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Maharashtra Institute of Technology, Aurangabad

Department of Plastics and Polymer Engineering

LABORATORY MANUAL

INSTRUMENTAL ANALYSIS OF POLYMERS MANUAL

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Maharashtra Institute of Technology, Aurangabad

Department of Plastics and Polymer Engineering

LABORATORY MANUAL

ACADEMIC YEAR: 2017-18 **PART: I**

COURSE: Instrumental Analysis of Polymer **COURSE COORDINATOR: Ms. P. N. Shindikar/Mr. A. Dey/Dr. S. Bhandari**

Experiment No.-1

1. Aim: Study of IR and FTIR for characterization of the structure of the polymers and interpretation of an IR spectrum obtained from the instrument.

2.Theory: Infrared radiation lies between the visible and microwave portions of the electromagnetic spectrum.Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves. The Infrared region is divided into: near, mid and far-infrared.Near-infrared refers to the part of the infrared spectrum that is closest to visible light and far-infrared refers to the part that is closer to the microwave region.Mid-infrared is the region between these two.The primary source of infrared radiation is thermal radiation (heat).It is the radiation produced by the motion of atoms and molecules in an object. The higher the temperature, the more the atoms and molecules move and the more infrared radiation they produce.

3. Apparatus:

a.Plates
b.Spatula
c.Dropper

4. Chemicals:

a. Common salt
b. Polymer sample

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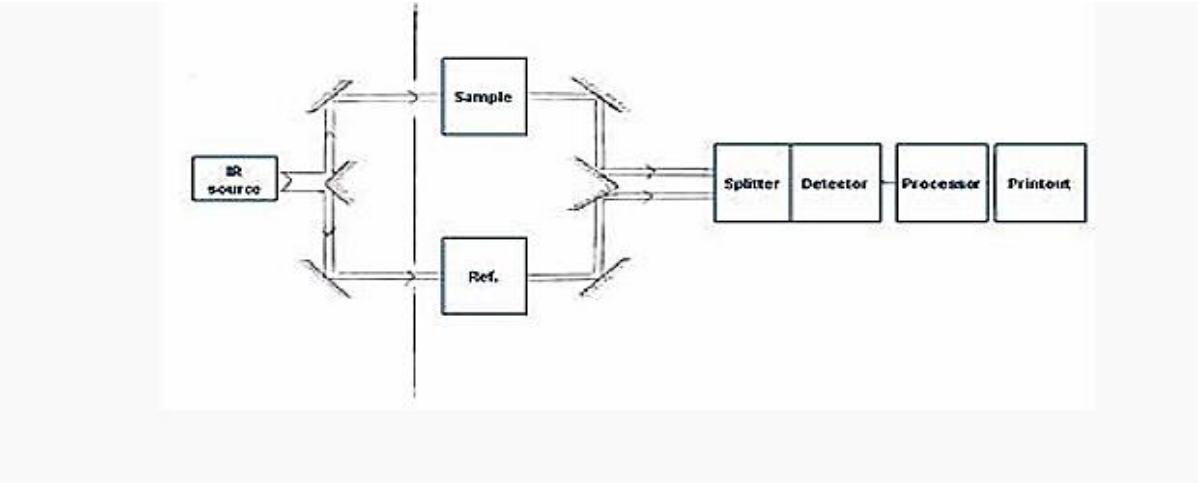
5. Procedure:



a.Take a liquid sample and add some drops of it between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride can also be used).
b.The plates are of transparent material and do not introduce any lines onto the spectra.
c.The thickness is adjusted according to the sample absorbance by inserting spacers between the aperture plates or by appropriately tightening the screws (without breaking the aperture plates). This type of cell is called a "liquid cell."
d.The infrared spectrum of the sample is recorded by passing a beam of infrared light through the sample.
e.Examination of the transmitted light reveals how much energy was absorbed at each wavelength.
f.A monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once is used here.
g.From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs.

6.Observation:

7. Result: The peaks in the Infrared spectrum correspond to the following ----------

8. Conclusion: As in the above spectrums one and two the following groups are present the sample might be

a. ----------

b.----------

9. Assignment Questions:

a. Explain how samples of different phases are prepared for being analysed by FTIR.

b. Briefly explain how to quantify the extent of modification of a polymer with incorporation of a functional group.

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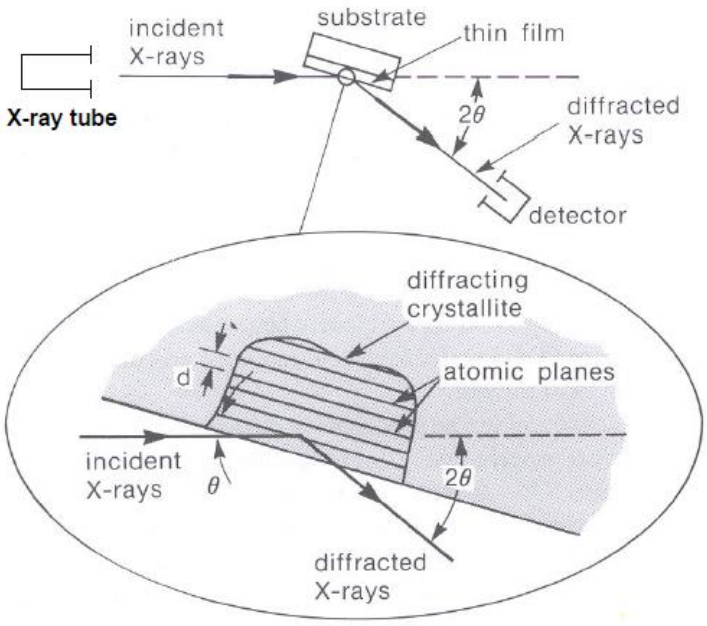
ACADEMIC YEAR: 2017-18 **PART: I**

COURSE: Instrumental Analysis of Polymer **COURSE COORDINATOR: Ms. P. N. Shindikar/Mr. A. Dey/Dr. S. Bhandari**

Experiment No.-2

1. Aim: Study of X-Ray scattering and X-Ray diffraction methods to determine crystallinity and orientation in polymers and analysis of a X-Ray diffraction pattern.

