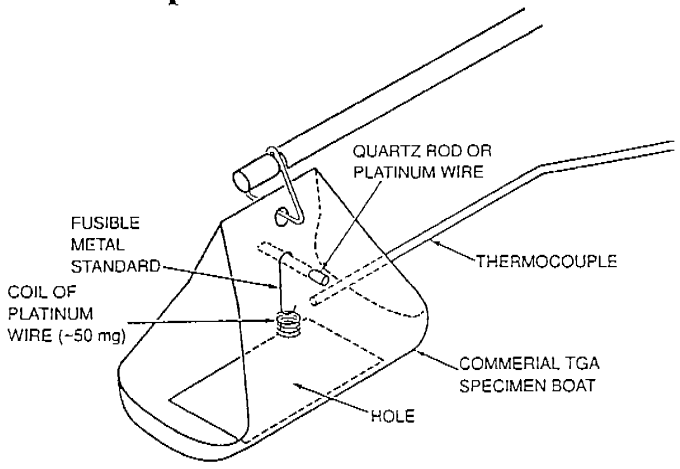
Methods:

- Curie point
- Fusible link (Hang down wire)
- Melting point method (SDT only)

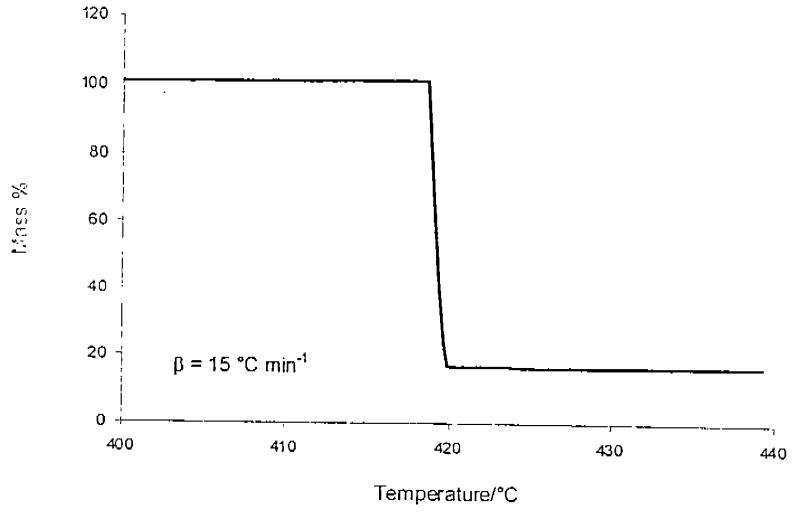
TG temperature calibration with Curie point
Example: nickel



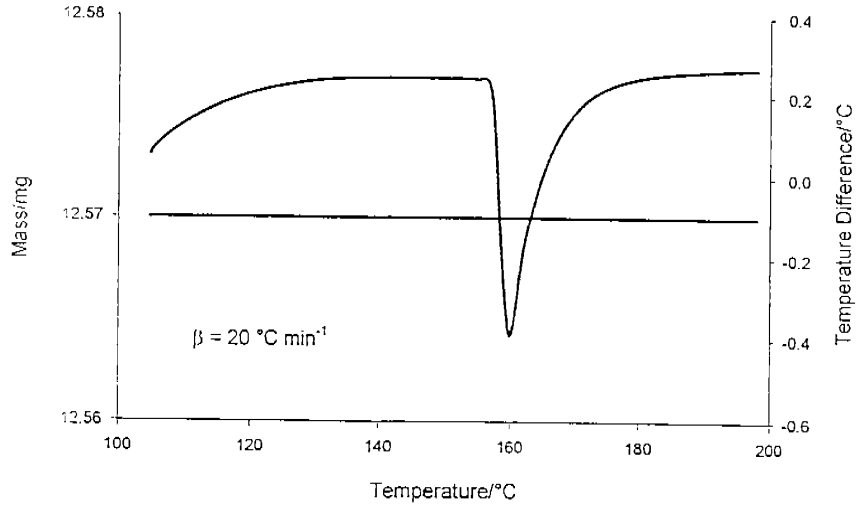
Modified pan for fusible link temperature calibration



TG temperature calibration with fusible link
Example: zinc

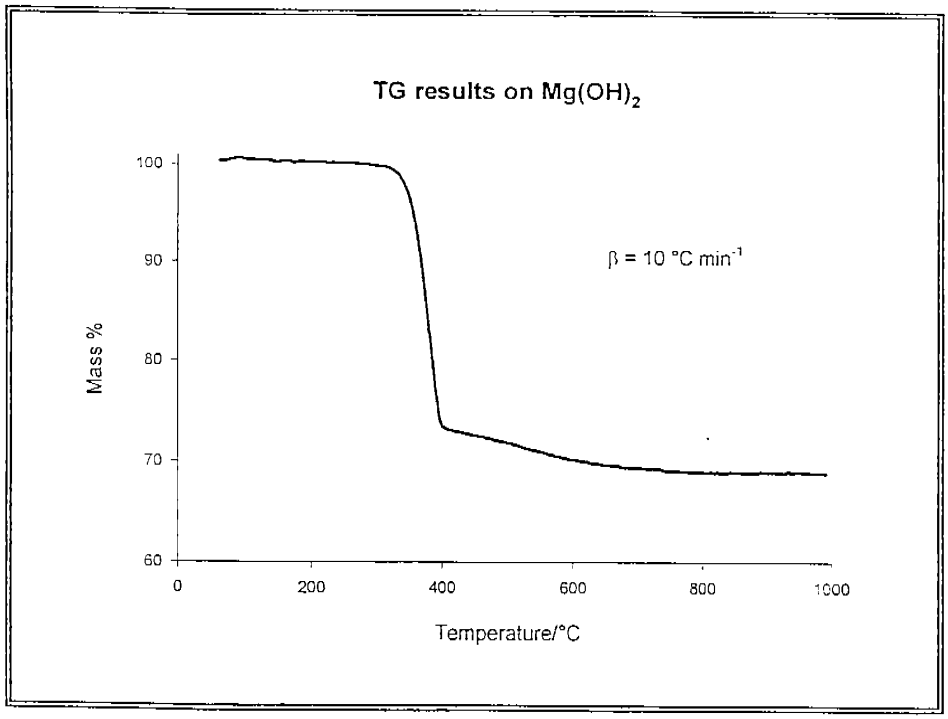


SDT temperature calibration with melting point method
Example: indium



TG – Applications

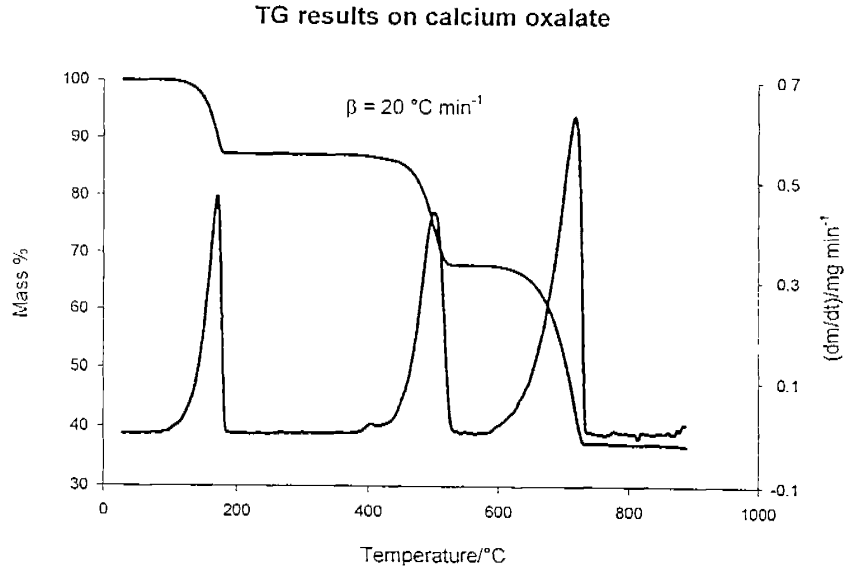
- Thermal stability
- Compositional analysis
- Reaction studies



