IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2014

PART X

and

M.Sc. in ADVANCED CHEMICAL ENGINEERING

For Internal Students of Imperial College London

This paper is also taken for the relevant examination
for the Associateship

PRODUCT CHARACTERISATION

Wednesday 21st May 2014: 10.00 – 11.30

Answer any **three** questions

All questions carry equal marks

or

Question 1 carries 25 marks (Answer in Red Booklet)
Question 2 carries 25 marks (Answer in Blue Booklet)
Question 3 carries 25 marks (Answer in Green Booklet)
Question 4 carries 25 marks (Answer in Orange Booklet)

Note: the paper will be marked out of 75 and the result expressed as a percentage

**THIS EXAMINATION PAPER HAS 5 PAGES IN TOTAL
WHICH INCLUDES THIS COVER SHEET**

TURN OVER FOR QUESTIONS

Question 1 **[25 marks]**

(a) Determine the number of vibrations (the normal modes of vibration) for the following molecules: HCl, C_6H_6 (Benzene), C_2H_2 (acetylene) and CH_4 (methane). State which of these molecules will be infrared (IR) active and explain why.

[6 marks]

(b) Quantitative analysis of tablets containing aspirin, phenacetin and caffeine is to be carried out using conventional IR spectroscopy in transmission. Each of these components show distinct carbonyl bands in chloroform solution and calibration data for known concentrations are listed below in Table 1:

Table 1. Calibration data for a drug mixture

Component	Concentration $mg \cdot mL^{-1}$	C=O wavenumber (cm^{-1})	Absorbance
Aspirin	90	1764	0.217
Phenacetin	65	1511	0.185
Caffeine	15	1656	0.123

Each of these standards was studied by using a 0.1 mm pathlength transmission cell. Given that absorbance values for an unknown drug mixture (tablet) produced under the same conditions are provided in Table 2, estimate the concentrations of aspirin, phenacetin and caffeine in the unknown tablet.

Table 2 Absorbance values for an unknown tablet

Wavenumber (cm^{-1})	Absorbance
1511	0.202
1764	0.207
1656	0.180

[10 marks]

(c) Which IR spectroscopic method would you use to measure the composition of layers of a polymeric laminate with a film of total thickness of 10 μm comprising of 4 different layers? Justify its use and explain the principles of the approach including any corresponding equations.

[9 marks]

END OF PAPER

Question 2 **[25 marks]**

(a) Determine which of these will be Raman active, explaining why: H_2O, C_6H_6 (Benzene), CO_2, Argon.

[8 marks]

(b) How can you non-destructively obtain quantitative spectroscopic information about the distribution of a dye in a polyester fibre of approximately 150 μm in diameter? Describe the key idea and practicalities of this method (schematics may be used).

[8 marks]

(c) Explain the principles of FT-IR spectroscopic imaging. How would you apply it to study tablet dissolution and drug release? Explain advantages and limitations of this methodology.

[9 marks]

END OF PAPER

Question 3 **[25 marks]**

(a)

(i) To determine the properties of particles outline **three** advantages of microscopic techniques, (light and/or electron) over scattering techniques (light, x-ray or neutron).

`

[6 marks]

(ii) To determine the properties of particles outline **three** advantages of scattering techniques (light, x-ray or neutron) over microscopic techniques, (light and/or electron)

[6 marks]

(b) Which **two** techniques would you choose to determine the particle size and particle size distribution of each of the following products? In all cases, explain your choice of methods and briefly describe how you would conduct the experiments.

(i) Oil droplets in mayonnaise (probably around 10 μm in diameter)

[3 marks]

(ii) Titanium dioxide particles in paint (probably around 100 nm in diameter)

[4 marks]

(iii) Calcium carbonate particles in Engine oils (probably around 10 nm in diameter)

[3 marks]

(iv) Lactose powder to be used in tableting (probably around 100 μm in diameter)

[3 marks]

END OF PAPER

Question 4 **[25 marks]**

(a) Describe the principles of X-ray Photoelectron spectroscopy XPS. (You do not need to describe the equipment used).

[5 marks]

(b) What is the difference between XPS and Auger electron spectroscopy, AES?

[5 marks]

(c) Why is such a technique only capable of determining the nature of the top 10 nm or so of a material?