2. Theory:

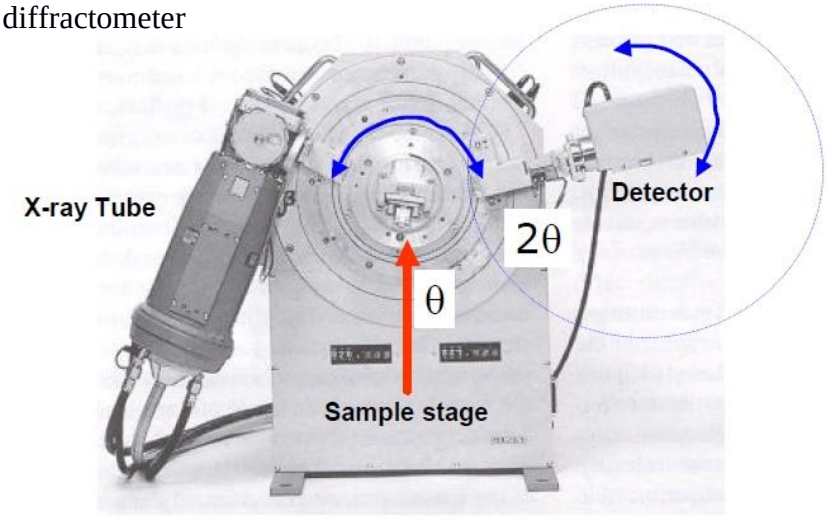


Powder x-ray diffraction (XRD) uses x-rays to investigate and quantify the crystalline nature of materials by measuring the diffraction of x-rays from the planes of crystal lattices within the material. It is sensitive to both the type of and relative position of atoms in the material as well as the length scale over which the crystalline order persists. It can, therefore, be used to measure the crystalline content of materials; identify the crystalline phases present (including the quantification of mixtures in favourable cases); determine the spacing between lattice planes and the length scales over which they persist; to study preferential ordering and epitaxial growth of crystallites; and to determine crystallite size, shape and internal stress of small crystalline regions. Moreover, for polymeric nanocomposites based on layered fillers, XRD is widely used to analyze the int It mayrcalation

and exfoliation of the nanolayers. It can analyze over the length scales from approximately sub angstroms to a few nm and is sensitive to ordering over tens of nanometres.
The samples for analysis are typically in the form of finely divided powders, but diffraction can also be obtained from surfaces, provided they are relatively flat and not too rough. Moreover the materials can be of a vast array of types, including inorganic, organic, polymers, metals or composites and the potential applications cover almost all research fields, e.g. metallurgy, pharmaceuticals, earth sciences, polymers and composites, microelectronics and nanotechnology. Powder XRD can also be applied to study the pseudo crystalline structure of mesoporous materials and colloidal crystals provided that the length scales are in the correct regime.
The analysis of crystallinity through XRD is based on the Bragg's law: $n\lambda=2d\sin\theta$ where n is a positive integer, λ is the wavelength of the incident beam, d is the d-spacing and θ is the scattering angle. The peaks in the diffractogram signifies crystalline region, whereas the broad halo indicates the amorphous region in the sample. The proportion of crystalline and amorphous region may be measured by peak deconvolution using appropriate software, or by measuring the ratio of the area as printed over homogeneous paper.
% crystallinity =
where A_c and A_a are the total area under crystalline peaks and amorphous halo respectively.

3. Apparatus:

a.X-ray diffractometer



4. Materials:

a) Crystalline/ semi-crystalline sample
b) Scissor or blade (required for crystallinity analysis from printed diffractogram)

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5. Procedure:

i) Sample loading

a) The sample should be placed horizontally.
b) Both film and powder samples may be analyzed using powder diffraction XRD.
c) Conventionally, for most of the polymeric samples Cu or Co target may be used.
d) For powder samples, the upper surface should be pressed with glass slide to have its outer surface smooth.
e) Maximum kV and mA settings are: 40 kV and 30 mA.
f) Lowest angle to be started can start from is 2θ=1° (small angle XRD) or 10° (wide angle XRD).
g) Maximum number of counts within 500,000 counts.
h) X-Ray window/shutter will not open if doors are not closed properly. Analysis will not start until doors are properly closed.
i) Emergency Stop buttons are located on both sides of the instrument. These will shut down the XRD in case of an emergency. Be careful not to touch these while analysis is in progress.
j) Do not use solvents and other chemicals that might damage surface of stage.
k) Only locked-coupled scans should be carried out. No detector scans.