Magnesium hydroxide

$Mg(OH)_2(s) = MgO(s) + H_2O(g)$

% Loss = 100 x $M(H_2O)/M(Mg(OH)_2)$
= 100 x 18.0/58.3
= 30.9 %



Calcium oxalate

$CaC_2O_4 \cdot H_2O(s) = CaC_2O_4(s) + H_2O(g)$

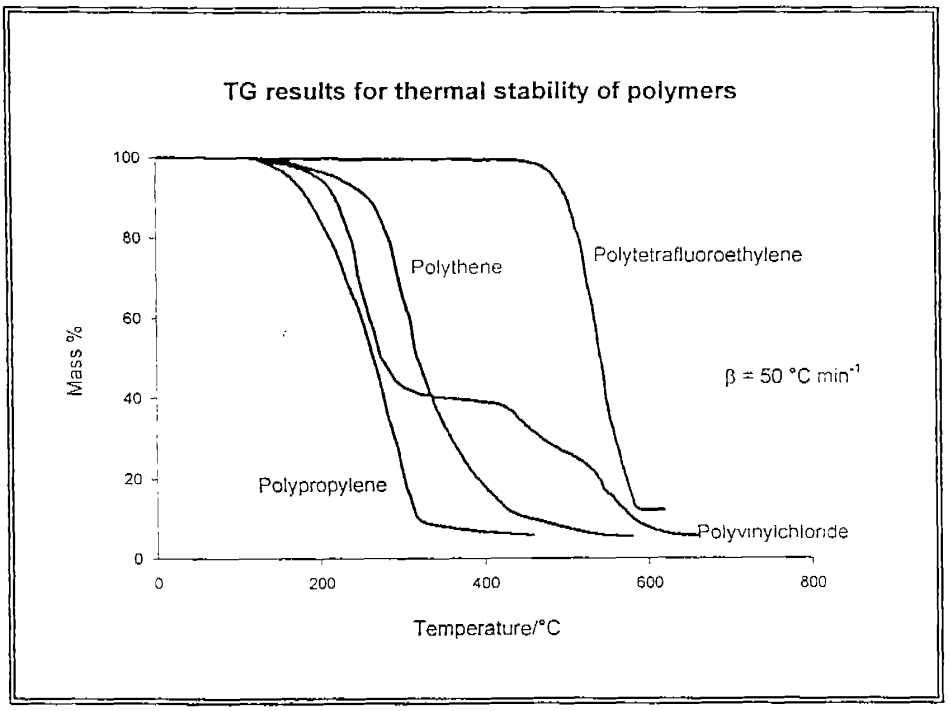
% Loss = 100 x 18.0/146.1 =12.3 %

$CaC_2O_4(s) = CaCO_3(s) + CO(g)$

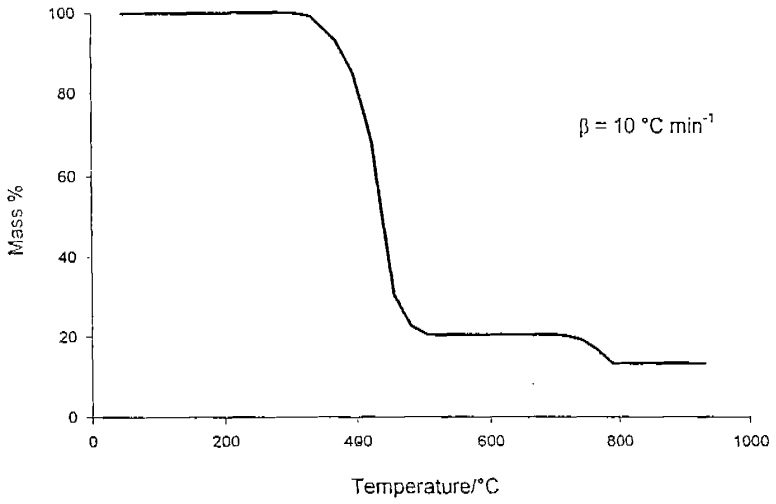
% Loss = 100 x 28.0/146.1 = 19.2 %

$CaCO_3(s) = CaO(s) + CO_2(g)$

% Loss = 100 x 44.0/146.1 = 30.1 %



TG results for compositional analysis
Example: mixture of polyolefin + $CaCO_3$



Mixture of polyolefin + $CaCO_3$

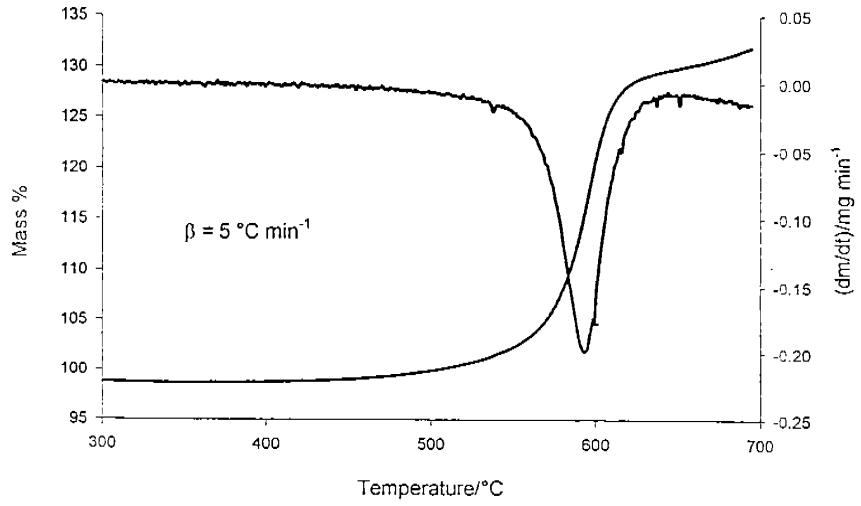
Decomposition of polyolefin

% Loss = 100 x 8.7/10.5 = 83 %

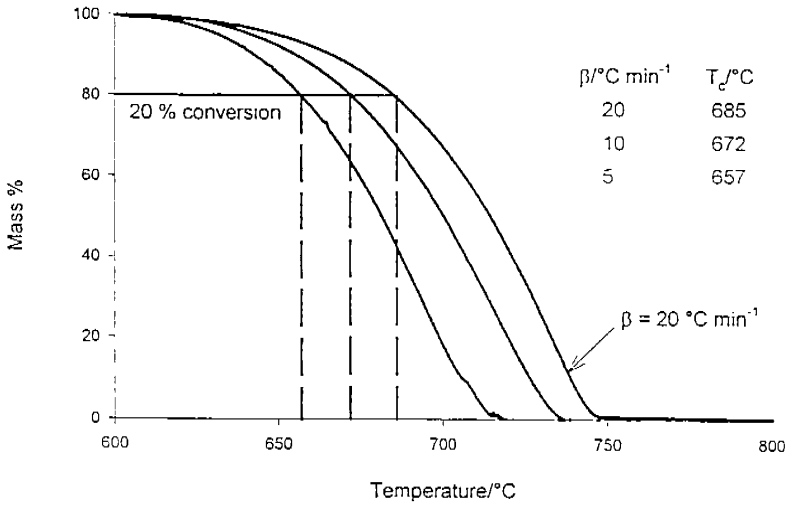
$CaCO_3(s) = CaO(s) + CO_2(g)$

% Loss = 100 x 0.8/10.5 = 7.4 %

TG results for reaction studies
Example: Al nanopowder in air



TG results for kinetic studies
Example: $CaCO_3$ in N_2



Differential Scanning Calorimetry (DSC) & Differential Thermal Analysis (DTA)

Differential Scanning Calorimetry (DSC)

A technique in which the difference in heat flow to a sample and to a reference is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

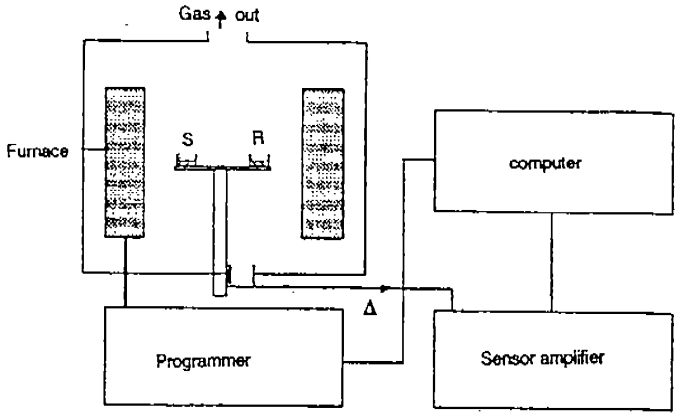
Differential Thermal Analysis (DTA)

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

DSC and DTA

The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these.

DSC/DTA – Schematic diagram



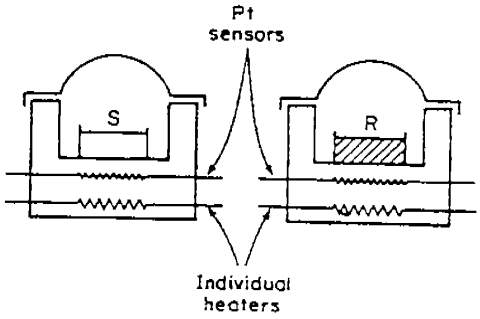
DSC/DTA – Measured signals

- Differential heat flow
- Temperature difference
- Temperature
- Time

Power-compensated DSC

where the sample and reference are heated by separate, individual heaters, and the temperature difference is kept close to zero, while the difference in electrical power needed to maintain equal temperature ($\Delta P = d(\Delta Q)/dt$) is measured.

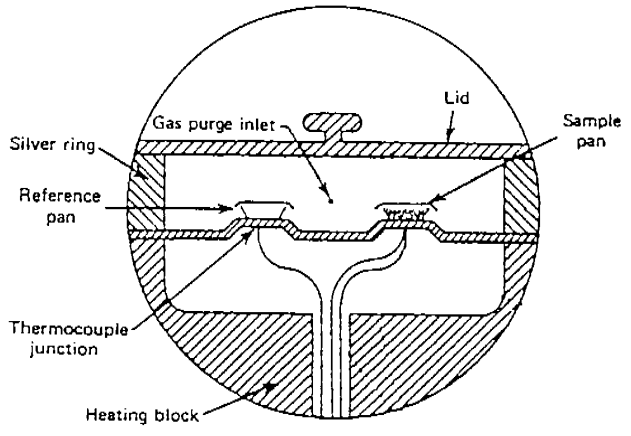
Power-compensated DSC



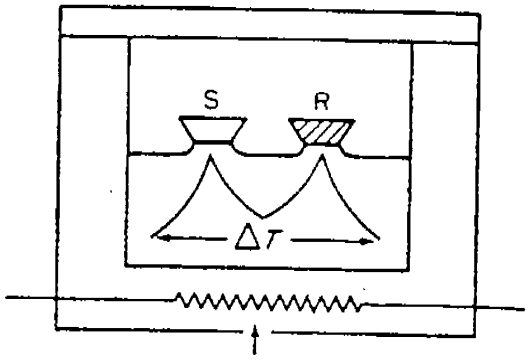
Heat flux DSC

where the sample and reference are heated from the same source and the temperature difference ΔT is measured. This signal is converted to a power difference ΔP using the calorimetric sensitivity.

Heat flux DSC



DTA



Single heat source

Comparison of DSC and DTA

- DTA sample holders are capable of much higher temperature, while DSC holders are limited to about 700 °C.
- DSC is easier to use for quantitative measurements of ΔH, because the calibration coefficient is independent of temperature.