[5 marks]

(d) A palladium surface is coated with a monolayer of a protein which is preventing the palladium acting as a catalyst. How could you use XPS to determine the thickness of the protein layer, (which is known to be less than 10 nm thick).

[5 marks]

(e) What other techniques (not XPS or AES) could be used to determine the nature of the surface of the palladium surface?

[5 marks]

END OF PAPER

IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2015

PART III and IV

and

M.Sc. in ADVANCED CHEMICAL ENGINEERING

For Internal Students of Imperial College London

This paper is also taken for the relevant examination
for the Associateship

PRODUCT CHARACTERISATION

Wednesday 13th May 2015: 10.00 – 11.30

Answer **ALL** questions

All questions carry equal marks

Note: the paper will be marked out of 75 and the result expressed as a percentage

**THIS EXAMINATION PAPER HAS FIVE PAGES IN TOTAL
WHICH INCLUDES THIS COVER SHEET**

TURN OVER FOR QUESTIONS

Question 1 **[25 marks]**

(a) Compare and contrast the major features of light and neutron scattering, and discuss when to employ each technique.

.

[10 marks]

(b) If you were designing a new dip to be had with nachos (a corn based crisp like snack) what type of rheological considerations would you need to take into account? Sketch the flow curve for such a fluid.

[5 marks]

(c) If you were designing a new paint, which would be a non-drip paint, what rheological characteristics would you require the paint to have? How would you achieve this.

[5 marks]

(d) The particle size of the titanium dioxide particles in the above paint needs to be 200 +/- 20 nm. You suspect that the particle size in some batches of titanium dioxide delivered to your plant is nearer 500 nm, describe two ways by which you could determine the particle size and which would you choose if you worked for a small company of around 25 employees, so that equipment costing more than £100,000 would be unavailable?

[5 marks]

Question 2 **[25 marks]**

Carbon sieves are porous materials containing mainly carbon atoms. They can be used as a catalyst support. At a production site, a carbon sieve product has been synthesized for this purpose and its properties have been analysed to ensure that the product meets the manufacturing criteria. The results of the N_2 sorption analysis and thermo-gravimetric analysis for this product are presented in Fig. 1 and Fig. 2, respectively.

(a) The phenomenon of adsorption plays an important part in catalysis. (i) What is adsorption? (ii) What are the two types of adsorption and their characteristics?

[5 marks]

(b) Considering Fig. 1: (i) What is the type of isotherm for the carbon sieve produced? (ii) Identify the different steps of the isotherm and describe what they correspond to physically. (You may re-sketch the isotherm and indicate the steps directly on this).

[5 marks]

(c) Show that the total pore volume (V_{tot}) of an adsorbent is: $V_{tot} = \frac{PV_{ads}V_m}{RT}$

[5 marks]

(d) Incipient wetness method is a method used to impregnate a porous material with a given compound A. It consists in adding to the porous material a volume of solution (containing compound A) equal to the total volume of pore of the material. The material and impregnated solution containing A are then dried to remove the solvent and leave only compound A on the surface of the porous material. Calculate the copper concentration of a solution to be used to impregnate 100 g of the carbon sieve and obtain a 10 wt% copper loading (weight percentage loading).

[6 marks]

(e) It is proposed to use the carbon sieve as a catalyst support for:
- selective catalytic reduction (i.e. conversion of NO or NO_2 to N_2) at 700 ^oC.
- dehydrogenation of methanol into formaldehyde at 300 ^oC.

Are these reasonable applications? Justify your answer.

[4 marks]

Data for Question 2:

Name	Symbol	Value	Units
Total pore volume	V_{tot}	-	$cm^3\ g^{-1}$
Standard pressure	P	10^5	Pa
N_2 gas volume adsorbed at Standard Temperature & Pressure conditions	V_{ads}	-	$cm^3\ g^{-1}$
Molar volume of liquid N_2 at 77 K	V_m	34.65×10^{-6}	$m^3\ mol^{-1}$
Standard temperature	T	273	K
Gas constant	R	8.314	$m^3\ Pa\ K^{-1}\ mol^{-1}$
Molecular weight of copper	-	63.5	$g\ mol^{-1}$

Figures for Question 2:

