

# Thermal Analysis Report

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## Part I

### Answer: (a)

Information that can be obtained from TGA analysis ...

1. **Thermal and/or Oxidative stability of sample** – through decomposition temperatures.
2. **Composition of the sample** – via the pathway of degradation, and by varying TGA evaluation atmosphere (inert to reactive).
3. **Amount of adsorbed/desorbed contents on the sample** – through % mass change.
4. **Decomposition Kinetics of the sample** – by observing the rate of % mass change.

### Answer: (b)

Effect of heating rate in the features in a TGA thermogram ...

1. High heating rate
  - 1.1. Upside: Smaller samples can be measured and signal-to-noise ratio is better.
  - 1.2. Downside: Too high a heating rate would result in a thermal lag in the thermogram, and overlaps any consequent transitions.
2. Low heating rate
  - 2.1. Upside: A low heating rate would ensure thermal equilibrium is approached, thereby enabling to resolve overlapping transitions in the thermogram. Larger samples can be measured (with good resolution).
  - 2.2. Downside: Poorer signal-to-noise ratio.

### Answer: (c)

DTG ...

Thermal analysis carried out by analysing the rate of change of mass (with time/temperature) for a sample w.r.t a reference, to the applied heat treatment. In mathematical notion, DTG is the first derivative of TG.

### Answer: (d)

Information that can be obtained from DSC analysis ...

1. **Phase transitions and corresponding temperatures (transition points) of the sample** – by analysing transition peaks (physical/allotropic/polymorphic) in the DSC thermogram.
2. **Enthalpy of phase transitions in the sample** – area covered by the DSC heat flux peak of the corresponding phase transition.

3. **Heat capacity of the sample** – ratio of the absolute value of the DSC heat flow to the heating rate, multiplied by the calibration constant for the DSC setup.
4. **Phase diagram (binary/ternary/..) of the sample** – by combining DSC thermograms of varying sample compositions.
5. **Degree of crystallinity in the sample** – ratio of the melting heat enthalpies of partially crystalline sample to the fully crystalline sample.

## Answer: (e)

### **Effect of heating rate in the features in a DSC thermogram ...**

Similar to Answer: (b) for TGA, too a high a heating rate may cause a thermal lag in the phase transition onset temperatures in the sample with poorer resolution; and a lower heating rate might take a longer time with better resolution in the thermogram.

## Answer: (f)

### **Typical transitions observed in polymeric materials in DSC thermograms ...**

1. Melting
2. Freezing
3. Glass Transition
4. Cross-linking
5. Oxidation/Reduction

## Answer: (g)

### **Quantification of the amount of polymer coating on a given nanopowder of ceramic/metallic material ...**

Using TGA analysis, one can measure the % mass lost due to just the oxidative thermal degradation of the polymer coating, by reaching temperatures at and above which the polymer degrades in air (but not high enough at which the ceramic/metallic nanopowder starts to melt and evaporate).

## Answer: (h)

### **Evaluation of crystallinity in a composite polymeric material ...**

The ratio of melting heat enthalpies of partially crystalline to the fully crystalline sample is indicative of the degree of crystallinity in the composite polymeric material, and melting enthalpies can only be obtained in a DSC. The amount of crystallinity is thus proportional to the area under the melting heat flux peak in DSC (which is in-turn its enthalpy of melting).

## Answer: (i)

### **Evaluation of thermal stability of a polymer-inorganic composite material with different inorganic content ...**

Any polymeric thermal stability measurement accompanies decomposition processes, which can be measured by TGA. Polymers decompose more readily than inorganics under heat. Hence, with the polymer-inorganic composite material, the effect of different inorganic content is reflected in the corresponding TGA thermograms – higher decomposition kinetics in the material leads to higher rate of % mass change and lower degradation temperature in the thermogram, and vice-versa.

## Part II

### Experimental Section

The objective of this experiment is to make a thermal analysis of an unknown sample using first TGA then DSC, and this sequence is followed so as to affirm the transitions observed in TGA and so that the sample can be destructively tested to watch out for any unexpected decomposition outbursts / flares / evaporation (which should not be allowed to happen in DSC apparatus).

