UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2010/2011

# KAA 507 – Surface and Thermal Analysis
## *[Analisis Permukaan dan Terma]*

Duration : 3 hours
*[Masa : 3 jam]*

Please check that this examination paper consists of FOURTEEN pages of printed material before you begin the examination.

**Instructions:**

Answer **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answer each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

In the event of any discrepancies, the English version shall be used.

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1. (a) Briefly discuss the basic principles of surface analysis by means of electron irradiation. Why high vacuum condition is essential in modern surface analysis especially those using electron and ion as a source of irradiation?

(6 marks)

(b) Compositional analysis by means of electron probe microanalysis (EPMA) produces more accurate and quantitative analysis as compared to scanning electron microscopy with X- ray energy dispersive mode (SEM-EDX).

i. Explain briefly how the X- ray is detected and analyzed in EPMA.

ii. Describe briefly FOUR advantages and disadvantages of EPMA analysis as compared to SEM-EDX.

iii. Explain, using diagrams, THREE types of artifacts or false X- ray signal that commonly occur in SEM-EDX analysis.

(8 marks)

(c) Transmission Electron Microscope (TEM) is capable of producing high resolution images and selected area electron diffraction. Explain the basic principles of electron diffraction technique in structural determination of materials. What are the differences in diffraction patterns between single crystal, polycrystalline and amorphous materials?

(6 marks)

2. (a) Discuss briefly the factors affecting the interaction volume when a specimen is bombarded with an electron beam.
Sketch the region of the interaction volume that generates the secondary electron, Auger electron and X-ray.

(6 marks)

(b) When FeO was heated at high temperature, parts of $Fe^{2+}$ were oxidized to $Fe^{3+}$ to produce $Fe_3O_4$ and $Fe_2O_3$.

i. Explain briefly the surface analytical technique that is required to determine the crystal structure of each of the iron oxides.

ii. Describe the analytical techniques to determine quantitatively the composition of $Fe^{2+}$ and $Fe^{3+}$ after a certain period of oxidation.

(7 marks)

(c) X-ray photoelectron spectroscopy (XPS) is a surface analytical technique with the capability to measure the binding energy variations of an atom in its chemical environment.

i. Explain briefly the basic principles of XPS with emphasis on the source of irradiation, signal detection and the pattern of the XPS spectrum.

ii. What is meant by chemical shift in XPS? Describe briefly, with an example, how chemical shift can be applied in the determination of molecular structure.

(7 marks)

3. (a) Describe the various types of solid surface imperfections due to the chemical nature of the solid and the way the solid was prepared.

(10 marks)

(b) Sketch the three types of hysteresis loop. Show how the relationship between desorption pressure, $p_d$, and adsorption pressure, $p_a$, for a given amount of gas adsorbed on the solid open-end cylindrical pores (Type A of hysteresis loop) is obtained.

(10 marks)

4. (a) Describe the criteria for choosing a suitable gas for surface area determination of a solid.
Other than nitrogen gas, argon is also frequently used for the determination of surface area of solids. Give reasons why argon gas is prefered.

(10 marks)

(b) Adsorption studies of argon on a mesoporous solid at 77 K produce isotherm of Type IV according to BET classification. From the BET plot obtained the BET constant c and monolayer capacity, $V_m$, are 250 and 740 $cm^3$ (STP), respectively. The area occupied by one argon molecule is 18.2 $Å^2$.

i. Determine the specific surface area of the solid.

ii. Estimate the net heat of adsorption.

iii. If the pore radius of solid is 2.30 x $10^{-7}$ cm, calculate the relative pressure when the capillary evaporation occurs. State the assumption used.

Given: The surface tension, $\gamma$, and density, $\rho$, of argon at 77 K are 8.75 dyne $cm^{-1}$ and 0.957 g $cm^{-3}$, respectively.

(10 marks)

5. (a) Consider a semi-crystalline sample such as nylon that is hydroscopic, melts at 120 ºC and degrades at 250 ºC. Sketch the weight versus temperature curve you would expect from a thermogravimetric analysis (TGA) instrument.