DSC – Temperature calibration

- ASTM E967
- Transition temperature of standards (eg. indium, lead etc)
- 2 - 5 calibration points

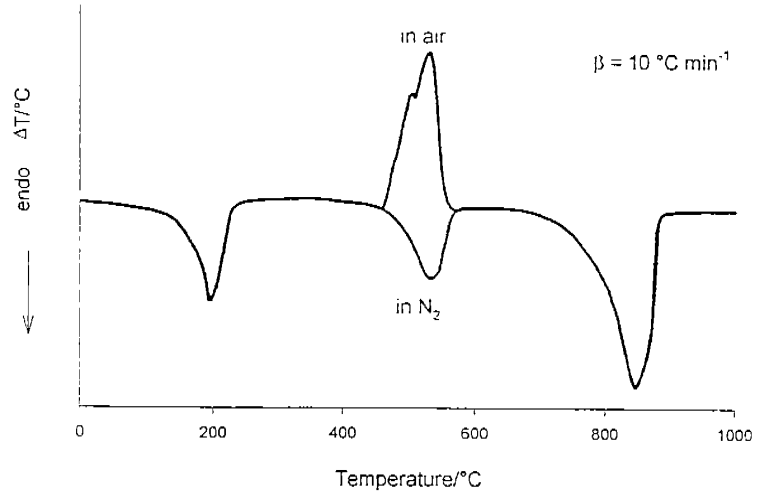
DSC – Heat Flow calibration

- $A = \pm \Delta H \cdot m \cdot K$
- ASTM E968
- Enthalpy of fusion standards (e.g indium)
- DSC: single point
- DTA: calibration over the entire temperature range of interest. ΔT recorded as function of time and T, hence K is a function of temperature.

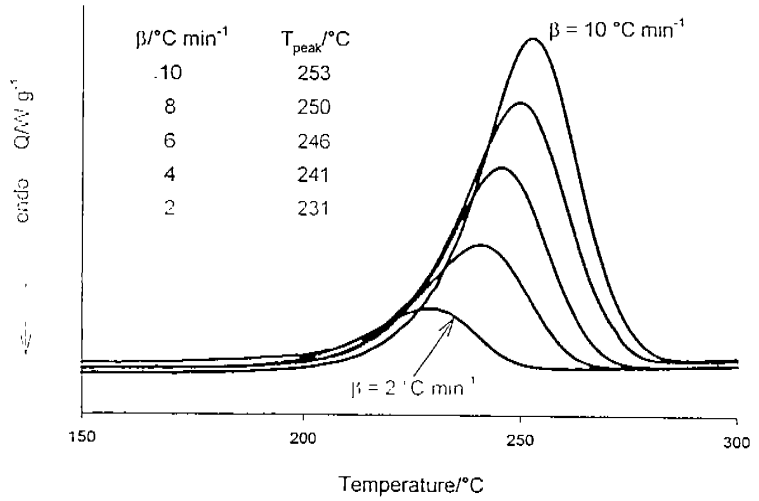
DSC – Heat Flow calibration

- $A = \pm \Delta H \cdot m \cdot K$
- ASTM E968
- Enthalpy of fusion standards (e.g indium)
- DSC: single point
- DTA: calibration over the entire temperature range of interest. ΔT recorded as function of time and T, hence K is a function of temperature.

Effect of atmosphere on the DTA curve
Example: calcium oxalate



Effect of heating rates on the peak temperature
Example: GAP

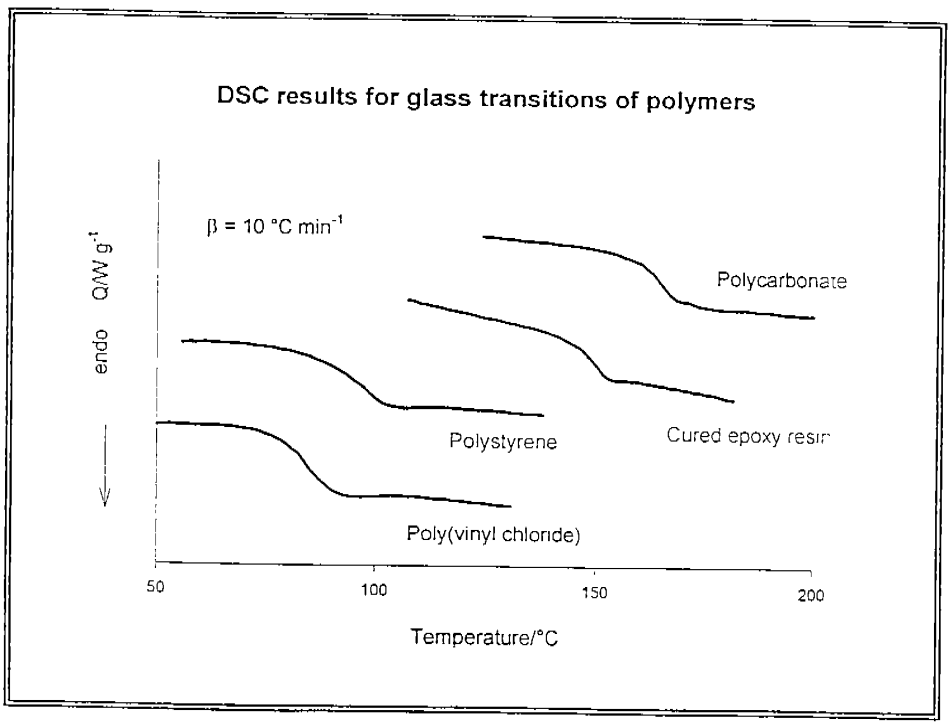


Optimization of conditions

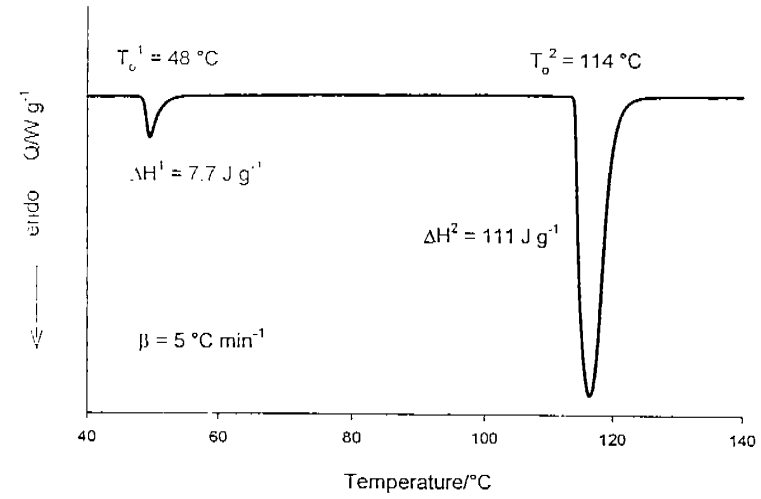
Parameter	Maximum Resolution	Maximum Sensitivity
Sample size	Small	Large
Heating rate	Slow	Fast
Sample holder	Block	Isolated container
Surface/volume of sample	Large	Small
Atmosphere	High heat conductivity (He, H_2)	Low heat conductivity (vacuum)

DSC – Applications

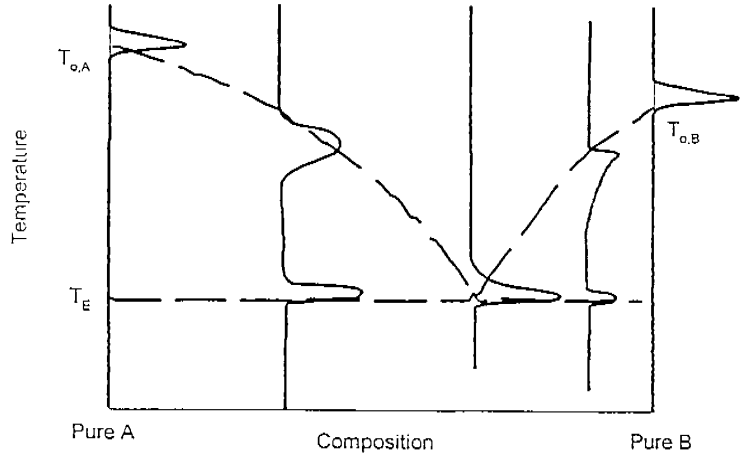
- Glass transitions
- Crystalline phase transitions
- Phase diagram
- Purity measurement
- Evaluation of ΔH
- Specific heat capacity
- Vapour pressure
- Oxidative/Thermal stability
- Reaction kinetics



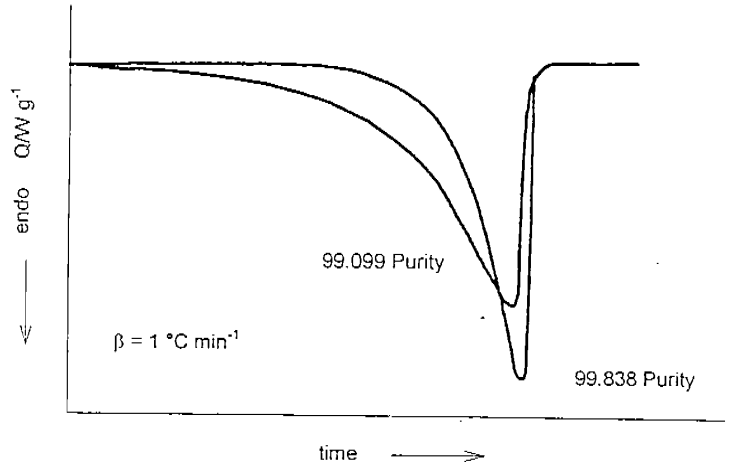
DSC results for phase transitions of DMNB



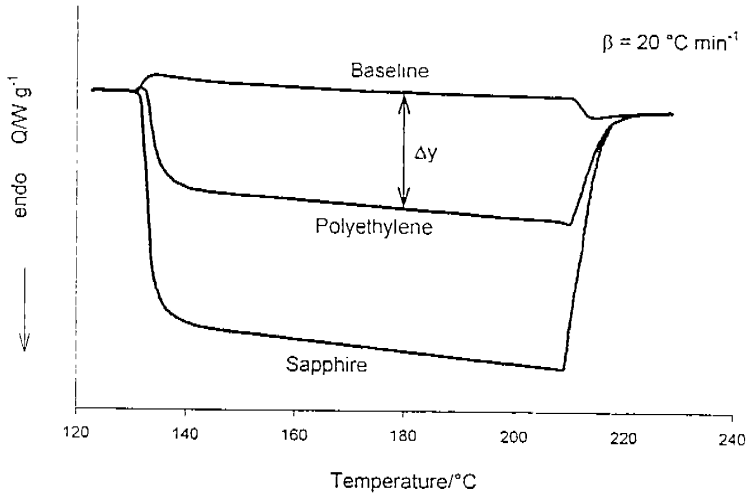
Eutectic phase diagram with superimposed DTA curves