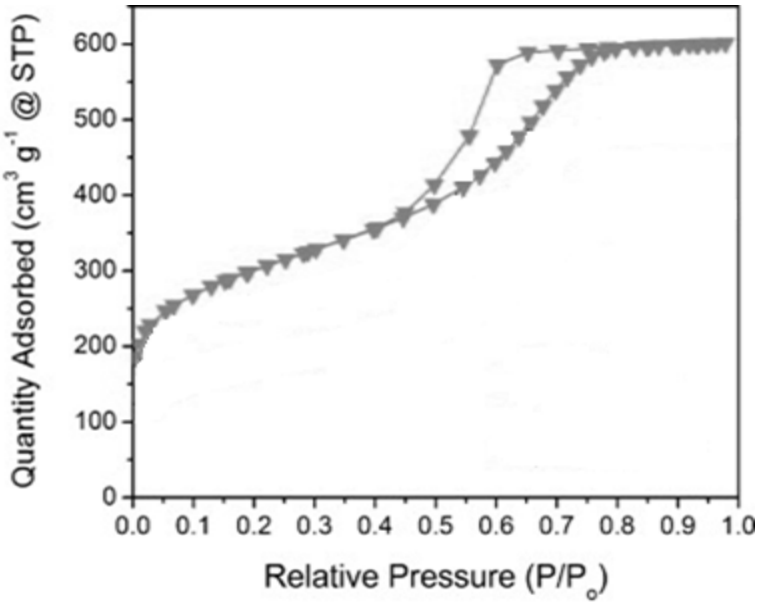

Fig. 1. N_2 isotherm of the carbon sieve at 77 K.

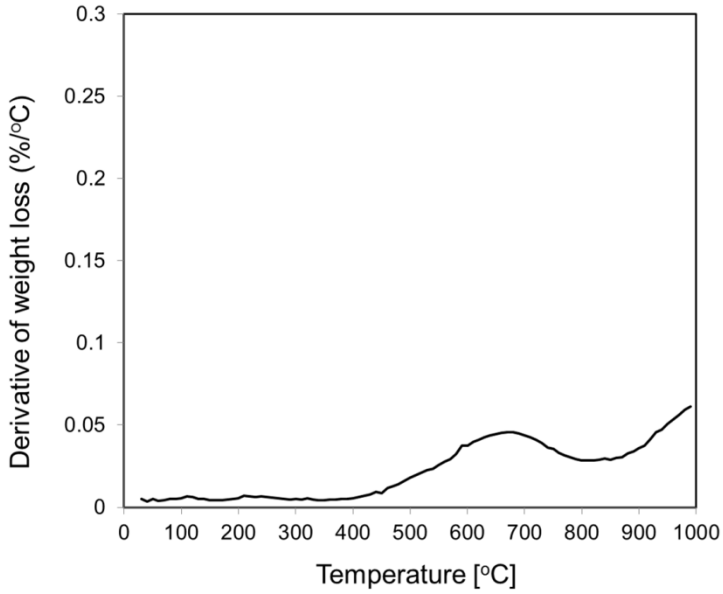

Fig. 2. Derivative of thermogravimetric curve of the carbon sieve under N_2 atmosphere.

Question 3 **[25 marks]**

(a) (i) Assuming that the vibrational wavenumber of hydrogen chloride $^{1}H^{35}Cl$ is 2886 cm^{-1} (frequency 8.652 x 10^{-13} s^{-1}) predict the vibrational wavenumber for $^{2}H^{35}Cl$. Assume that the molecule is an ideal harmonic oscillator and that force constant does not change upon isotopic substitution.

[4 marks]

(ii) What is the energy of the first excited state of vibration of $^{1}H^{35}Cl$ molecule? (Planck's constant) is 6.626 x 10^{-34} J s).

[2 marks]

(iii) Which type of spectroscopy would you use to observe vibrations in $^{1}H^{35}Cl$, $^{2}H^{35}Cl$ and $^{35}Cl^{35}Cl$ molecules and why?

[3 marks]

(b) Which spectroscopic imaging method would you use to characterise dissolution of pharmaceutical tablet? Justify its use and explain the principles, including the fields of view and spatial resolution obtained.

[7 marks]

(c) You are provided with 0.5 mm thick polymer film. Which Raman and Infrared spectroscopic methods would you use to assess quantitatively the chemical composition of this film? Describe the reasons for your choice and explain the principles of these methods with corresponding equations or/and schematics as appropriate.