(4 marks)

(b) A polypropylene resin manufacturer had made two batches (A and B) of product. They were suspected to be of different quality. Conventional heating experiments were conducted, but failed to show any difference. The isothermal crystallization test (shown in the figure below) was tried and was able to show the difference clearly between the two batches. Account for the observed differences in crystallization rates and explain why conventional heating experiments were unable to detect any difference.

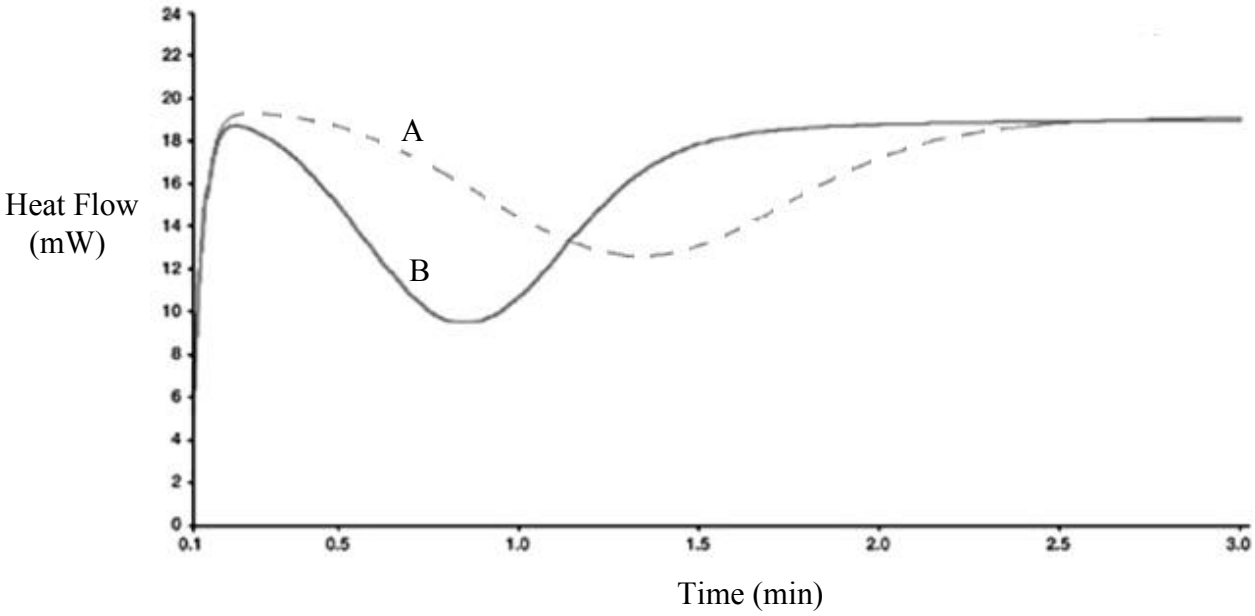



Figure: Isothermal Crystallization at 140 °C

(8 marks)

(c) Two samples of lactose were used for the study of $T_g$ exhibited by amorphous and crystalline lactose. The first sample was a spray-dried lactose of 100% amorphous content and the second was a fully crystalline sample of the α-lactose monohydrate. Sketch the DSC curves of both samples using a heating rate of 500 °C $min^{-1}$ with the $T_g$ in the range 80-100 °C. Explain the difference in the step height of the $T_g$ for both the samples.

(8 marks)

6. (a) Draw a schematic diagram of a dynamic mechanical analysis (DMA) instrument and explain how the instrument may be used to measure the following parameters for a material.

