MAT 312
Material Characterization

Thermal Analysis

lecture notes at
http://people.sabanciuniv.edu/~mpapila/mat312.htm

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Online seminar by Perkin Elmer

• Introduction to Thermal Analysis for Materials Characterization

http://las.perkinelmer.com/Registration/FormBuilderThankYou.htm?Text=ASOSS02

(Included in the exam!!!)
Differential Thermal Analysis- DTA

• The edge of DTA is being concerned with measurement of energy changes in materials.

• Applicable to variety of phenomena since every physical or chemical change involves a change in energy.
Differential Thermal Analysis- DTA

- Thermocouples measuring respective temperatures of S (sample) and R (reference material) exposed to the same heating/cooling schedule via symmetric arrangement in the same furnace
- The difference in the temperature profiles of S and R as the cycle progresses also recorded

http://www.anasys.co.uk/library/dsc1.htm
Differential Thermal Analysis- DTA

- When sample experiences energy change associated with a physical/chemical phenomena, the difference in the temperature profiles of S and R identifies the transition

- If, for instance, the sample melts, its temperature will lag behind $T_R$ as it absorbs the heat energy necessary for melting
  - $\Delta T$ against time, or more often, sample temperature. The curve shows an endothermic (heat-absorbing) peak.

http://www.anasys.co.uk/library/dsc1.htm
Classical DTA

- A single block with symmetrical cavities for the sample and reference is heated in the furnace
- **Fig 4.1a** ([Introduction to thermal analysis.](/Brown, Michael E , e-book))

- Heat sinking block and sample holder of low thermal conductivity placed on the block ensure an adequate differential temperature signal
- During a thermal event sample temperature will depart from reference temperature
  - Endothermic event (e.g. melting), $\Delta H > 0$ and $T_s < T_r$
  - Exothermic event (e.g. oxidation), $\Delta H < 0$ and $T_s > T_r$
- **Fig 4.1c** ([Introduction to thermal analysis.](/Brown, Michael E , e-book))
Classical DTA

- Reference material
  - Should not undergo thermal events over the operating temp range
  - Should not react with the sample holder or thermocouple
  - Thermal conductivity and heat capacity should be similar to the sample material

- DTA instruments are still valuable, particularly at higher temperatures (>1000°C), or in aggressive environments, where true heat-flux DSC instruments may not be able to operate.
Differential Scanning Calorimetry-DSC

- Calorimetry: measurement of the heat changes that occurs during a process
- Sample and reference are placed on a thermally conducting bases attached to the thermocouples (S and R materials standing free) properties of the sample
- Quantitative measurements of enthalpies of transformations are also possible
- Practical difference between DTA and DSC: Nature of the signal from the equipment
  - DTA, proportional to $\Delta T$
  - DSC, proportional to difference in thermal power between sample and reference $\frac{d(\Delta q)}{dt}$
Differential Scanning Calorimetry - DSC

• The differential scanning calorimeter (DSC) is an analytical tool that measures the heat flux to a material sample as it is maintained at a constant temperature or along a linear temperature ramp. The DSC operates by comparing the heat transfer to the sample pan with the heat transfer to a reference pan. From this heating data, physical properties such as melting point, glass transition point, and reaction kinetics can be determined.

• DSC is used for instance
  – (a) in an isothermal mode to determine the cure kinetics of a thermoset resin and
  – (b) in the varying temperature mode to identify the thermal transitions of various thermoplastic polymers.
Differential Scanning Calorimetry-DSC

- Measure the energy necessary to establish a nearly-zero temperature difference between the S and R while the two are subjected to an identical Temperature schedule.

- Two types
  - Power-compensation
  - Heat-flux
Differential Scanning Calorimetry-DSC

- **Power-compensation DSC: fig 4.2** ([Introduction to thermal analysis.](#) / Brown, Michael E , e-book) ([fig 2, Haines](#))
  - Individual microheaters and temperature sensors for both S and R are employed
  - The background heating of the block is provided by a separate heater/cooler
  - This separate system tries to keep the average temperature of the sample and heater at a set temperature $T_p$.
  - Vary the power input to the two furnaces, energy associated with the power changes is a measure of the enthalpy or heat capacity changes
Differential Scanning Calorimetry- DSC

• Heat-Flux DSC:
  – S and R in pans are enclosed in the same furnace, and placed on a metal block of high thermal conductivity (constantan, silver) which ensures a good heat flow path between the two. A good thermal contact between sample, pan and heat flux plate is provided.
  – The enthalpy or heat capacity changes lead to temperature differences relative to R resulting in a heat-flow between S and R.
  – Note the provision for establishing a gas flow through the cell, to sweep away volatiles, provide the required atmosphere, and to assist in heat transfer.