#### **Measurement Procedure ...**

##### **TGA**

1. First, N<sub>2</sub> was selected to be purged in the sample chamber, and then flow rates for the balance and furnace were set in the TGA acquisition software.
2. A Pt pan was selected as the sample holder and inspected for residues on its inner surface. If found, the holder's inner surface was then cleaned with a Q-tip wet in Acetone and further burned to remove any excess residue.
3. The clean pan was then placed in the autosampler to tare. When complete, the pan was then loaded with 10-20 mg of the unknown sample such that it fits the holder and the surface flat.
4. The details of the sample are then entered in the TGA acquisition software, and the ramp rate, temperature range are set. This program was then run, and after completing the analysis, the TGA instrumentation was set to equilibrate and cool down before the sample was unloaded.

##### **DSC**

1. N<sub>2</sub> was purged in the sample chamber with appropriate flow rate, and flange temperature set to be within -80 °C and -90 °C, for 10 minutes.
2. An Al pan was selected as the sample holder, and placed in the sample chamber to be tared and calibrated upto 5 significant digits.
3. Via the DSC acquisition software, details of the sample were then entered along with the ramp rate and temperature range. This program was then run. After completion of the analysis, DSC instrumentation was set to return 40 °C, after which sample was unloaded, N<sub>2</sub> purge turned off.

# Results

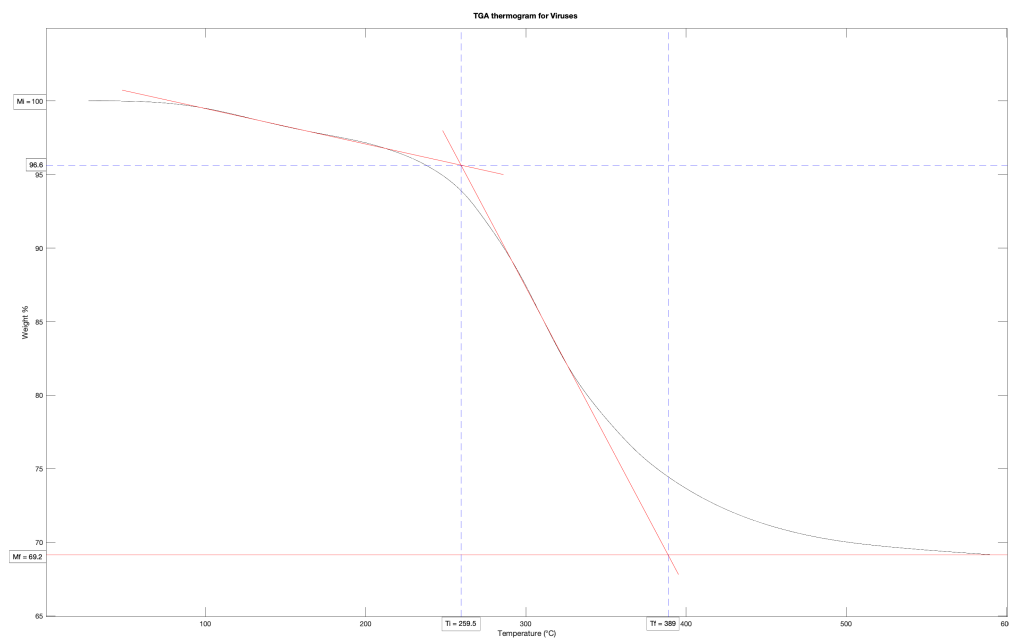


Figure 1: TGA thermogram for Pyrolysis of Viruses.

% C content in Viruses = Residual mass left after pyrolytic decomposition = 69.2% (Mf in Figure 1).