ii) Basic controls

a) Close shutter in XRD Commander.
b) Open the doors of diffractometer.
c) Turn on internal light. Green switch below emergency button on left side of instrument.
d) Place sample on centre of stage. Use holes as a guide (equal number of holes around sample). Turn on vacuum to hold sample in place.
e) Lower knife edge to 0.000mm (knife edge micrometer counter clockwise).
f) Raise sample up to knife edge (stage micrometer clockwise direction). Use the torch to watch the gap between knife edge and sample disappear. Make sure knife edge remains at 0.000mm. If number changes it means knife edge is hitting your sample.
g) Raise knife edge up to 1.200mm (micrometer clockwise).
h) Close doors.

iii) Sample removal

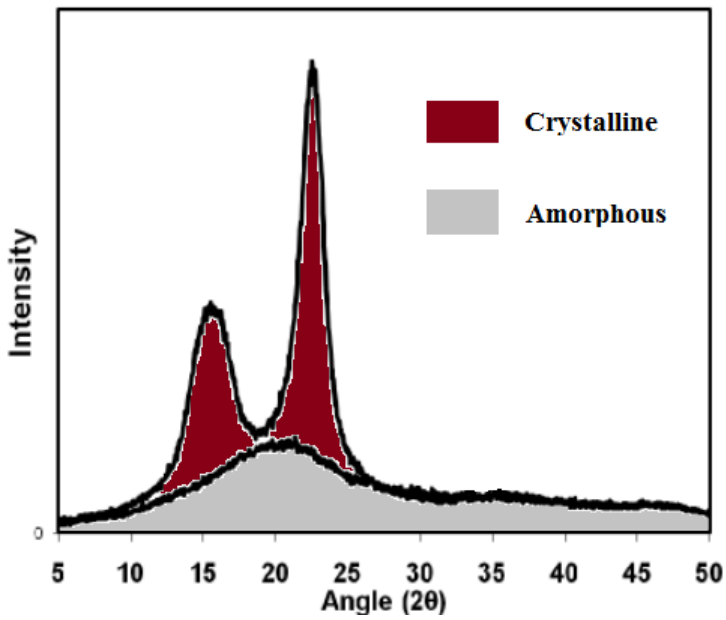
a) Open doors.
b) Turn off vacuum.

c) Remove sample from stage. Clean holder then return to box.
d) Close doors properly.

iv) Shut down - end of session

a. Close all programs.
b. Turn off monitor.

6. Observation and analysis:



a) Take the result of the diffractogram printed on a paper (homogeneous in weight/ unit area)
b) Draw the amorphous halo considering the highest point of crest of the crystalline peaks as the apex of the halo
c) Cut along the lines to separate out the total crystalline and amorphous regions
d) Measure the weights of the two regions, which will be proportional to the area of the respective regions
e) Calculate percent crystallinity from the ratio using the formula stated in the theory section.

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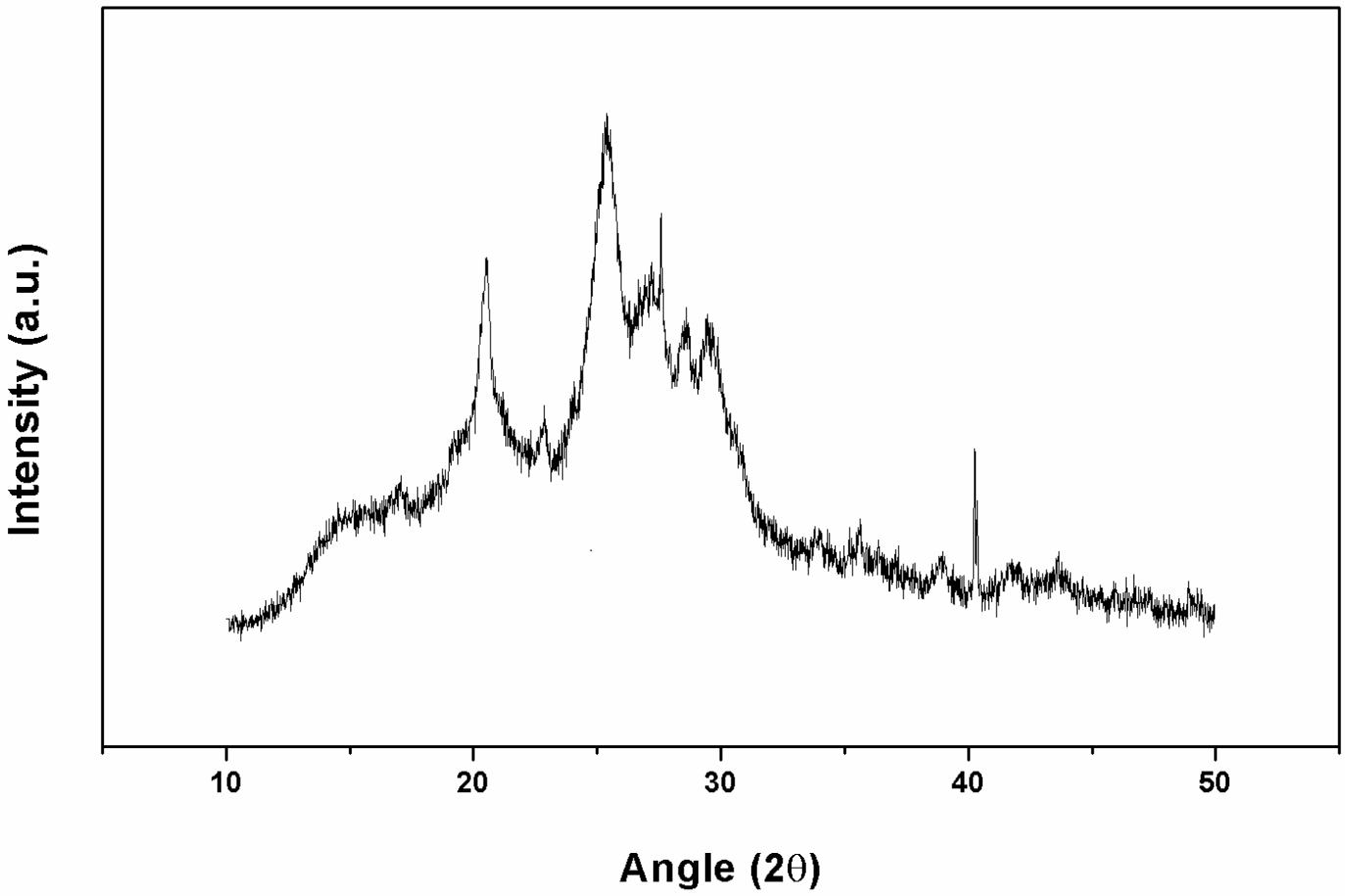