http://www.anasys.co.uk/library/dsc1.htm
Differential Scanning Calorimetry - DSC

- **Heat-Flux DSC:**

![Diagram of Heat-Flux DSC](image)

http://www.anasys.co.uk/library/dsc1.htm
Differential Scanning Calorimetry-DSC

- Both types make use of two crucibles of 5-6 mm in diameter
- One for the sample, one for the reference (empty or inert material in it)
- Most are heat flux type

[Diagram of DSC setup]
Differential Scanning Calorimetry-DSC

• Terminology relating to the results from DSC

![Diagram of DSC curve]

An offset, **O**, is usually apparent, which is due to an imbalance in the thermal capacities of the sample pan and its contents, and the reference pan and contents.

In the absence of any discrete physical or chemical transformations, the baseline signal, as at **B** above, is related to the heat capacity of the sample.

The DSC/DTA curve may show a step change, as at **S** in the curve, reflecting a change in heat capacity not accompanied by a discrete enthalpy change.

http://www.anasys.co.uk/library/dsc1.htm
Differential Scanning Calorimetry-DSC

- Greatest impact: study of polymer materials. Crystallinity, melting, glass transition, curing processes

- http://pslc.ws/macrog/dsc.htm
Differential Scanning Calorimetry - DSC

Sample: Polyethylene terephthalate (PET)
Temperature increase rate: 20°C/min
Temperature range: 30°C - 300°C
# DSC- Enthalpy Changes

<table>
<thead>
<tr>
<th>Process</th>
<th>Exotherm</th>
<th>Endotherm</th>
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</thead>
<tbody>
<tr>
<td>Solid-solid transition</td>
<td>*</td>
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<tr>
<td>Crystallisation</td>
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<td>Melting</td>
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<td>Vaporisation</td>
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<td>Adsorption</td>
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<tr>
<td>Desorption</td>
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<tr>
<td>Desolvation (drying)</td>
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<td>*</td>
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<tr>
<td>Decomposition</td>
<td>*</td>
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<td>Solid-solid reaction</td>
<td>*</td>
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<tr>
<td>Solid-liquid reaction</td>
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<tr>
<td>Solid-gas reaction</td>
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<tr>
<td>Curing</td>
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<tr>
<td>Polymerisation</td>
<td>*</td>
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<tr>
<td>Catalytic reactions</td>
<td></td>
<td>*</td>
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</tbody>
</table>

http://www.anasys.co.uk/
Glass Transition

• The temperature below which molecules have little relative mobility.
• Usually applicable to wholly or partially amorphous phases such as glasses and polymers.
• For inorganic or mineral glasses, such as common glass, it is the mid-point of a temperature range in which they gradually become more viscous and change from being liquid to solid.
• Thermoplastic (non-crosslinked) polymers are more complex because, in addition to melting point, Tm, above which all their crystalline structure disappears, such plastics have a second, lower Tg below which they become rigid and brittle, and can crack and shatter under stress.
• Above Tg, the secondary, non-covalent bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery and capable of elastic or plastic deformation without fracture. This behavior is one of the things which make most plastics useful.
Glass Transitions

- characterized by change in heat capacity (no heat absorbed or evolved)
- transition from a disordered solid to a liquid
- appears as a step (endothermic direction) in the DSC curve
- gradual enthalpy change may occur, producing an endothermic peak superimposed on the glass transition

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Definition of Transition Temperature

- **Extrapolated onset temperature**: 156.50°C
- **Peak melting temperature**: 157.81°C
- **Heat Flow (W/g)**
- **Temperature (°C)**
Enthalpy of Fusion

156.50°C
28.87 J/g

157.81°C

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Crystalline Structure of PVDF film

- DSC Results (solution cast films)

transformation to $\beta$-phase favorable for piezoelectricity

stretching introduced $\beta$-phase transformation
- **DSC Results – (Electrospun fiber mats)**

  - Close to thermal behavior of stretched solution cast films
  - Effect of stretching by e-spin
  - No significant change in the melting point when electrospun randomly oriented fiber mats are additionally stretched
DSC-Heat Capacity

\[
\frac{D\ (\text{sample})}{D\ (\text{sapphire})} = \frac{C_p\ (\text{sample}) \times \text{mass of sample}}{C_p\ (\text{sapphire}) \times \text{mass of sapphire}}
\]
Differential Scanning Calorimetry-DSC

- **Identity of a component in a mixture can be confirmed:**
  - Add the suspected mineral into reference crucible
  - Repeat the analysis
  - Relevant peak should diminish
Recognizing Artefacts