DSC results for purity measurement (ASTM E928)
Example: pharmaceutical compounds



DSC measurement of specific heat capacity (ASTM E1269)
Example: polyethylene



Specific heat capacity of PE

$$C_p = \frac{K \cdot \Delta y}{(dT/dt) \cdot m}$$

for sapphire at 445 K

$\Delta y(S) = 75.0$ mm

$C_p(S) = 0.997\ J \cdot K^{-1} \cdot g^{-1}$

$$K = \frac{(0.997 J \cdot K^{-1} \cdot g^{-1})(133.6 \times 10^{-3} g)(20 K \cdot min^{-1})}{75.0 mm}$$

$$K = 3.552 \times 10^{-2} J \cdot min^{-1} \cdot mm^{-1}$$

Specific heat capacity of PE (cont'd)

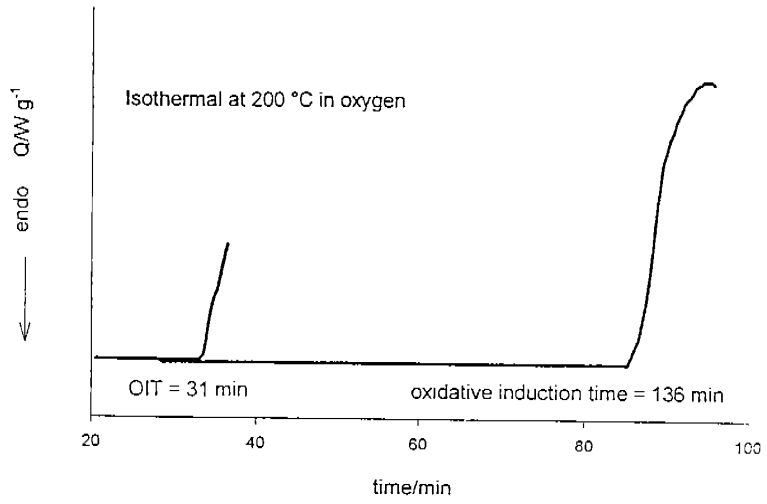
For polyethylene

$\Delta y(PE) = 34.0$ mm

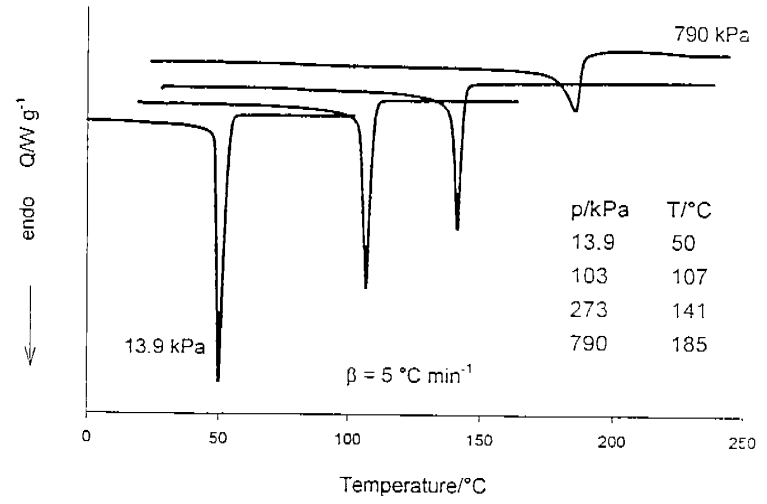
$$C_p(PE) = \frac{(3.552 \times 10^{-2} J \cdot min^{-1} \cdot mm^{-1})(34.0 mm)}{(20 K \cdot min^{-1})(23.14 \times 10^{-3} g)}$$

$$C_p(PE) = 2.61 J \cdot K^{-1} \cdot g^{-1}$$

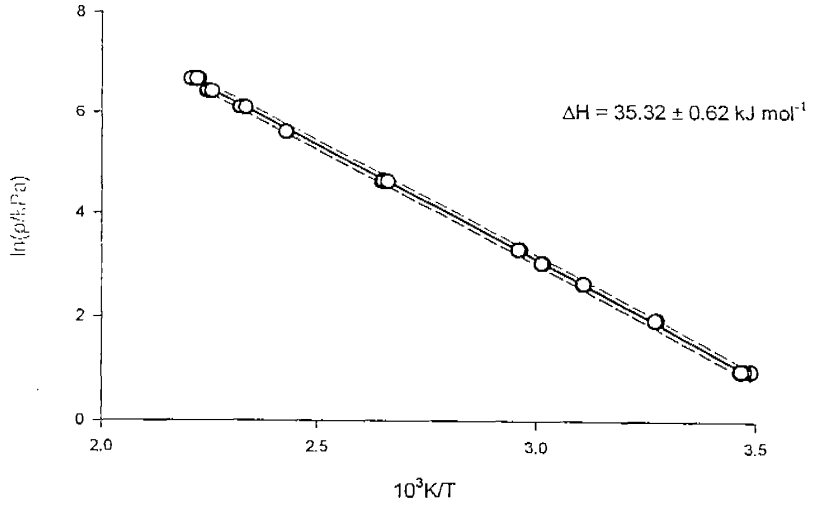
DSC results for oxidative stability studies
Example: polyethylene with different antioxidants



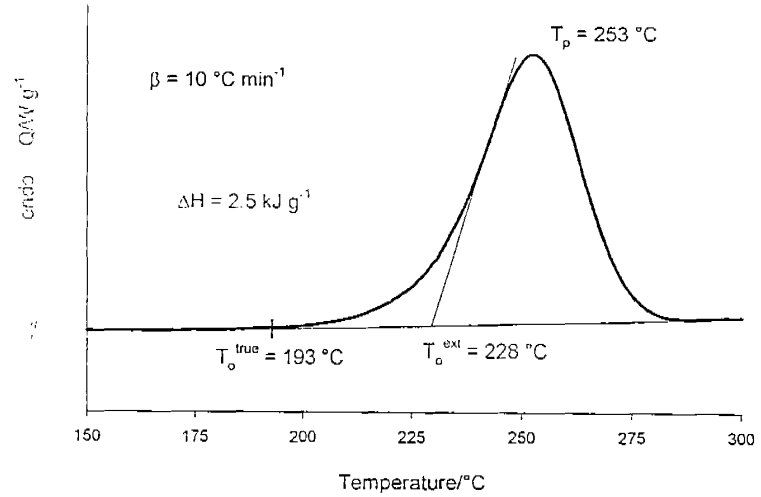
DSC results for vapour pressure measurement (ASTM E1782)
Example: Isopropylnitrate



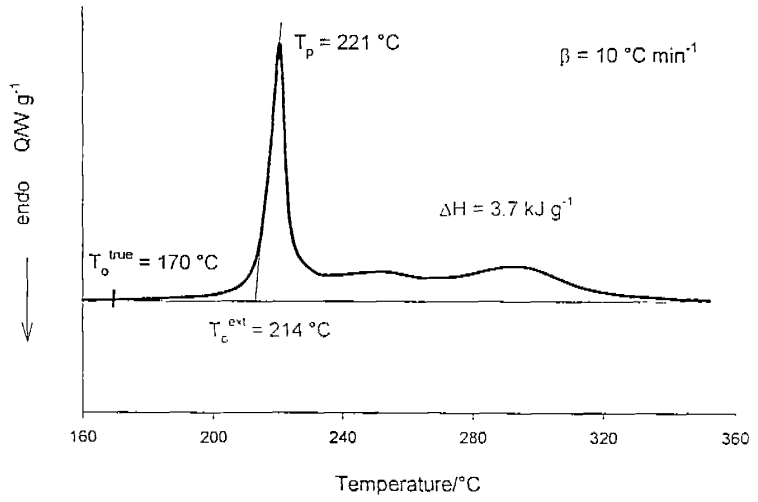
Clausius-Clapeyron plot for DSC vapour pressure results
Example: Isopropylnitrate



DSC results for decomposition studies
Example: GAP



DSC results for reaction studies
Example: KDNBF



KINETICS

Rate Law for Chemical Reactions

The rate law can be expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

where α is the fraction of sample reacted (converted) and $d\alpha/dt$ is the rate of reaction.

Rate Law for Chemical Reactions (cont'd)

For a n-th order process

$$f(\alpha) = (1-\alpha)^n$$

The order, n is determined by experiments and generally has no relationship to the stoichiometry of the chemical reaction.

Kinetic Equations for Various Models

Type	f(α)
P1 power law (m=1/2)	α^{1-m}
E1 exponential law	α
B1 Prout-Tompkins	α(1-α)
F1 first order	1-α
R3 contracting volume	$3(1-\alpha)^{2/3}$
FIX constant rate	1
A033 Avrami-Erofeev (n=1/3)	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
D1 one-dimensional diffusion	1/α
D2 one-dimensional diffusion	$[\ln(1-\alpha)]^{-1}$

Temperature Dependence of k

Arrhenius Equation (empirical)

$$k(T) = Z \exp\left(-\frac{E}{RT}\right)$$

$$\ln[k(T)] = \ln Z - \frac{E}{RT}$$

NON ISOTHERMAL METHODS

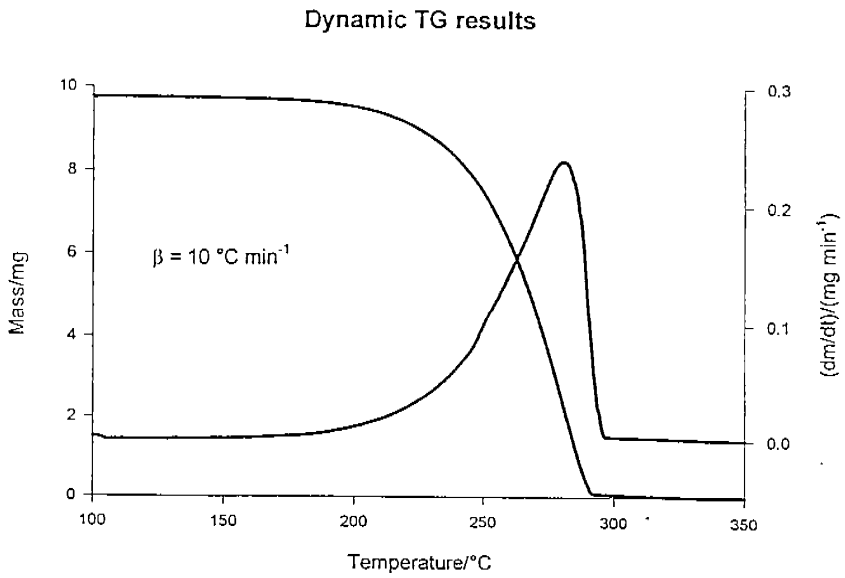
Thermogravimetry

Direct measure of α and $d\alpha/dt$

$$\alpha = \frac{m_i - m(t)}{m_i - m_f}$$

where m_i, m_f and m(t) are the masses initially, finally and at time t and $\Delta m = m_i - m_f$

$$\frac{d\alpha}{dt} = -\frac{1}{\Delta m}\left(\frac{dm}{dt}\right)$$



Thermogravimetry (cont'd)

For a linear heating rate, $\beta = dT/dt$ = constant

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT}$$

Note: if substantial heat given off during course of reaction, $\beta = \beta(t)$, ie β is no longer linear.