7. Result: a) In the X-Ray diffraction pattern of the sample _____ the crystalline peaks appear at _____.

b) The weight of the cut-out part of the paper indicating total crystalline region is _____ and total amorphous halo is _____.
(Attach the cut-out parts of crystalline and amorphous regions for the given sample)

c) Total crystallinity is calculated as

8.Conclusion: From above patterns we conclude that the samples may be of the type

_____.

9.Assignment Questions:

a. Briefly explain how X-Ray diffraction is used to study orientation and crystallinity in polymers.

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ACADEMIC YEAR: 2017-18 **PART: I**

COURSE: Instrumental Analysis of Polymer **COURSE COORDINATOR: Ms. P. N. Shindikar/Mr. A. Dey/Dr. S. Bhandari**

Experiment No.-3

1.Aim: To find T_g, T_c, T_m of given resin and interprete and analyse isothermal crystallization by using DSC.

2.Theory: DSC is a thermal method of analysis to study the thermal behaviour and thermal properties of materials (typically polymers). The material is sealed in a sample pan and subjected to a controlled temperature programme. The resulting thermograph can yield much valuable information about the properties of the material analysed.

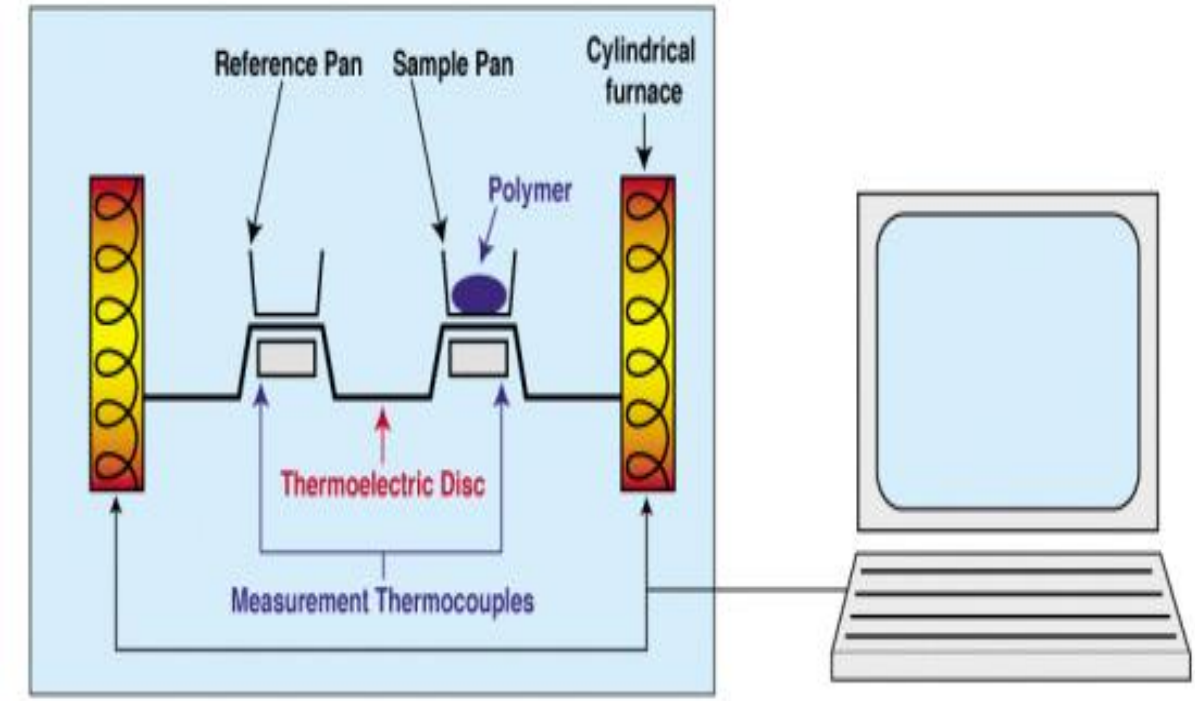
- **Differential:** sample relative to reference
- **Scanning:** temperature is ramped
- **Calorimeter:** measures heat

- DSC measurements are both **qualitative** and **quantitative** and provide information about physical and chemical changes involving:
  - Endothermic processes – sample absorbs energy
  - Exothermic processes – sample releases energy
  - Changes in heat capacity

3.Chemicals:

a.Sample

4. Procedure:



a. Place sample inside a crucible and then place it inside the measurement cell (furnace) of the DSC system along with a reference pan which is normally empty (inert gas may be used).
b. Apply a controlled temperature program (isothermal, heating or cooling at constant rates), and accordingly phase changes can be characterized and/or the specific heat of a material can be determined.
c. Heat flow quantities are calculated based on calibrated heat flow characteristics of the cell.