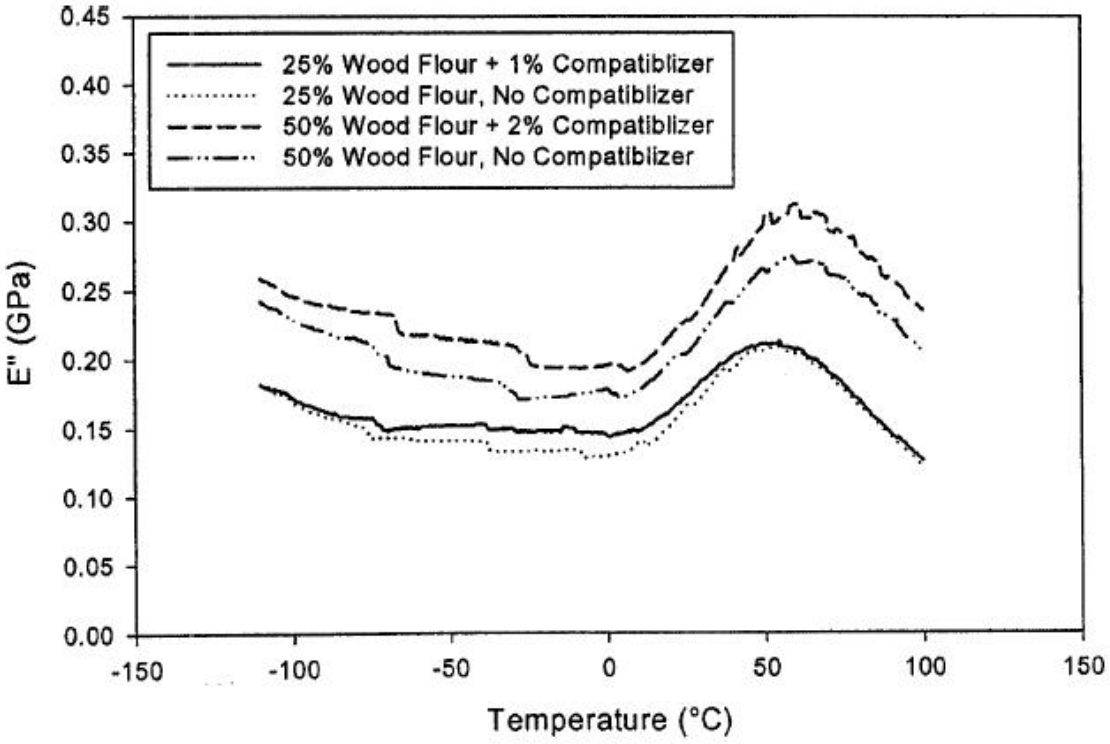
i. storage modulus (E')

ii. loss modulus (E")

iii. loss tangent (tan δ)

(6 marks)

(b) The effect of maleic anhydride polyethylene (MAPE) as the compatibilizer on the mechanical properties of wood-flour polyethylene composites has been investigated by using dynamic mechanical analysis (DMA). Composites were made at 25% and 50% fiber content and 1% and 2% compatibilizer by weight respectively. The loss modulus plot of the high density polyethylene (HDPE)/wood flour composites is shown in the figure below. What inference can be drawn about coupled composites with varying fibre and compatibilizer content with regard to loss modulus and glass transition temperature?




(8 marks)

(c) Composite materials are increasingly being introduced as replacement materials for parts previously manufactured from metals. As such, the thermal expansion behavior of a composite part becomes a critical design parameter. Draw a schematic diagram of a thermomechanical analysis (TMA) instrument and explain how this technique may be used to obtain the coefficient of thermal expansion of the composite material.

(6 marks)

1. (a) Jelaskan dengan ringkas prinsip asas analisis permukaan dengan menggunakan penyinaran elektron. Mengapa keadaan vakum yang tinggi amat perlu dalam analisis permukaan moden terutamanya yang menggunakan elektron dan ion sebagai sumber penyinaran.

(6 markah)

(b) Analisis komposisi dengan mikroanalisis prob electron (EPMA) menghasilkan keputusan yang lebih tepat dan kuantitatif berbanding dengan mikroskop electron imbasan dengan mod penyerakan electron (SEM-EDX).

i. Jelaskan dengan ringkas bagaimana sinar-X dikesan dan dianalisis pada EPMA.

ii. Nyatakan dengan ringkas, EMPAT kelebihan dan kekurangan EPMA berbanding dengan SEM-EDX.

iii. Terangkan dengan bantuan gambar rajah, TIGA jenis artifak atau kekeliruan isyarat sinar-X yang biasanya berlaku semasa analisis menggunakan SEM-EDX.