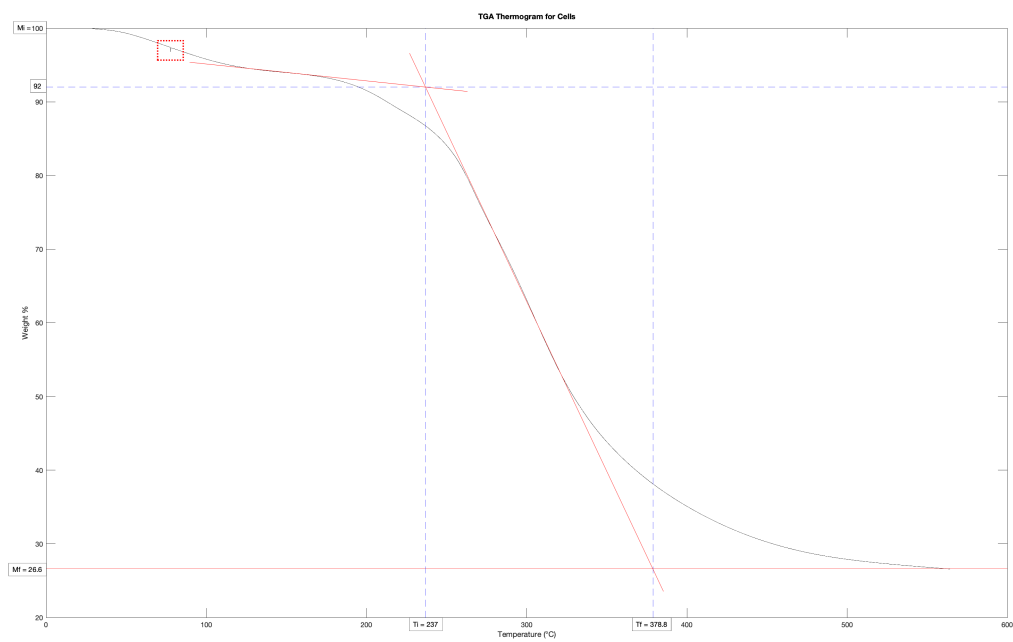


Figure 2: TGA thermogram for Pyrolysis of Cells.

% C content in the Cells = Residual mass left after pyrolytic decomposition = 26.6% (Mf in Figure 2).

The red dotted box in Figure 2 identifies an abrupt change (dip) in the data, and this may occur due to any vibrational interference from outside the apparatus during TGA.

## Part III

### Solutions to Assignments

#### Answer: 1

Percentage organic component in  $\text{Fe}_3\text{O}_4$  nanoparticles coated with a layer of aminopropyl triethoxy silane (APTES) ...

Assuming there is no decomposition of the ceramic phase,

$$\% \text{ organic component} = \%m_i - \%m_f = 100\% - 88\% = 12\%$$

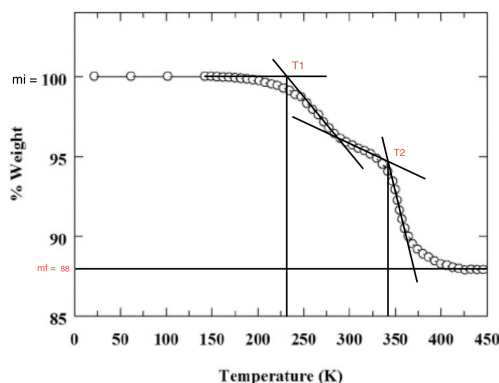


Figure 3: Inset for initial and final sample masses in the given TGA thermogram.

If DSC analysis was performed on the same sample, then information on the phase transitions (and corresponding enthalpies) at T1 (230 K) and T2 (340 K) can be obtained in addition to TGA.

#### Answer: 2

MgO-MgCO<sub>3</sub> nanopowder mix ...