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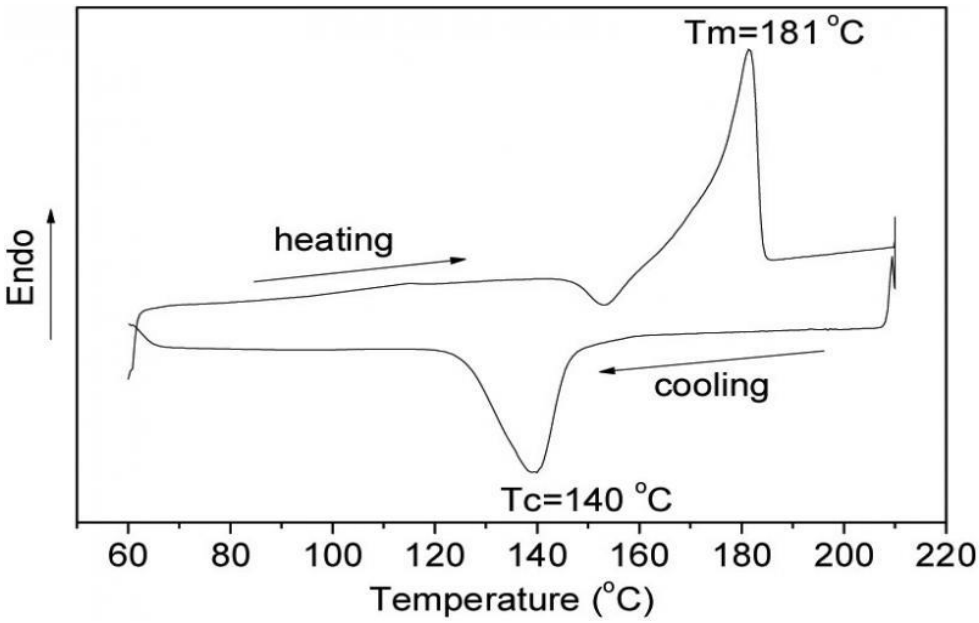
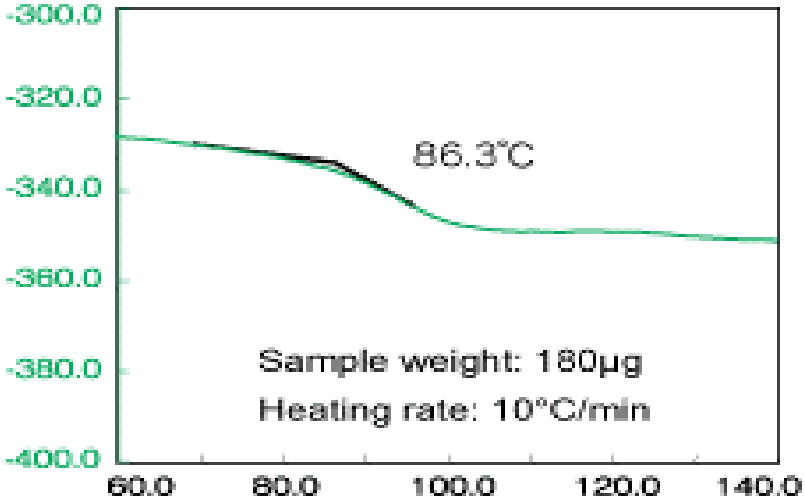
5.Observation:





6.Result: 1.After analyzing the first graph we can infer that the sample might be ----------

2.From the T_g value of second graph the sample might be ----------.

7.Conclusion: Hence the samples tested for thermal properties by DSC are:

a. ----------

b.----------

8.Assignment Questions:

a. Discuss briefly how to determine the proportion in the composition of a known blend of two polymers with diferent T_g values.

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ACADEMIC YEAR: 2017-18 **PART: I**

COURSE: Instrumental Analysis of Polymer **COURSE COORDINATOR: Ms. P. N. Shindikar/Mr. A. Dey/Dr. S. Bhandari**

Experiment No.- 4

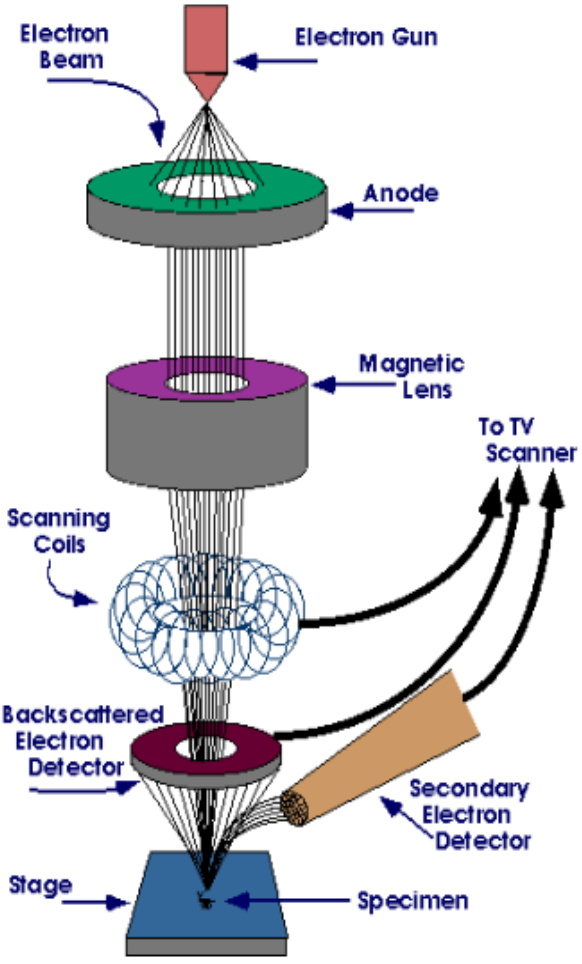
1. Aim: To study scanning electron microscopy and interprete a SEM photograph.