(8 markah)

(c) Elektron Mikroskop Transmisi (TEM) berupaya menghasilkan imej resolusi tinggi dan difraksi elektron pada kawasan terpilih. Jelaskan prinsip asas difraksi elektron dalam penentuan struktur suatu bahan. Apakah perbezaan corak difraksi elektron bagi bahan hablur tunggal, polihablur dan amorfus?

(6 markah)

2. (a) Bincangkan dengan ringkas faktor yang mempengaruhi isipadu interaksi akibat pancaran elektron ke atas permukaan spesimen.
Lakarkan isipadu interaksi tersebut dan tandakan kawasan yang memberikan isyarat elektron sekunder, elektron Auger dan sinar-X.

(6 markah)

(b) Apabila FeO dipanaskan pada suhu tinggi, sebahagian $Fe^{2+}$ teroksida kepada $Fe^{3+}$ bagi menghasilkan $Fe_3O_4$ dan $Fe_2O_3$.

i. Terangkan dengan ringkas teknik analisis permukaan yang diperlukan untuk menentukan struktur hablur bagi setiap oksida besi tersebut.

ii. Nyatakan teknik analisis bagi menentukan secara kuantitatif komposisi $Fe^{2+}$ dan $Fe^{3+}$ selepas masa tertentu pengoksidaan.

(7 markah)

(c) Spectroskopi fotoelektron sinar-X (XPS) merupakan teknik analisis permukaan yang berupaya mengukur perubahan tenaga ikatan suatu atom dalam persekitaran kimianya.

i. Terangkan dengan ringkas prinsip analisis XPS dengan penekanan kepada sumber pancaran, pengesanan isyarat dan corak spektrum yang dihasilkan.

ii. Apakah anjakan kimia dalam XPS? Jelaskan dengan ringkas, berserta contoh, bagaimana anjakan kimia boleh digunakan untuk menentukan struktur molekul.

(7 markah)

3. (a) Huraikan berbagai jenis kecacatan permukaan pepejal yang diakibatkan oleh tabii kimia pepejal dan cara pepejal tersebut disediakan.

(10 markah)

(b) Lakarkan tiga jenis gelung histeresis. Tunjukkan bagaimana hubungan di antara tekanan penyaherapan, $p_d$, dan tekanan penjerapan, $p_a$, bagi sejumlah gas terjerap pada pepejal berliang silinder hujung terbuka (gelung histeresis Jenis IV) diperoleh.

(10 markah)

4. (a) Huraikan kreteria bagi memilih suatu gas yang sesuai untuk penentuan luas permukaan suatu pepejal.
Selain gas nitrogen, argon juga sering digunakan untuk penentuan luas permukaan pepejal. Beri alasan-alasan mengapa gas argon dipilih.

(10 markah)

(b) Kajian penjerapan argon keatas suatu pepejal mesoliang pada 77 K menghasilkan isoterma Jenis IV berdasarkan pengelasan BET. Daripada plot BET diperolehi pemalar c bagi BET dan muatan ekalapisan, $V_m$, masing-masing adalah 250 dan 740 $cm^3$(STP). Luas yang ditempati oleh satu molekul argon ialah 18.2 $Å^2$.

i. Tentukan luas permukaan tentu pepejal.

ii. Anggarkan haba penjerapan net.

iii. Jika jejari liang pepejal ialah $2.30 \times 10^{-7}$ cm, kiralah tekanan relatif apabila penyejatan rerambut terjadi. Nyatakan andaian yang digunakan.