Thermogravimetry (cont'd)

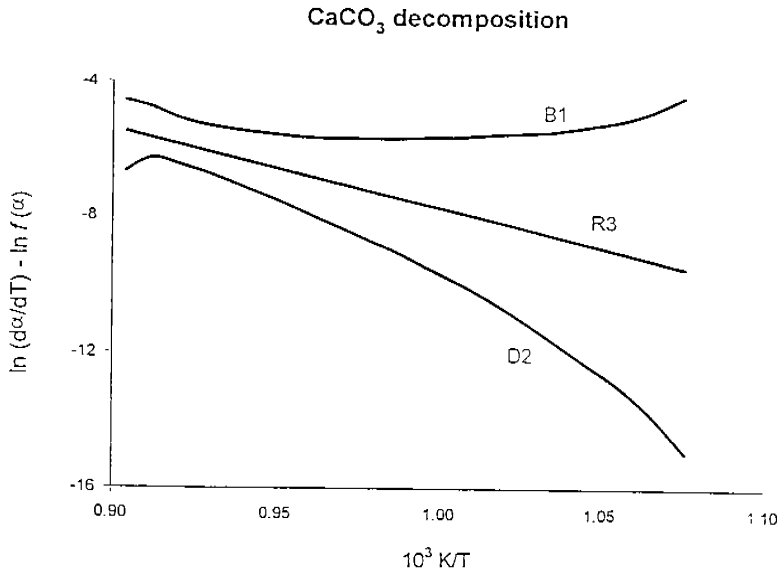
$$\frac{d\alpha}{dT} = \frac{Z}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha)$$

or

$$\ln\left(\frac{d\alpha}{dT}\right) - \ln f(\alpha) = \ln\left(\frac{Z}{\beta}\right) - \frac{E}{RT}$$

? plot L.H.S. against 1/T

? must decide which f(α) to use



Thermogravimetry (cont'd)

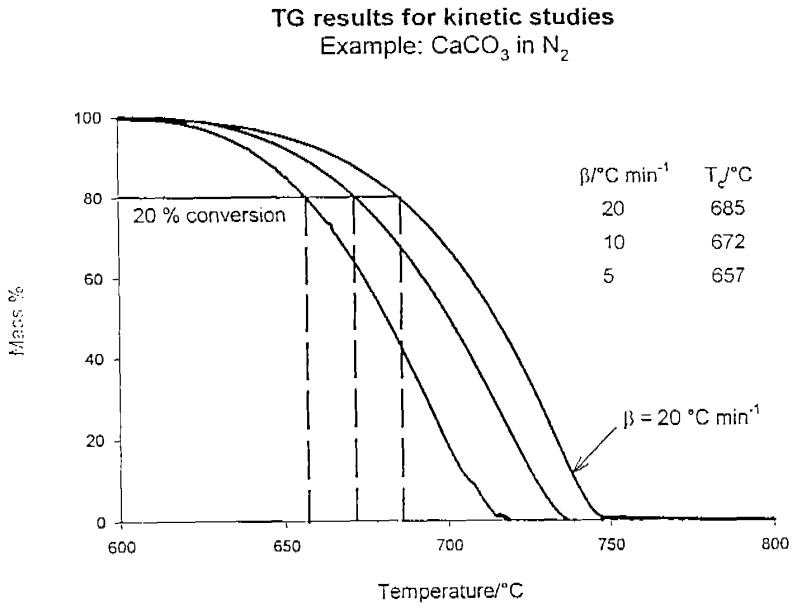
For a linear heating rate, β

$$\ln\beta = \ln Z + \ln[f(\alpha)] - \ln\left(\frac{d\alpha}{dT}\right) - \frac{E}{RT}$$

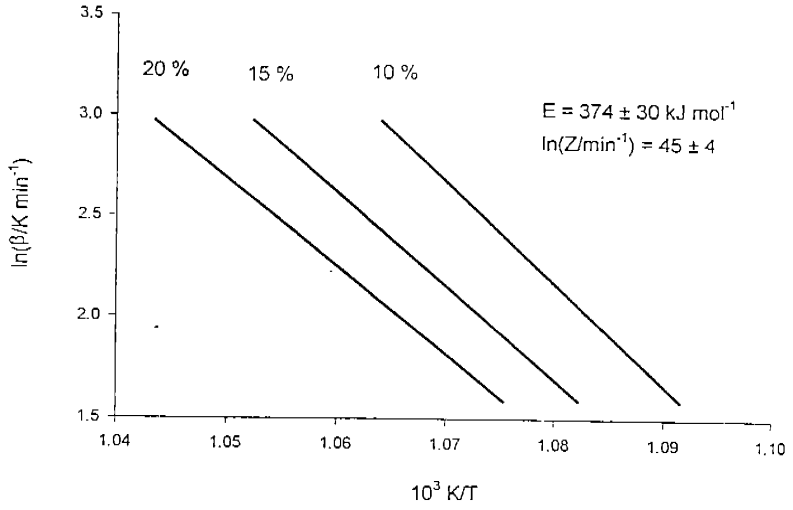
At constant conversion ie α = constant first 3 terms on R.H.S. are constant

> plot ln β against 1/T

Also, applies to processes involving mass gain eg. oxidation.



TG kinetic studies (ASTM E1641)
Example: $CaCO_3$ decomposition



Analysis of n-th Order Reactions

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

$$= Z\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n$$

Assume that maximum rate occurs when

$$\frac{d\left(d\alpha/dt\right)}{dt} = 0$$

Analysis of n-th Order Reactions

This corresponds with the maximum deflection in the thermal curve at a peak temperature, T_p

ie $(dm/dt)_p$ for TG curve

and $(dQ/dt)_p$ for DSC curve

(assuming that there is a mass change)

Analysis of n-th Order Reaction (cont'd)

if $dT/dt = \beta$, a constant

$$\ln\left(\frac{\beta}{T_p^{\,2}}\right) = \ln\left[\frac{R}{E} Zn(1-\alpha)^{n-1}\right] - \frac{E}{RT_p}$$

First term on R.H.S. is independent of T

> plot $\ln(\beta/T_p^2)$ against $1/T_p$ gives E for nth order reaction

Analysis of n-th Order Reaction (cont'd)