[9 marks]

END OF PAPER

IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2016

PART III and IV

and

M.Sc. in ADVANCED CHEMICAL ENGINEERING

For Internal Students of Imperial College London

This paper is also taken for the relevant examination
for the Associateship

PRODUCT CHARACTERISATION

Monday 16th May 2016: 10.00 – 11.30

Answer any **three** questions

All questions carry equal marks

Note: This examination is marked out of 75. The coursework project is marked out of 25. The results will be added to give a mark out of 100.

**THIS EXAMINATION PAPER HAS SIX PAGES IN TOTAL
WHICH INCLUDES THIS COVER SHEET**

Before starting, please make sure that the paper is complete. Ask the invigilator for a replacement if your copy is faulty

TURN OVER FOR QUESTIONS

Question 1 **[25 marks]**

CO_2, a greenhouse gas, is released as part of the flue gas emitted from power plants. Among the proposed ways to capture CO_2 from a flue gas stream, one can cite adsorption. Here, a solid microporous polymer is tested as a potential CO_2 adsorbent at P = 1 bar. The polymer is tested in a simplified set-up with a mixture of CO_2 and N_2 only.

(a) (i) Define what an adsorbent is and outline the main characteristics of a 'good' adsorbent. (ii) Why would a microporous material be a potentially 'good' adsorbent for CO_2 under the pressure condition cited above?

[4 marks]

(b) The polymer sample is analysed by N_2 sorption at 77 K. The resulting isotherm is shown in Figure 1.1. Explain, step-by-step and indicating all assumptions made, how you would determine the BET surface area of the sample using Figure 1.1.

[7 marks]

(c) The N_2 and CO_2 adsorption isotherms at 298 K for the polymer sample are shown in Figure 1.2. Following what is called the Ideal Adsorption Solution Theory, one can define the ideal selectivity as being the ratio between the adsorption capacity for a given species to the adsorption capacity for another species. (i) Estimate the CO_2 adsorption capacity and N_2 adsorption capacity of the polymer sample at 298 K and 1 bar [1.5 marks]. (ii) Estimate the selectivity of the polymer sample towards CO_2 under the same conditions [1.5 marks].

[3 marks]

(d) Could one use a thermogravimetric analyser to measure the CO_2 adsorption capacity of the polymer sample? If so, how (describe all the steps and the shape of the expected curve)? Would there be any limitations? If so, indicate which ones.

[4 marks]

(e) An important parameter of CO_2 capture is the energy required to regenerate the sorbent, which is typically performed *via* heating at about 120 ^oC. Part of this energy requirement is caused by the heat capacity of the sorbent. A DSC scan was performed to measure the heat capacity of the polymer sample following the

reference method using sapphire (Figure 1.3). (i) Derive an expression for the specific heat capacity of the sample as a function of the specific heat capacity of the reference. Indicate all the steps [3 marks]. (ii) Calculate the specific heat capacity of this material at 120 ^{o}C [2 marks]. (iii) The most mature technology for CO_2 capture is based on the use of aqueous solvents. The specific heat capacity of water is 4.248 J g^{-1} K^{-1} at 120 ^{o}C. Using the information given, would you say that the polymer material allows a higher or lower energy requirement for sorbent regeneration compared to aqueous solvents [2 marks]?

[7 marks]

Data for Question 1:

Specific heat capacity of sapphire at 120 ^{o}C: $0.9340\ Jg^{-1}K^{-1}$

BET equation: $\frac{V}{V_m} = \frac{C \times \frac{P}{P_0}}{\left(1-\frac{P}{P_0}\right)\left(1-\frac{P}{P_0}+C\times\frac{P}{P_0}\right)}$ with:

V: Volume of gas adsorbed

V_m: Volume corresponding to the monolayer coverage

P: Pressure of gas at equilibrium

P_0: Saturation pressure

C: Constant

Figures for Question 1:

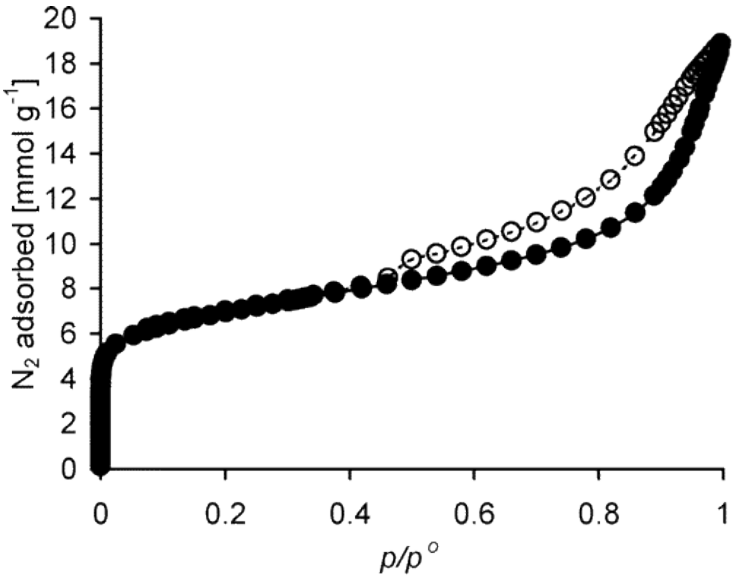

Fig.1.1. N_2 isotherm of the polymer sample at 77 K.

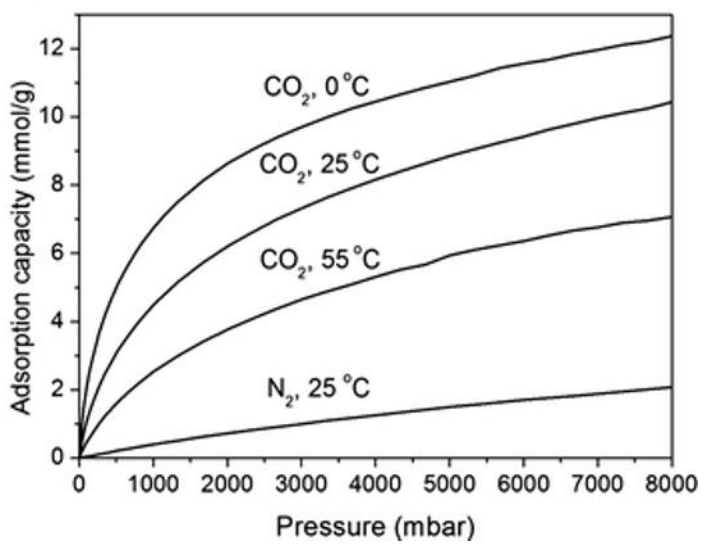

Fig. 1.2. CO_2 adsorption isotherms at 0 °C, 25 °C and 55 °C and N_2 adsorption isotherm at 25 °C for the polymer sample.

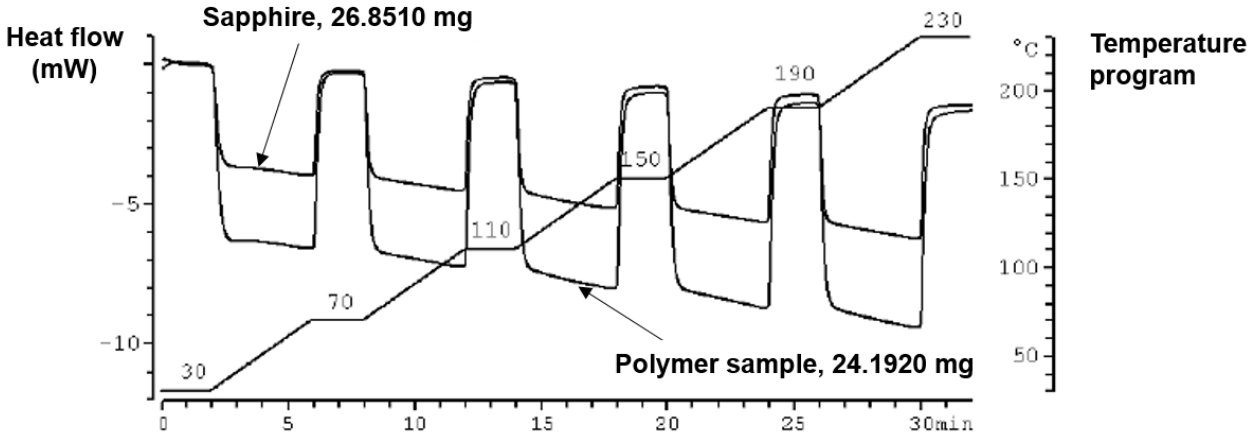

Fig. 1.3. DSC traces obtained for the polymer sample and the reference sample (sapphire) for a specific temperature program.