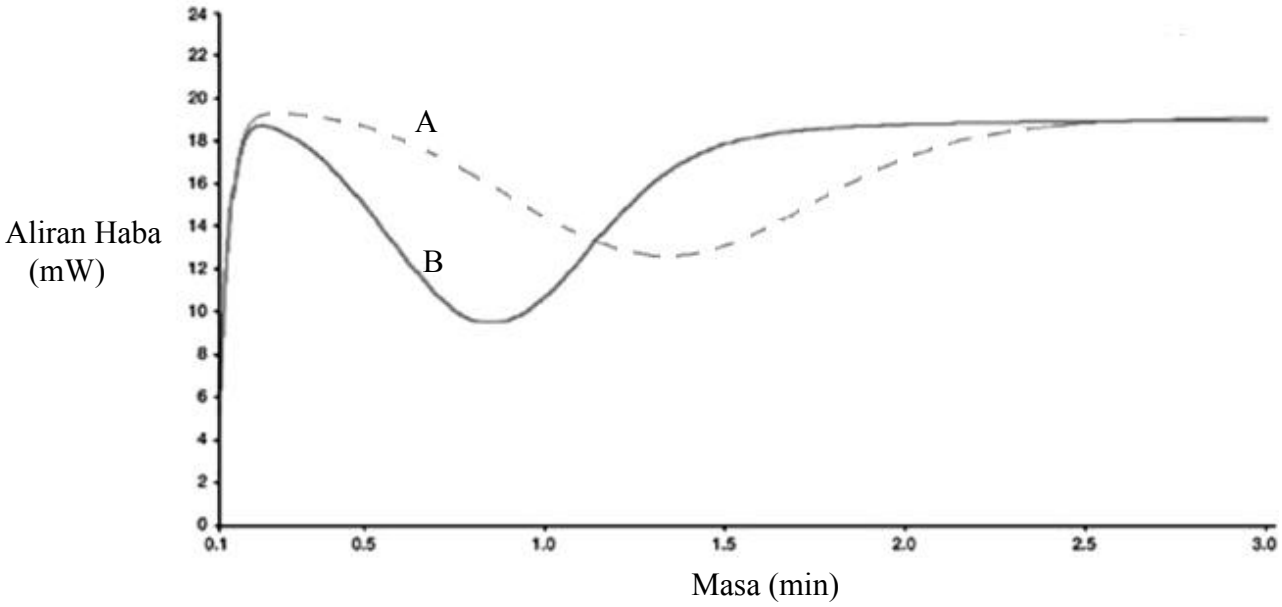
Diberi: Tegangan permukaan, $\gamma$, dan ketumpatan, $\rho$, argon pada 77 K masing-masing adalah 8.75 dyne $cm^{-1}$ dan 0.957 g $cm^{-3}$.

(10 markah)

5. (a) Pertimbangkan suatu sampel separuh hablur seperti nilon yang berhidroskopik, lebur pada 120 ºC dan berurai pada 250 ºC. Lakarkan keluk berat lawan suhu yang dijangkakan daripada alat analisis termogravimetrik (TGA).

(4 markah)

(b) Suatu pengilang resin polipropilena telah mengeluarkan dua kumpulan produk (A and B). Produk itu disyaki mempunyai kualiti berbeza. Eksperimen pemanasan biasa dijalankan, tetapi gagal menunjukkan perbezaan. Ujian penghabluran isotermal (ditunjukkan dalam gambarajah di bawah) dicuba dan didapati boleh menunjukkan dengan jelas perbezaan antara dua kumpulan itu. Beri penjelasan bagi perbezaan dalam kadar penghabluran yang diperhatikan dan terangkan mengapa eksperimen pemanasan biasa tidak dapat mengesan sebarang perbezaan.




Rajah: Penghabluran Isotermal pada 140 °C

(8 markah)

(c) Dua sampel laktosa digunakan untuk kajian $T_g$ bagi laktosa amorfous dan berhablur. Sampel pertama adalah laktosa tersembur kering dengan kandungan 100% amorfous dan sampel kedua adalah sampel berhablur lengkap bagi α-laktosa monohidrat. Lakarkan keluk kalorimeter pengskanan diferensial (DSC) bagi kedua-dua sampel dengan menggunakan kadar pemanasan 500 °C $min^{-1}$ dengan $T_g$ dalam julat 80-100 °C. Jelaskan perbezaan dalam ketinggian tingkat bagi $T_g$ untuk kedua-dua sampel.

(8 markah)

6. (a) Lukiskan gambarajah skema bagi suatu penganalisis mekanikal dinamik dan jelaskan bagaimana alat itu boleh digunakan untuk mengukur parameter berikut bagi suatu bahan.