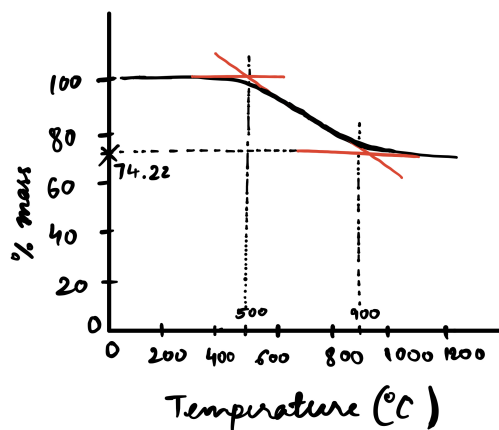


Figure 4: Hypothetical TGA thermogram for MgO-MgCO<sub>3</sub> nanopowder mix according to said data.

- (a) % mass after decomposition =  $100 - \left( \frac{125.3-93}{125.3} \times 100 \right) = 74.22$ .
- (b)  $\therefore$   $\text{MgCO}_3$  is the only decomposing component into (most likely)  $\text{CO}_2$  and  $\text{MgO}$ .  
 $\therefore$  %  $\text{MgO} = \frac{\text{mass left}}{\text{initial mass}} \times 100 = \frac{93}{125.3} \times 100 = 74.22$ .
- (c) In the DSC thermogram of this sample, one would observe a single peak for this single transition (from 500 - 900 °C) observed in TGA. This DSC peak would then correspond to the endothermic decomposition of  $\text{MgCO}_3$  into  $\text{MgO}$  and  $\text{CO}_2$ , the enthalpy of which can be calculated from the area under this DSC decomposition peak.

## Answer: 3

### Interpretation of TGA thermograms of a) $\text{TiO}_2$ , b) PCz and c) PCz/ $\text{TiO}_2$ -8 nanocomposite

- (a)  $\text{TiO}_2$ :  
 Pure  $\text{TiO}_2$  has negligible effect on its weight change upon heating, upto its boiling point of 2,972 °C. The observed % weight change in the corresponding TGA thermogram may then be due to desorption/drying of any surface contaminants.
- (b) PCz:  
 Pure Polycarbazole (PCz) shows dual-stage decomposition at T1 and T2 (marked red in Figure 5). Thereafter at higher temperatures, it rapidly decomposes to a smaller weight% (<10%). Based on this observation on its initial and final weight %, it may be concluded that this analysis was carried out in atmospheric air (atleast from T1 if not before), leading to the rapid loss in PCz weight mainly as  $\text{CO}/\text{CO}_2$  upon consequent heating. The transition at T1 can be better resolved with a slower heating rate. The initial weight loss (until T1) may be due to desorption and/or pyrolytic breakdown of PCz in inert atmosphere.
- (c) PCz/ $\text{TiO}_2$ -8 nanocomposite:  
 As can be observed in Figure 5, due to the presence of  $\text{TiO}_2$  in the PCz nanocomposite, the corresponding transition temperatures (T3 and T4) shifted to higher temperatures when compared to T1 and T2 respectively. This may be due to adherence of  $\text{TiO}_2$  (a high melting material) to the PCz composite matrix, leading to a delay in the dual-stage decomposition mechanism. The final weight loss (from T4) can also be observed to be substantially less than that of pure PCz, and this can again be attributed to the presence of  $\text{TiO}_2$  in PCz matrix.
- As discussed in (b), the initial weight loss until T3 may be due to desorption and/or pyrolytic breakdown of PCz in inert atmosphere. And the final weight loss from T4 may be due to atmospheric oxidation of PCz breakdown products.

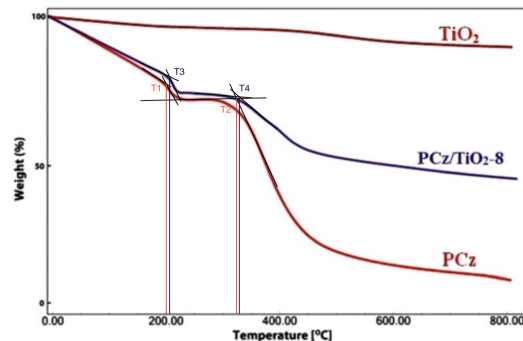


Figure 5: TGA thermograms of (a)  $\text{TiO}_2$  (b) PCz (c) PCz/ $\text{TiO}_2$  nanocomposite.