- Sample movement in pan
- Sample pan distortion
- Pan moves in furnace
- Mechanical shock / knock bench
- Cool air entry into cell
- Electrical effects, power spikes, etc.
- Atmosphere changes
- Burst of pan lid
- Cooling / opening pan hole, e.g. sublimation

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DSC-Theory

Introduction to thermal analysis. / Brown, Michael E

Page 59 (e-book)
Modulated DSC

• Conventional linear heating ramp(s) modulated by superimposing a wave function of small amplitude
• A linear change in average temperature with time

• Allows separation of reversing processes (glass transition) from non-reversing processes (cure reactions)
Modulated DSC (MDSC)

- introduced in 1993; “heat flux” design
- sinusoidal (or square-wave or sawtooth) modulation is superimposed on the underlying heating ramp
- total heat flow signal contains all of the thermal transitions of standard DSC
- Fourier Transformation analysis is used to separate the total heat flow into its two components: reversing and non-reversing heat flow
- increased sensitivity, resolution and the ability to separate multiple thermal events

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MDSC for Polymorph Characterization

Heat capacity
(reversing heat flow)
glass transition
melting

Kinetic
(non-reversing heat flow)
crystallization
decomposition
evaporation

reversing heat flow
Lot A
Lot B

non-reversing heat flow
Lot A
Lot B

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‘Hyper’ DSC

- Fast scanning DSC
- Only possible with power compensated
- Normal equipment ≈ 100 °C/min
- Specialised up to 500 °C/min
- Increased sensitivity, loss of resolution
- e.g. amorphous content in mainly crystalline sample
  - change of specific heat at Tg is linear relationship to the amorphous content
  - Conventional DSC 10% amorphous limit of detection
  - Hyper DSC <1% amorphous easily detected

Sample Preparation

- accurately-weighed samples (~3-20 mg, usually 3-5 mg for simple powders)
- small sample pans (0.1 mL) of inert or treated metals (Al, Pt, stainless)
- several pan configurations, e.g., open, pinhole, or hermetically-sealed pans
- same material and configuration should be used for the sample and the reference
- material should completely cover the bottom of the pan to ensure good thermal contact
- avoid overfilling the pan to minimize thermal lag from the bulk of the material to the sensor

* small sample masses and low heating rates increase resolution, but at the expense of sensitivity

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Best Practices for Thermal Analysis

- proper instrument calibration
- use purge gas (N₂ or He) to remove corrosive off-gases
- small sample size
- good thermal contact between the sample and the temperature-sensing device
- proper sample encapsulation
- start temperature well below expected transition temperature
- slow scanning speeds
  (Unless aiming to obscure thermal transitions, e.g. fast scan DSC)
- avoid decomposition in the DSC
  (Run TGA first – it’s easier to clean up!)

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Dynamic Mechanical Analysis (DMA)

- [http://www.anasys.co.uk/library/macrot.htm](http://www.anasys.co.uk/library/macrot.htm)

Introduction to DMA

• DMA is simply described as applying an oscillating force to a sample and analyzing the material’s response to that force.

• In late 1970’s Murayama, Read, Brown wrote a book, uses of DMA for material characterization

• Applied force $\rightarrow \sigma$

• Response $\rightarrow \varepsilon$ (or $\delta$)
DMA Structure in general

How the DMA works:
- Constant inputs and outputs function as in the TMA
- A sine wave current is added to the force coil
- The resultant sine wave voltage of the LVDT is compared to the sine wave force
- The amplitude of the LVDT is related to the storage modulus, $E'$ via the spring constant, $k$.
- The phase lag, $\delta$, is related to the $E''$ via the damping constant, $D$.

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
• There are different clamping geometries;

- Single Cantilever Bending
- Dual Cantilever Bending
- 3 Point Bending
- Tension
- Compression
- Shear
• If the specimen is a bar → Single or dual cantilever bending modes are used

• If the samples are soft and thick → Shear measurements are used

• Fibres and films are mounted in tension
Hooke’s Law

- Model is the spring
- As k increases the material becomes stiffer

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
Liquid like flow: Viscous limit

- Newtonian Model, dashpot
- Many oils, fluids are Newtonian

The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
Figure 2  (a)When a sample is subjected to a sinusoidal oscillating stress, it responds in a similar strain wave provided the material stays within its elastic limits. When the material responds to the applied wave perfectly elastically, an in-phase, storage, or elastic response is seen (b), while a viscous response gives an out of phase, loss, or viscous response (c). Viscoelastic materials fall in between these two extremes as shown in (d). For the real sample in (d), the phase angle, $\delta$, and the amplitude at peak, $k$, are the values used for the calculation of modulus, viscosity, damping, and other properties.
Dynamic Stress

Force (dynamic)

F (static)

Stress = FA

Material response

Phase angle = \( \delta \)

Amplitude = k

Strain = \( y^o/y \)

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
Why? Let’s bounce a ball.