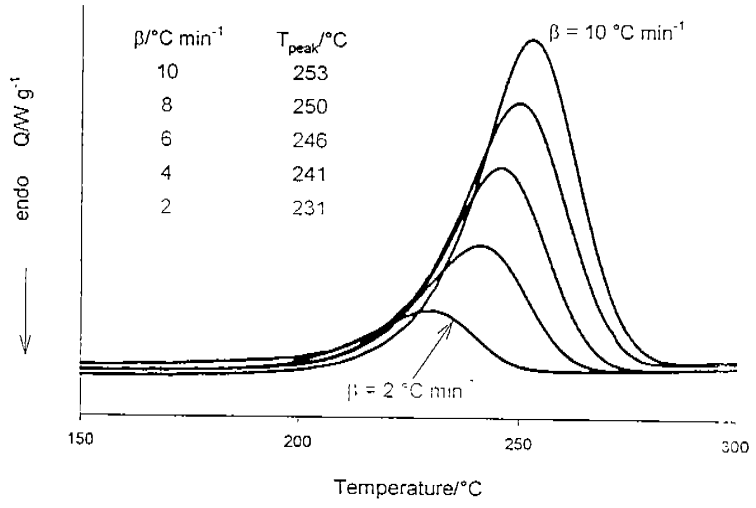
if n = 1

$$Z = \frac{\beta E}{RT_p^{\,2}} \exp\left(\frac{E}{RT_p}\right)$$

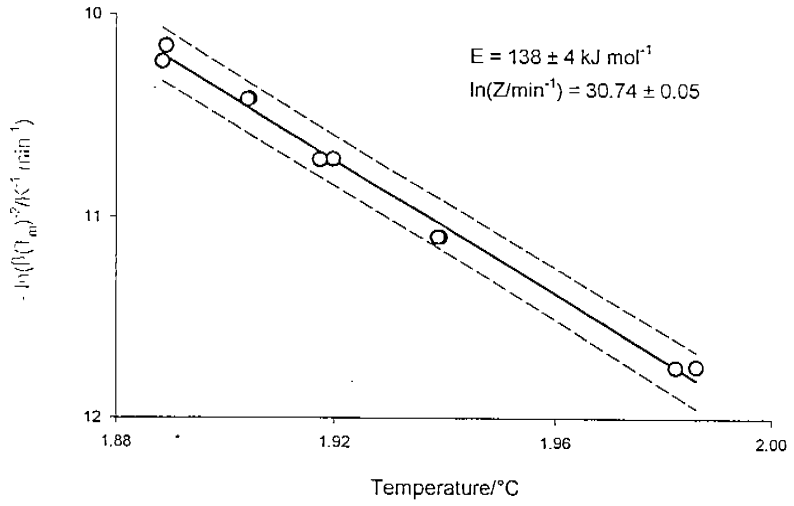
> ASTM E698

> Application to DSC results for GAP

DSC results for kinetic studies
Example: GAP



DSC kinetics studies (ASTM E 698)
Example: GAP decomposition

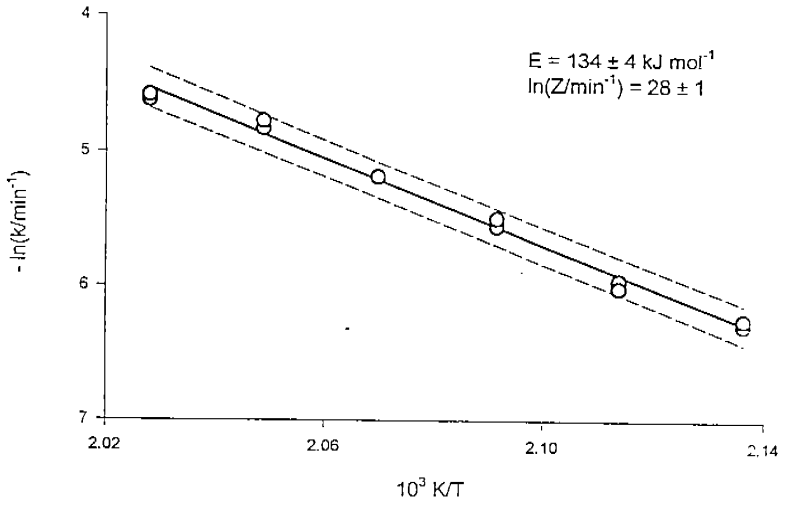


ISOTHERMAL METHODS

Direct method – TG

A multiple linear regression is carried out with $\ln(d\alpha/dt)$ as the dependant variable and $1/T$, $\ln\alpha$ and $\ln(1-\alpha)$ as independent variables.

TG isothermal kinetics studies
Example: GAP decomposition

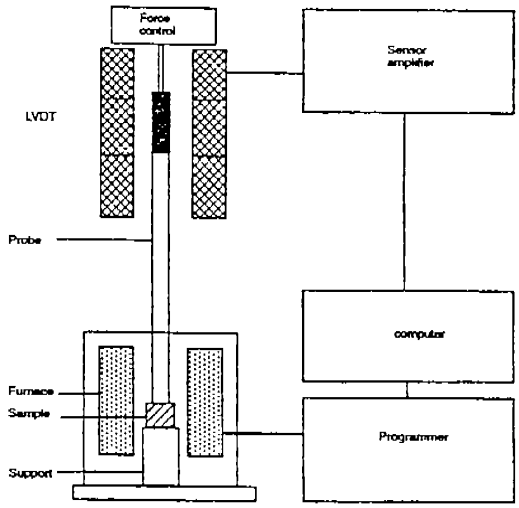


Thermomechanical Analysis (TMA)

Thermomechanical Analysis (TMA)

A technique in which the dimension of a sample is monitored against time, temperature and applied force, while the temperature of the sample, in a specified atmosphere, is programmed.

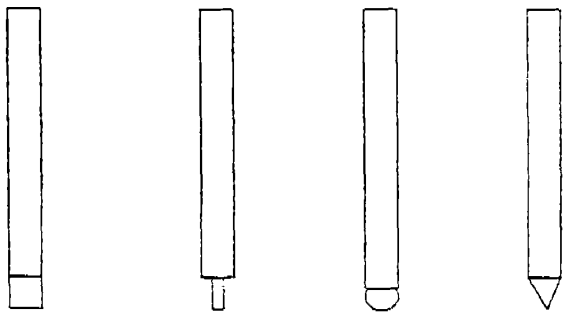
TMA – Schematic diagram



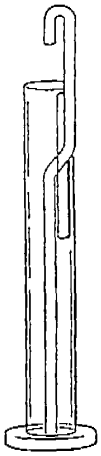
TMA – Measured signals

- Length (probe position) relative to set position
- Rate of length change
  - > dL/dt = Creep (flow)
  - > dL/dT = Coefficient thermal expansion (CTE)
- Stress (applied force)
- Temperature
- Time

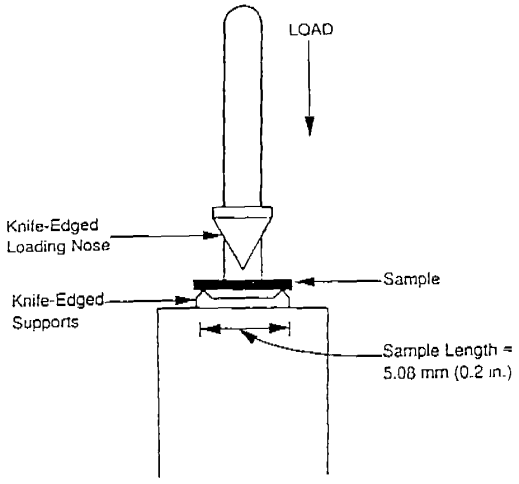
TMA probe configurations



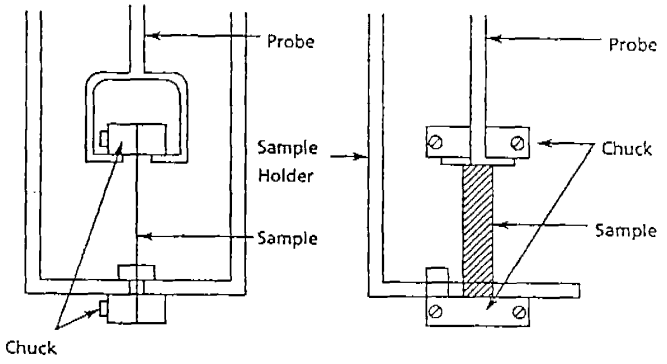
Standard expansion probe configuration



Flexure probe and stage



Tension mounted sample



TMA – Calibration

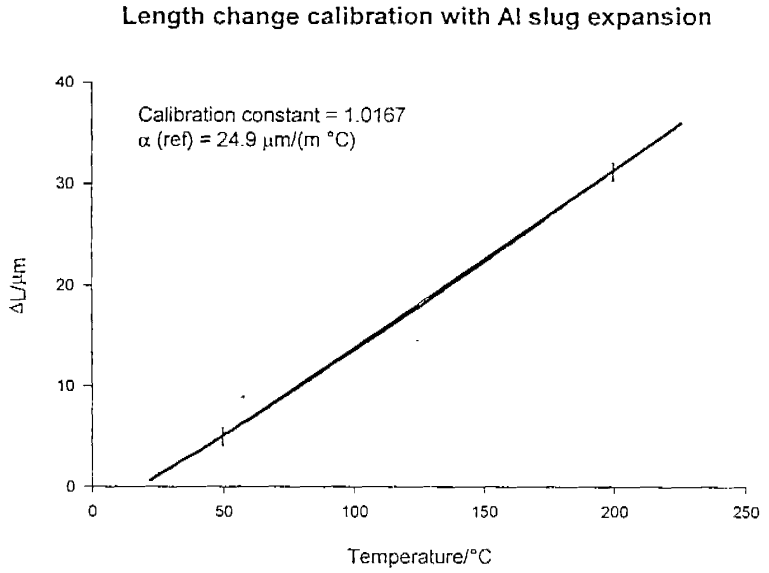
- Sample length and stress
- Linear variable differential transformer (change in sample length)
- Temperature

TMA – Sample length and stress calibration

- usually done electronically as part of module calibration
- the procedures varies from one instrument design to another

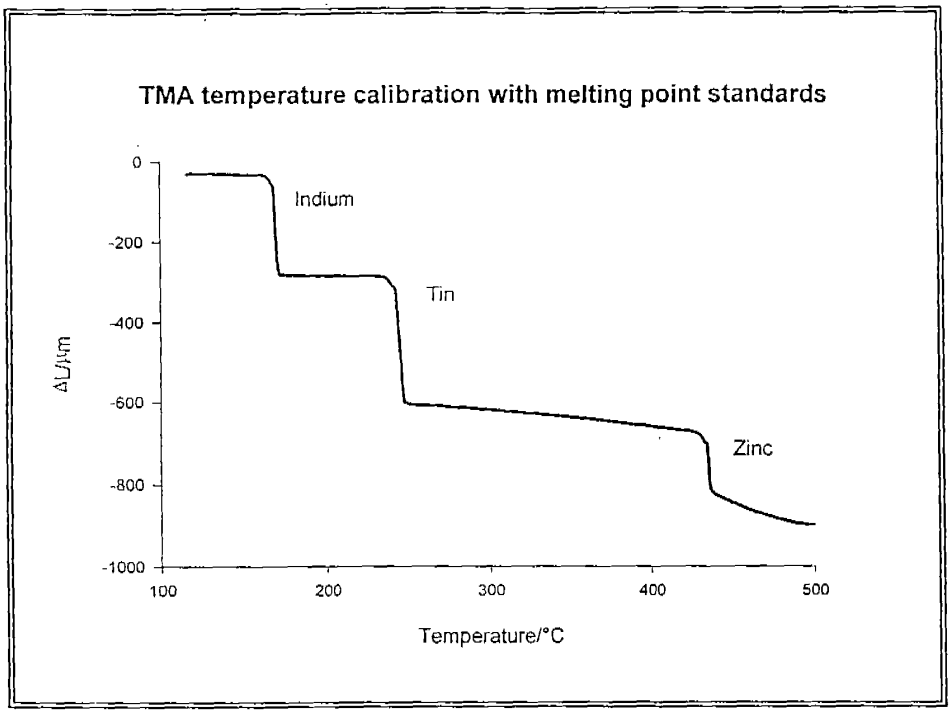
TMA – Length change calibration

- ASTM E831
- using Al, Pt, Cu standards
- often called "cell constant" or "expansion calibration factor"
- check baseline (no sample) to determine effect on CTE measurements



TMA – Temperature calibration

- typically done with melting point standards in form of foil and expansion probe with 5-10 g load
- standards in form of wire can be used for fiber and film probes (tension mode)
- calibration procedures often lead to significant errors in glass transition temperature compared to DSC