END OF QUESTION 1

Question 2 **[25 marks]**

(a) Describe (with the aid of a diagram if helpful) two experiments that can be used to assess the thixotropy of a complex fluid.

[**10 marks]**

(b) What is the difference between atomic force microscopy (AFM) and scanning tunnelling electron microscopy (STM) with regard to the type of sample that can be imaged?

[5 marks]

(c) What is the difference between scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with regard to the type of sample that can be imaged?

[5 marks]

(d) What is the difference between x-ray scattering and neutron scattering, with regard to the type of sample that can be studied?

[5 marks]

END OF QUESTION 2

Question 3 **[25 marks]**

(a) Interactions between CO_2 and polymers are important for polymer processing with high-pressure or supercritical fluid CO_2. Why is the degeneracy of the bending vibrational mode of CO_2 removed when it is absorbed into polymers that contain carbonyl functional groups? Explain how it is observed spectroscopically and the implications of such interactions.

[7 marks]

(b) Which spectroscopic technique would you use to observe symmetric stretching vibration of CO_2? Explain why.

[4 marks]

(c) What is the difference between Attenuated Total Reflection (ATR)-FTIR spectroscopy and confocal Raman microscopy with regard to the probing depth into polymeric samples that can be analysed by these techniques? Support explanations with corresponding equations and/or schematics as appropriate.

[7 marks]

(d) Explain the main differences between micro ATR-FTIR spectroscopic imaging and macro ATR-FTIR spectroscopic imaging. What are the main applications of each of these methods?

[7 marks]

END OF PAPER

.

IMPERIAL COLLEGE LONDON

M.Eng EXAMINATION IN CHEMICAL ENGINEERING 2017

PART III and IV

and

M.Sc. in ADVANCED CHEMICAL ENGINEERING

For Internal Students of Imperial College London

This paper is also taken for the relevant examination
for the Associateship

PRODUCT CHARACTERISATION

Wednesday 10th May 2017: 10:00-11:30

Answer all four questions

All questions carry equal marks

Note: This examination is marked out of 75. The coursework project is marked out of 25. The results will be added to give a mark out of 100.

**THIS EXAMINATION PAPER HAS SIX PAGES IN TOTAL
WHICH INCLUDES THIS COVER SHEET**

Before starting, please make sure that the paper is complete. Ask the invigilator for a replacement if your copy is faulty

TURN OVER FOR QUESTIONS

Question 1

[25 marks]

a) Briefly answer the following questions

i) What is meant by the term thixotropic fluid? Give an example
ii) What is the cause of non-Newtonian behaviour of concentrated colloidal dispersion?
iii) What are the shear rates experienced when squeezing a tube of toothpaste?
iv) What are the shear rates experienced when spraying an aerosol can?
v) Describe the die swell phenomenon, what is its cause?

[2 marks for each section]

b) Figure 1 shows the curves for two paints - a non-drip gloss and a gloss finish which have been analysed using stress viscometry.