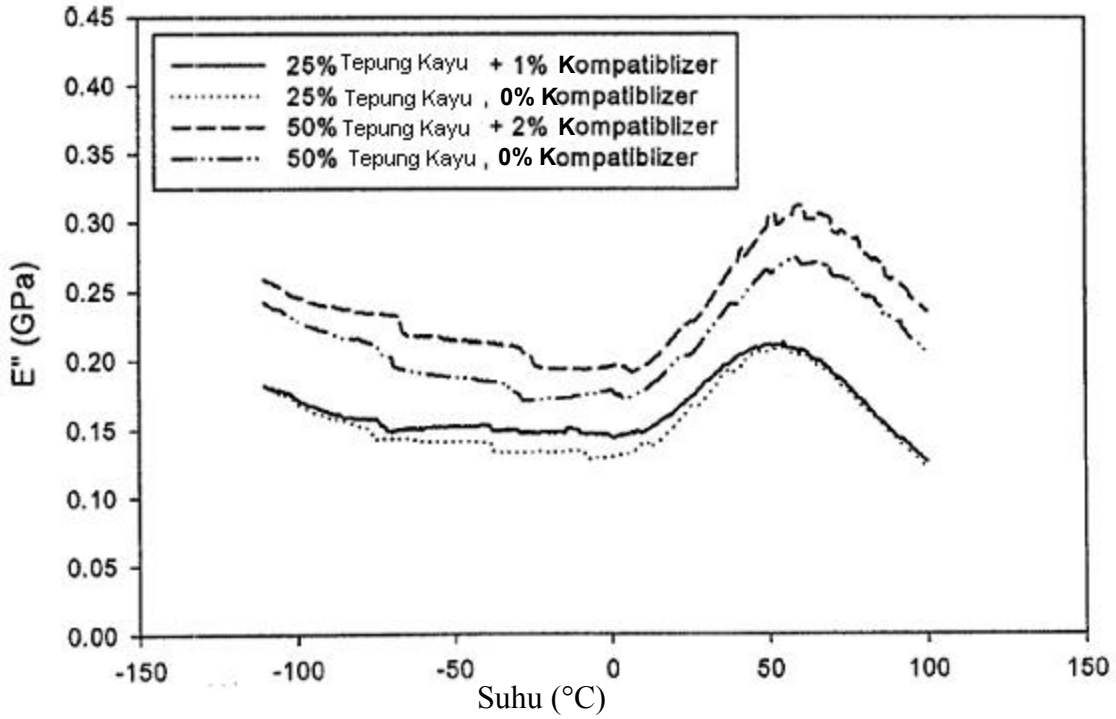
i. modulus penstoran (E')

ii. modulus kehilangan (E")

iii. tangen kehilangan (tan δ)

(6 markah)

(b) Kesan maleik anhidrida polietilena (MAPE) sebagai kompatibilizer pada sifat mekanikal bagi komposit polietilena tepung kayu telah dikaji dengan menggunakan analisis mekanikal dinamik (DMA). Komposit dibuat pada 25% dan 50% kandungan serat dan 1% dan 2% kompatibilizer mengikut berat masing-masing. Plot modulus kehilangan bagi komposit polietilena ketumpatan tinggi (HDPE)/tepung kayu ditunjukkan dalam gambarajah di bawah. Apakah inferens yang boleh buat mengenai hubungan komposit berkupel dengan kandungan serat dan kompatibilizer berbeza terhadap modulus kehilangan dan suhu peralihan kaca?




(8 markah)

(c) Pengunaan bahan komposit sebagai bahan gentian untuk komponen yang dahulu dibuat daripada logam makin bertambah. Oleh itu, kelakuan pengembangan termal bagi suatu bahagian komposit menjadi suatu parameter perekaan kritikal. Lukiskan gambarajah skema bagi suatu penganalisis termomekanikal (TMA) dan jelaskan bagaimana teknik ini boleh digunakan untuk memperolehi koefisien pengembangan termal bagi bahan komposit itu.

(6 markah)

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