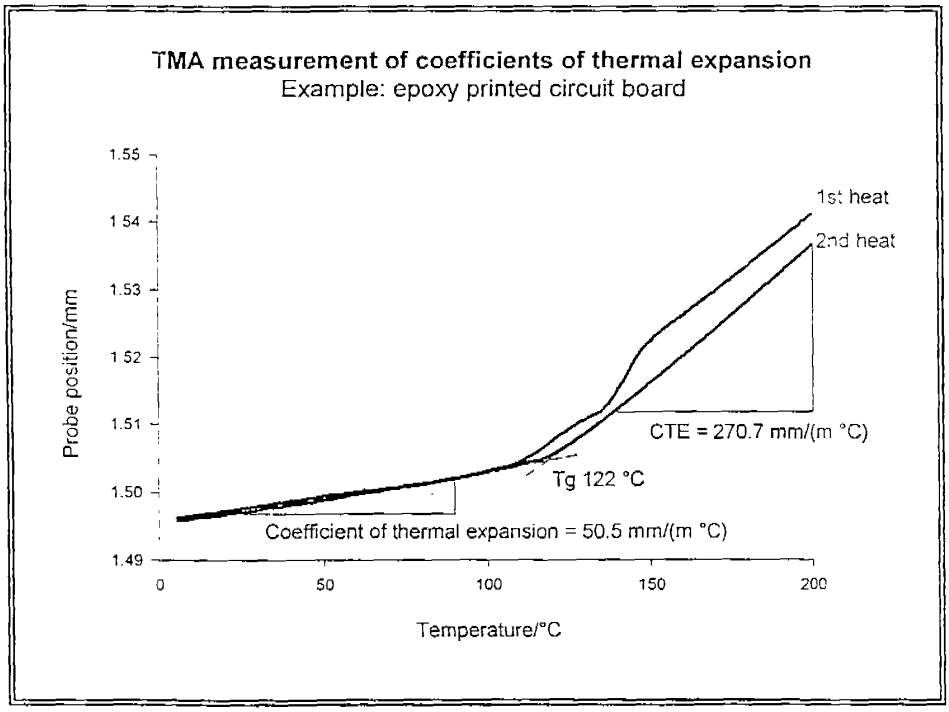


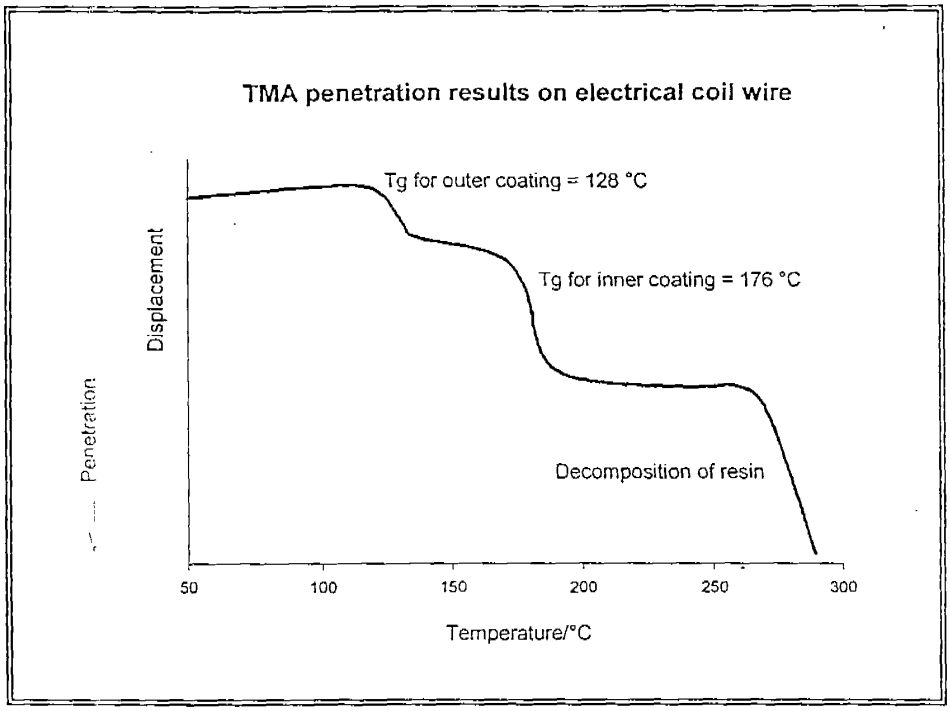
TMA – Applications

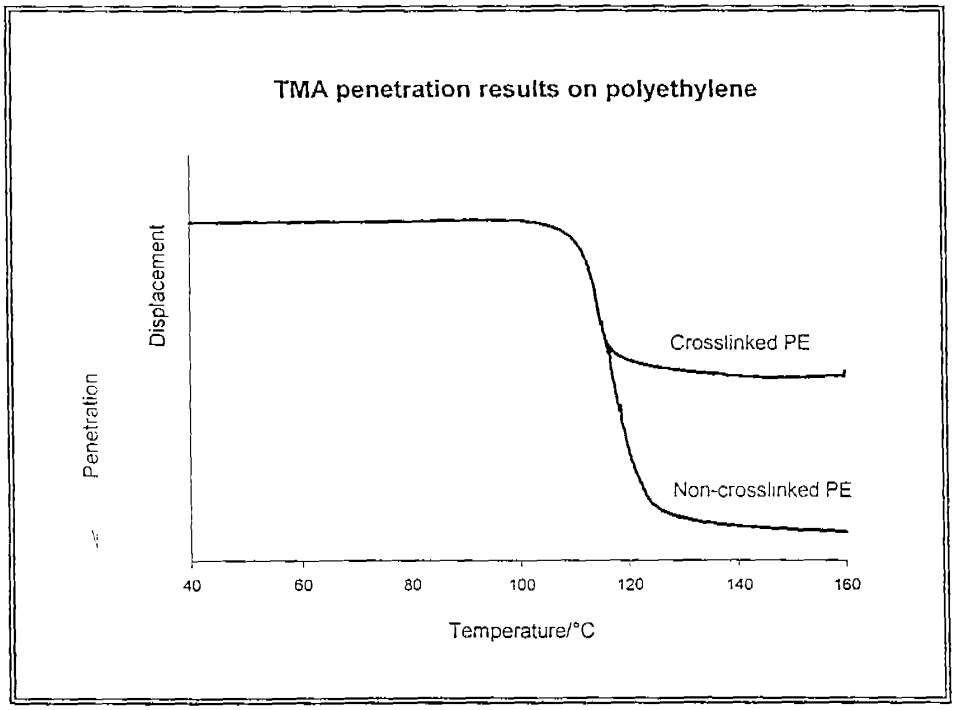
- Coefficients of thermal expansion
- Glass transition temperature
- Softening temperature
- Phase transitions
- Thermal stability
- Chemical reactions
- Liquid-solid interactions

Coefficient of thermal expansion

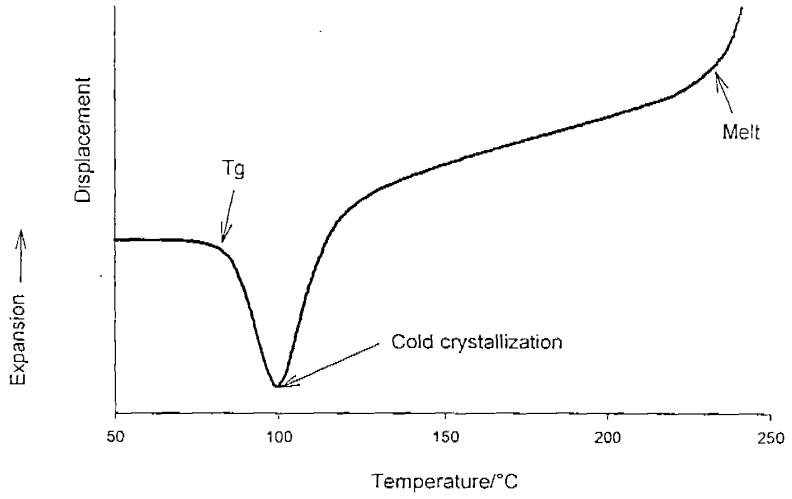
- quantitative measurement of ΔL with ΔT
- important in many applications but especially in composite structures
- results can vary significantly with samples having orientated structure due to processing (tension, pressure, cooling rate etc.)
- high accuracy/reproducibility usually obtained with samples > 5 mm thick



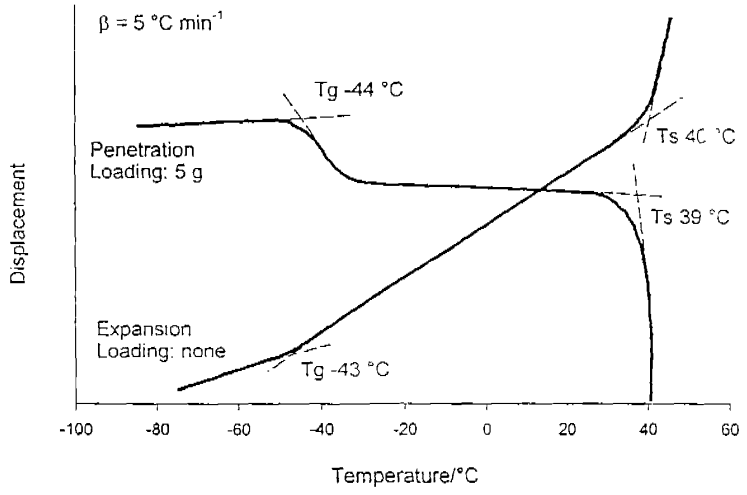

TMA penetration results on electrical coil wire
Tg for outer coating = 128 °C
Tg for inner coating = 176 °C
Decomposition of resin
Displacement
Penetration
50
100
150
200
250
300
Temperature/°C