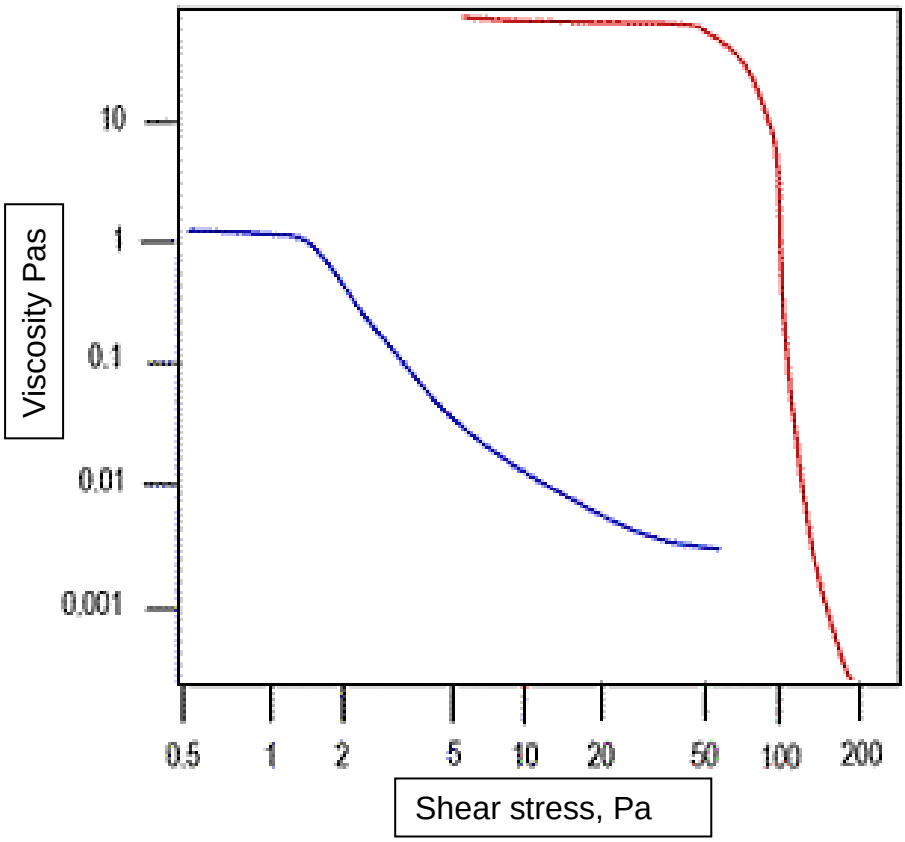

Figure 1. *Stress Viscometry of non drip gloss paint (red curve) and a free flowing gloss finish paint (blue curve)*

i) Describe the differences in the rheology of these paints
ii) Why does the non-drip paint have a higher low shear viscosity?
iii) Which paint would be easier to apply and why?
iv) Which paint would be easier to dip the brush into the paint and why?
v) Which paint is more likely to sediment and why?

[3 marks for each section]

[end of question 1]

Question 2 **[25 marks]**

a) With the aid of diagrams as appropriate describe the principles of

i) An atomic force microscope

ii) A scanning electron microscope

[3 marks for each part]

b) The types of images that you can obtain with these two microscopes are similar, discuss the advantages and disadvantages of using an atomic force microscope over a scanning electron microscope.

[6 marks]

c) With the aid of diagrams if appropriate describe the principles of

i) Dynamic light scattering

ii) Static (also known as low angle) light scattering

Note that no detailed equations are expected in the answer

[4 marks for each part]

d) These two instruments are generally used to measure different sized particles, what range of particles do they typically measure and why is one method much better for measuring small particles and the other method large particles.

[5 marks]

Question 3 **[25 marks]**

(a) Interactions between CO_2 and polymers are important for polymer processing with high-pressure or supercritical CO_2. Explain how you would spectroscopically measure and then quantitatively assess the amount of CO_2 sorbed by a polymer and the degree of polymer swelling, as the result of CO_2 sorption. State any assumptions that have been made and explain briefly the implications of such phenomena.

[9 marks]

(b) Which spectroscopic technique would you use to observe vibrations of nitrogen, oxygen and methane molecules? Explain why.

[7 marks]

(c) How would you analyse the relative distribution of polymer crystallinity and the distribution of a dye in a polymer film of 1 mm thickness? Support your explanations with corresponding equations and/or schematics as appropriate.

[9 marks]

END OF PAPER

Question 4 **[25 marks]**

(a) Define the theoretical limit of the spatial resolution in infrared microscopy or imaging, describe how you would assess the actual spatial resolution achieved in a spectroscopic measurement. How would the spatial resolution be different in transmission mode compared to that achieved in micro ATR-FTIR imaging? Explain why.

[8 marks]

(b) Explain the principles of macro ATR-FTIR spectroscopic imaging, describe its fields of view (measured areas), its lateral spatial resolution and depth resolution. Describe one representative example of using this imaging approach for studies of a dynamic system and the type of information obtained. Support your explanations with corresponding equations and/or schematics as appropriate.

[8 marks]

(c) Which optical aberration may occur when measuring samples in aqueous solution in an optical transmission cell using FTIR spectroscopic imaging and how would it be possible to rectify such aberration effect? Support explanation with schematics and provide examples of some systems where using such approach would be beneficial.

[9 marks]

END OF PAPER