2. Theory:

Scanning electron microscopy is used for inspecting surface morphology of specimens at very high magnifications. SEM magnifications may reach beyond 300,000X. It is often used to analyze surface cracks and defects, continuity of phases, filler dispersion shape and size identification etc. Apart from morphological analyis, SEM is also used for elemental analysis using Energy Dispersive Spectrometer (EDS) detector.

During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal.

To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected. Finally, the image is shown on a CRT.

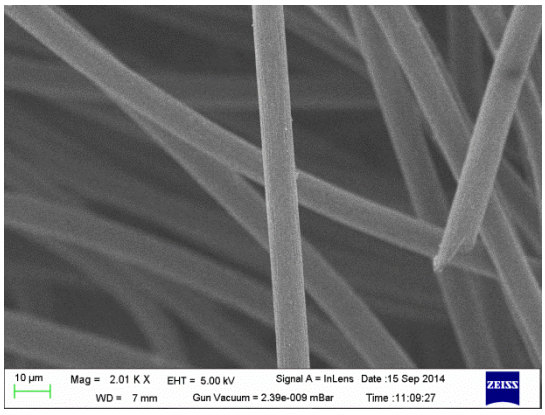


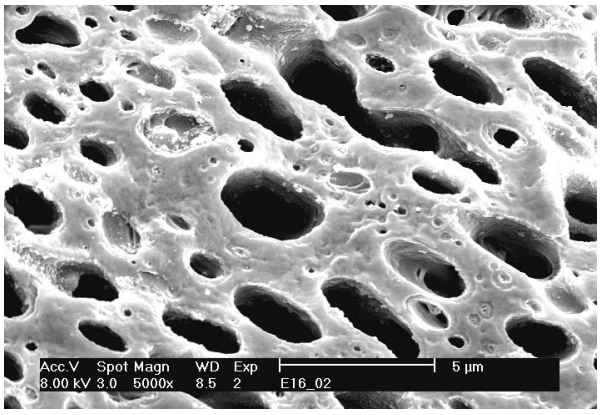
3. Procedure:

1. Non-conducting samples are coated with ultra-thin layer of gold (thickness in several angstrom level).

2. The virtual source at the top represent the electron gun, producing a stream of monochromatic electrons.
3. Standard SEM chamber pressure is nearly 10^{-6} Torr.
4. The stream is condensed by first condensing lens. This lens is used to form the beam and limit the amount of current in the beam. It works in conjunction with aperture to eliminate the high candle electron in the beam.
5. The beam is then constricted by the condenser aperture, eliminating some high angle electron.
6. The second condenser lens forms a electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob".
7. A user selectable objective aperture further eliminates the high angle electrons from the beam.
8. A set of coils then scan and sweep the beam in a grid fashion (like a television) dwelling or points for a period of time determined by the scan speed.
9. The final objective lens focuses the scanning beam onto the part of the specimen desired.
10. If surface roughness is more, then at higher magnification the problem of uneven brightness arises.

4.**Observation:**





SEM images of (a) carbon fibre and (b) 25/75 blend of PEO/PVDF after dissolution and etching of PEO phase.

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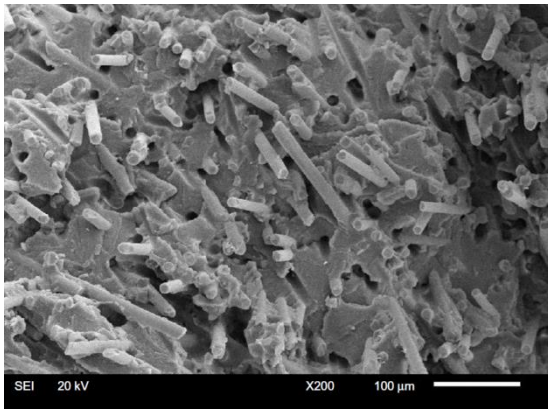

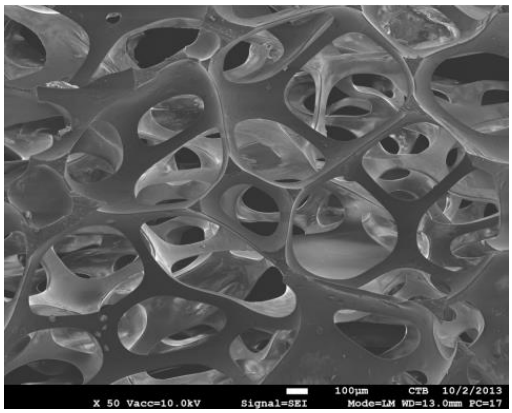

SEM images of glass fibre filled polyamide and (d) polyurethane foam

5.Result: From the images provided,

- the approximate diameter of carbon fibre is found to be _____
- the range of the pore size of the PVDF phase is_____
- the approximate diameter of the glass fibre is found to be _____
- the approximate pore size of the PU foam is found to be _____.