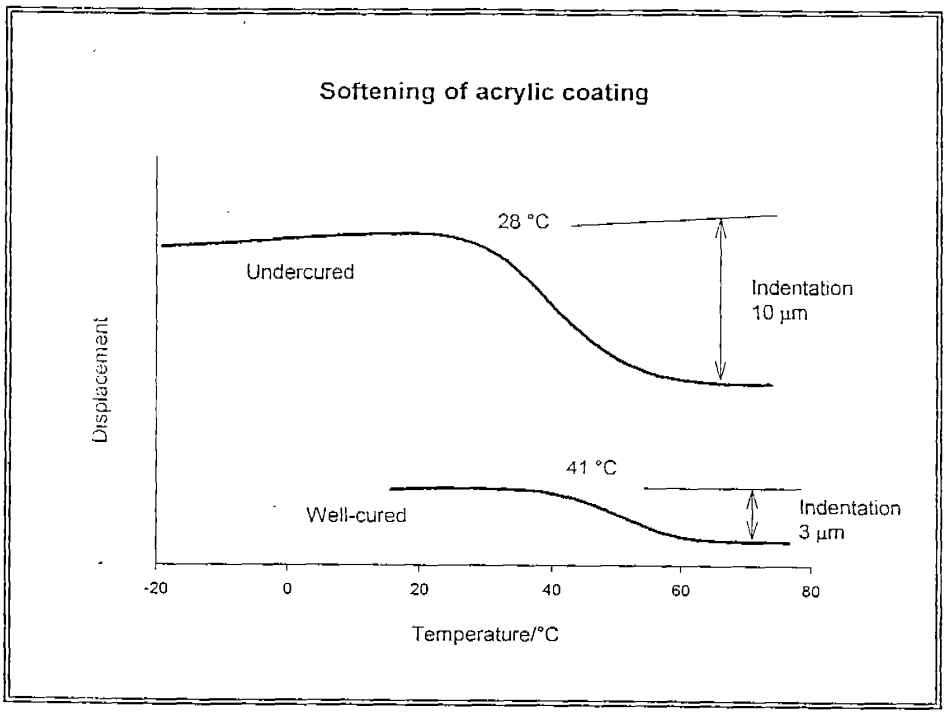

TMA penetration results on polyethylene
Crosslinked PE
Non-crosslinked PE
Displacement
Penetration
40
60
80
100
120
140
160
Temperature/°C

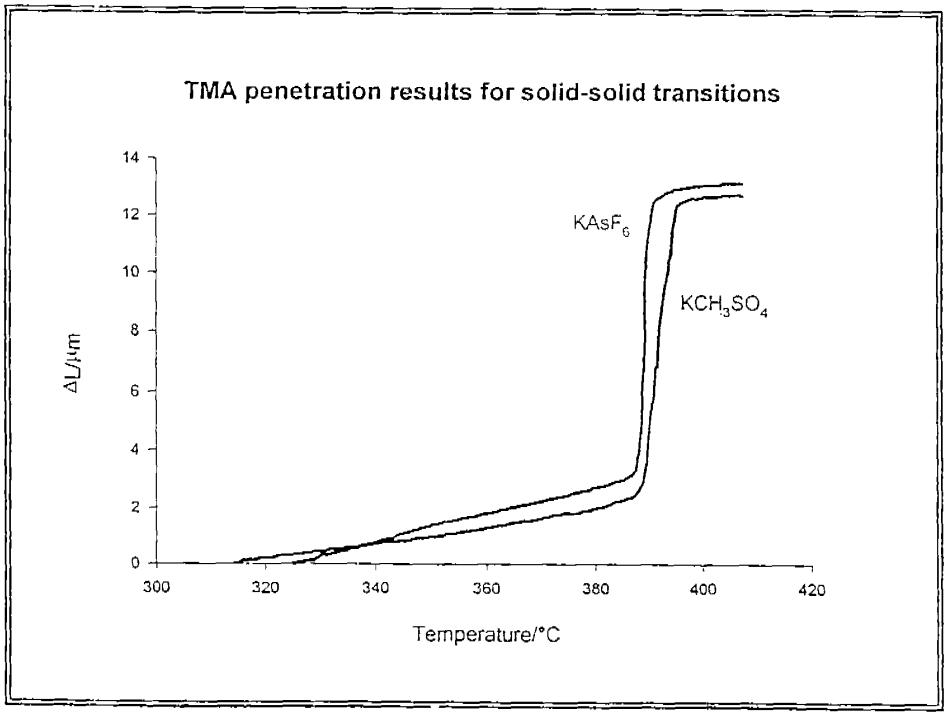
TMA extension results on polyester partially oriented fibers

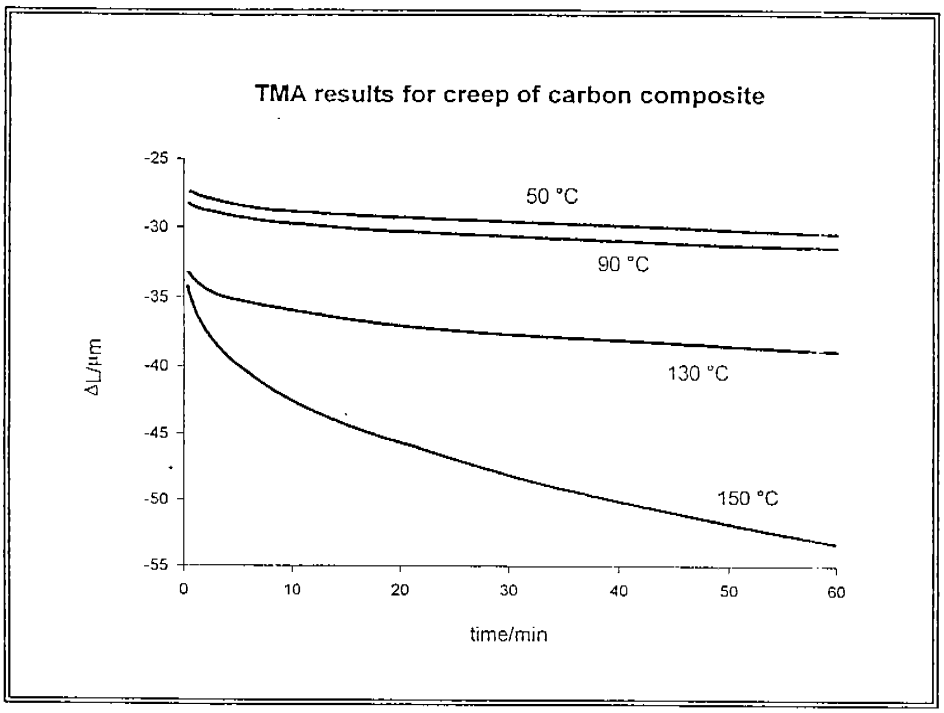


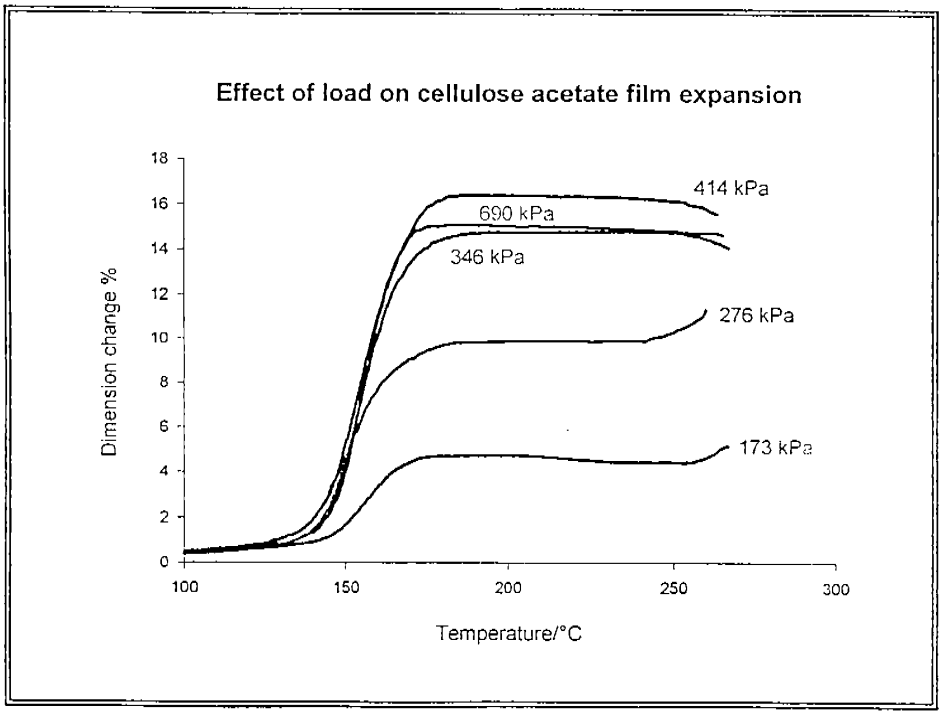
TMA measurement of glass transitions and softening points




Softening of acrylic coating
28 °C
Undercured
Indentation
10 µm
Displacement
41 °C
Well-cured
Indentation
3 µm
-20
0
20
40
60
80
Temperature/°C


TMA penetration results for solid-solid transitions
14
12
10
8
6
4
2
0
ΔL/µm
KAsF6
KCH3SO4
300
320
340
360
380
400
420
Temperature/°C


TMA results for creep of carbon composite
-25
-30
-35
-40
-45
-50
-55
ΔL/μm
50 °C
90 °C
130 °C
150 °C
0
10
20
30
40
50
60
time/min


Effect of load on cellulose acetate film expansion
18
16
14
12
10
8
6
4
2
0
Dimension change %
414 kPa
690 kPa
346 kPa
276 kPa
173 kPa
100
150
200
250
300
Temperature/°C

Summary

- Thermal analysis defined and a number of instrumental and sample parameters which affect results described.
- General features of TG, DTA/DSC and TMA outlined.
- In the discussion of TG, the different modes of operation, errors that may occur, calibration and various applications presented.

Summary (cont'd)

- Types of DSC discussed and DSC and DTA compared. Calibration of DSC, optimization of parameters and various applications presented.
- Application of TG and DSC to determination of kinetic parameters outlined and illustrated.
- Description of TMA includes measured signals, different types of probes, calibration and various applications.

Conclusions

- The thermal techniques, TG, DTA/DSC and TMA are very useful for characterization of a variety of materials.
- The apparatus must be carefully calibrated and the operating conditions optimized to get the best information from the techniques.
- Often, combining these techniques with other characterization tools maximizes the information obtained.