$E'' \sim$ energy loss in internal motion

$E' \sim$ elastic response

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
All this is calculated from $\delta$ and $k$:

- From $k$, we calculate $E'$ (storage modulus)
- From $\delta$, we calculate $E''$ (loss modulus)
- then:

$$\tan \delta = \frac{E''}{E'}$$

$$E^* = E' + iE'' = \sqrt{E'^2 + E''^2}$$

$$G^* = \frac{E^*}{2(1+\nu)}$$

$$\eta = 3G^*/\omega$$

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
To apply this to materials...

Since each part of the ramp has a sine wave stress associated with it, we get:

\[
\tan \delta = \frac{E^*, E', E''}{\eta}
\]

for each data point!!

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
DMA and DSC curves

Introduction to thermal analysis. / Brown, Michael E

Page 59 (e-book)

• Fig 4.6

• Fig 4.7
Time Temperature Scans at a Fixed Frequency

- hold frequency constant and vary temperature or time at temperature
- allows detection of transitions in material
- allows one to study cures
- most sensitive method for finding Tg
- can also get changes in dimension (TMA) while collecting DMA data
- Best probe of polymer relaxations as function of temperature

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
Tg are easily seen, as in PET Film

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
or in PP fishing line.

Sample prep can be minimal if only temperatures are needed.

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
Transitions are clearly seen in highly crosslinked samples

This $T_g$ is undetectable in the DSC !!!!!

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
as well as in blends.
Curing of Thermosets

- can be studied at constant temperature or by a temperature ramp
- can get minimum viscosity, gelation point (time) from DMA curve
- cure studies are not limited to polymeric systems but include food products like cakes and cookies
DMA is also used to study the behaviour of thermosetting polymers that are undergoing cross-linking due to chemical reaction;

- The large peak in heat flow at the start is due to the chemical reaction. The mechanical properties do not start to change until about 5 minutes into the crosslinking process as a network of polymer molecules begins to form (gel point). Even after nearly an hour, the DMA detects that curing is still continuing.

- Results from such experiments can be used to construct diagrams showing the changes in a thermoset’s properties which occur as a function of cure time and temperature.

http://www.anasys.co.uk/
Analysis of a Cure by DMA

- E’-E” Crossover ~ gelation point
- $10^6$ Pa ~ Solidity
- Vitrification point
- Curing
- Minimum Viscosity (time, length, temperature)

Postcure studies allow process optimization:

Source: Dynamic Mechanical Analysis, Basis and Beyond, Dr. Lin Li, Perkin Elmer Inc, 2000
QC can often be done by simply fingerprinting the resin.

\[ \eta^* \]

Note the different slopes and the different curve shapes.
DMA, can be used to study the effects of blending two polymers together or adding plasticisers to polymeric systems;

• The diagram near shows; idealised DMA curves of two homopolymers A and B. When they are blended together a completely miscible system results and the glass transition of the resulting system is situated between the Tg's of the parent materials in proportion to the amount of each phase present in the blend.
• The position of the Tg can be predicted from the Fox equation:

\[ \frac{1}{T_{g_{\text{blend}}}} = \frac{W_A}{T_{g_A}} + \frac{W_B}{T_{g_B}} \]

• Where WA & WB are the weight fraction of each polymer who's glass transition temperatures are TgA TgB respectively.

http://www.anasys.co.uk/
Frequency Scans

• hold temperature constant and vary frequency
• allows one to look at trends in material
• can estimate changes in MW and MWD
• looks at both tack-like and peel-like behavior
• can use data for Time Temperature Superposition to extend frequency range or predict age life.

As the mechanical frequency is increased, the position of the glass-rubber transition moves to a higher temperature since the polymer chains need more energy (i.e. the sample needs to be hotter) to respond to the shorter timescale stresses imposed at higher frequencies. Thus time and temperature can be seen to be interchangeable.

Figure 13. DMA results for poly(ethylene terephthalate) film measured in tension at different frequencies shown. The measurements were performed isothermally in 5°C increments and the apparatus allowed to come to thermal equilibrium for 5 minutes before the sequence of measurements was performed.

- As the mechanical frequency is increased, the position of the glass-rubber transition moves to a higher temperature since the polymer chains need more energy (i.e. the sample needs to be hotter) to respond to the shorter timescale stresses imposed at higher frequencies. Thus time and temperature can be seen to be interchangeable.