6.Conclusion:

7.Assignment:

1.Briefly explain how to analyze the surface morphological characteristics of a polymeric blend.

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Academic year: 2019-20 **Part: I**

Course: Instrumental Analysis of Polymer **Course Coordinator**: Ms. A.S.Dutta

Experiment no.- 5

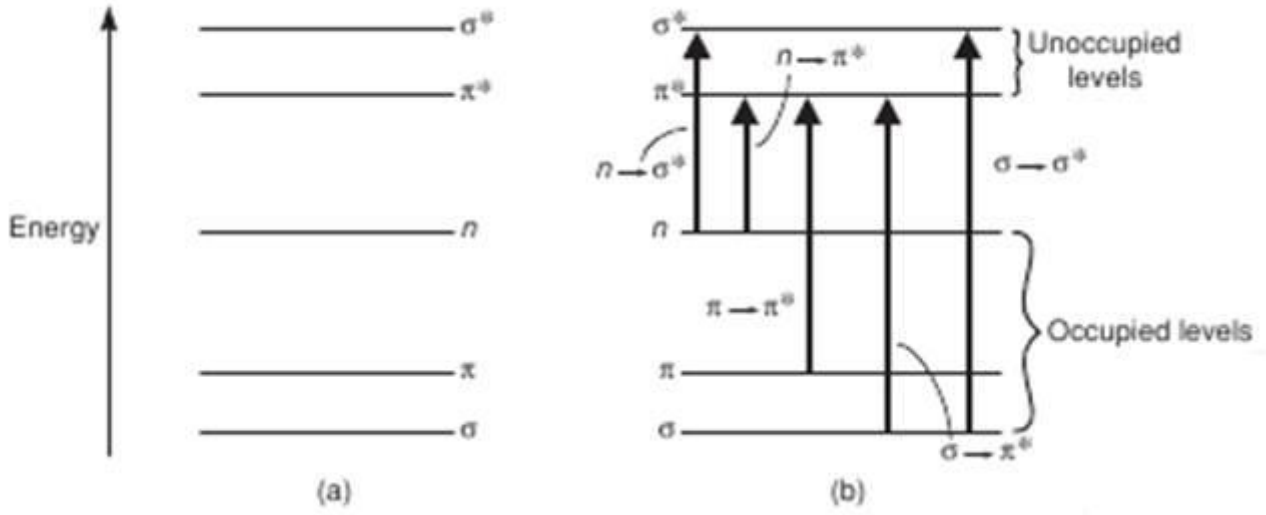
1.Aim: To characterize a polymer solution through uv-vis and analyze the spectrum.

2.Theory: Originally spectrum referred to the dispersion of visible light according to its wavelength by a prism. In modern science spectroscopy refers to the study of the interaction between matter (viz., atoms, molecules, ions, and solids) and electromagnetic radiation as a function of the radiation energy (often expressed in terms of frequency or wavelength of radiation). When light passes through a medium, some of the light energy may be absorbed, in addition to other processes such as scattering, surface reflectance, etc. If there is a fractional absorption of radiation (energy) and the rest of the radiation passes through the medium, then the medium is called a transparent medium to that particular transmitting radiation. When a portion of the radiation is absorbed from a passing continuous radiation through a transparent substance, the absorbed wavelengths remain absent from the residual emerging radiation spectrum. Thus an analysis of the transmitting radiation produces an absorption spectrum. Spectrophotometers are devices used to measure the wavelength distribution of absorbed or transmitted light. In UV-Visible absorption spectroscopy, samples absorb ultra-violet or visible radiations. UV-Visible absorption spectroscopy provides useful qualitative and quantitative information regarding solid, liquid and gaseous samples and many physical and chemical processes that occur in these samples.

Absorption of light energy involves a transfer of energy from the radiation field to the absorber resulting in transition of the absorber from a lower to a higher energy level. Absorption of the UV-visible light may lead to excitation of electrons from one energy level to another (subject to other conditions). The study of the electronic transitions under UV-visible light excitation is known as UV-visible absorption spectroscopy. In a molecule, the energy spacing between the ground and excited electronic energy states is determined by the bonding strength between the nuclei and the electrons. Therefore, the characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atoms. The group of atoms causing such absorption is called a chromophore. Substituents with unshared pair e's like OH, NH, SH, etc. when attached to a π chromophore generally move the absorption maximum to longer wavelength. These substituents are called auxochromes. Substituents may have any of the following four effects on a chromophore: (i) Bathochromic shift (red shift) – a shift to longer wavelength (λ) or lower energy. (ii) Hypsochromic shift (blue shift) – shift to shorter λ or higher energy. (iii) Hyperchromic effect – an increase in absorbance (intensity) of a band. (iv) Hypochromism: decrease in absorbance (intensity) of a band. Different substances absorb different wavelengths of light.

Therefore, the wavelength of maximum absorption by a substance is one of the characteristic properties of that substance.

The most probable transition often occurs from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In polyatomic molecules, it is convenient to classify the electronic transitions by specifying the initial and final orbitals. For example, if an electronic transition occurs from a bonding pi (π) orbital to antibonding pi orbital (π^*), we call it a $\pi \rightarrow \pi^*$ transition and similarly for a transition from nonbonding orbital (n) to an antibonding pi orbital (π^*) is known as $n \rightarrow \pi^*$ transition. The following Figure schematically shows some such transitions



Typical electronic transitions and light absorptions.

In the cases of atoms, such transitions should result in very narrow absorbance spectral bands at wavelengths characteristic of the difference in involved energy levels of the absorbing species. However, broad spectral bands are often observed in the cases of molecules. Since electronic energy is more than the vibrational and rotational energies, vibrational and rotational energy levels are superimposed on the electronic energy levels. Therefore, any electronic transition may be associated with many vibrational and rotational transitions (subject to some conditions) with different energies giving rise to broadened bands .The solvent-solute interactions also broaden the spectral band.

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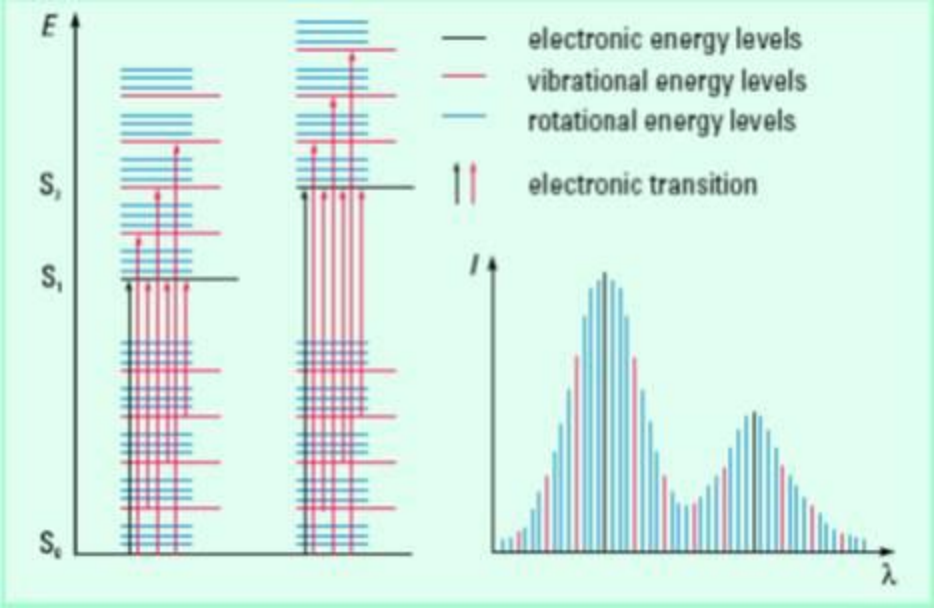

Electronic transitions in molecules and origin of UV-visible spectral band. S stands for singlet electronic energy state.

Charge-transfer transition is another type of electronic transition that is responsible for the intense color of many transition metal complexes and inorganic pigments. In charge transfer transitions, an electron transfers from the d orbitals of the metal to one of the vacant orbitals in ligands or vice versa. For example, an electron transfer from an O atom to the Mn atom causes the intense purple color of aqueous permanganate ion, $MnO4^-$.

A typical UV-visible spectrophotometer should have the following design components: a light source (that generates light at a specific wavelength or wavelengths), a dispersion device (causes different wavelengths of light to be dispersed at different angles), sample chamber, and one or more detector(s). VU-visible spectrophotometers may have two light sources: one for the UV range (e.g. a deuterium arc lamp) and the other for the visible range (e.g., tungsten-halogen lamp).

The dispersion device disperses source light into a "rainbow" of wavelengths (i.e., into different wavelengths of light), which are then directed to the sample. Prisms and holographic gratings are two dispersion devices commonly used in UV-visible spectrophotometers. In a conventional spectrophotometer, the entrance slit and an exit slit surrounding the dispersion device together constitute the monochromator. Light coming out of the

monochromator passes through the sample blank and/or sample. The intensity of the transmitted light is measured with a photodetector. Photomultiplier tubes (PMTs) or photodiodes (photodiode array) are commonly used as detectors. The photodetector behind the sample receives the light stimulus and generates an analog electronic current, which is then converted to a usable format and fed into a computer for further analysis. In a conventional spectrophotometer, the spectrum is obtained in a sequential manner, one wavelength after another, as a function of time. In a diode array spectrophotometer, polychromatic light after passing through the sample is focused on the entrance slit of the polychromator. This transmitted light is then dispersed onto the diode array where each diode measures a portion of the spectrum. That is, in a diode array spectrophotometer, the detector sees all of the wavelengths simultaneously.

Depending on the light beam, there are two different kinds of spectrophotometers used: single-beam and double-beam spectrophotometers. Single-beam includes both conventional and diode array spectrophotometers where a single light beam is used to illuminate first the sample blank and then the sample separately. A double beam instrument splits the light beam between the reference (sample blank) optical path and sample optical path and compares the light intensity between them. The splitting of the beam is accomplished in two ways. In a static method, a partially transmitting mirror is used that allows the light to be sent to the reference cell and sample cell simultaneously. In some spectrophotometers, a "chopper" alternates the light path. Both the spectrophotometers have a few advantages over the other. One expects a better stability of the light source, detectors and associated electronic devices with a double beam instrument. The disadvantages include the precision required in recombining the beams prior to reaching the monochrometer. The quality of the mirrors, other optics and their coatings and the dust buildup on these devices make the double beam instruments somewhat more difficult to maintain than single beam devices. In single beam instrument, only one cuvette holder is present, therefore, two measurements necessary. The sample and the sample blank (reference) are scanned simultaneously in one measurement with a double beam instrument, which has two cell holders. Diode Array spectrophotometer is a multichannel instrument, though requires two measurements, but measurements are very fast (0.1s) and have low resolution.

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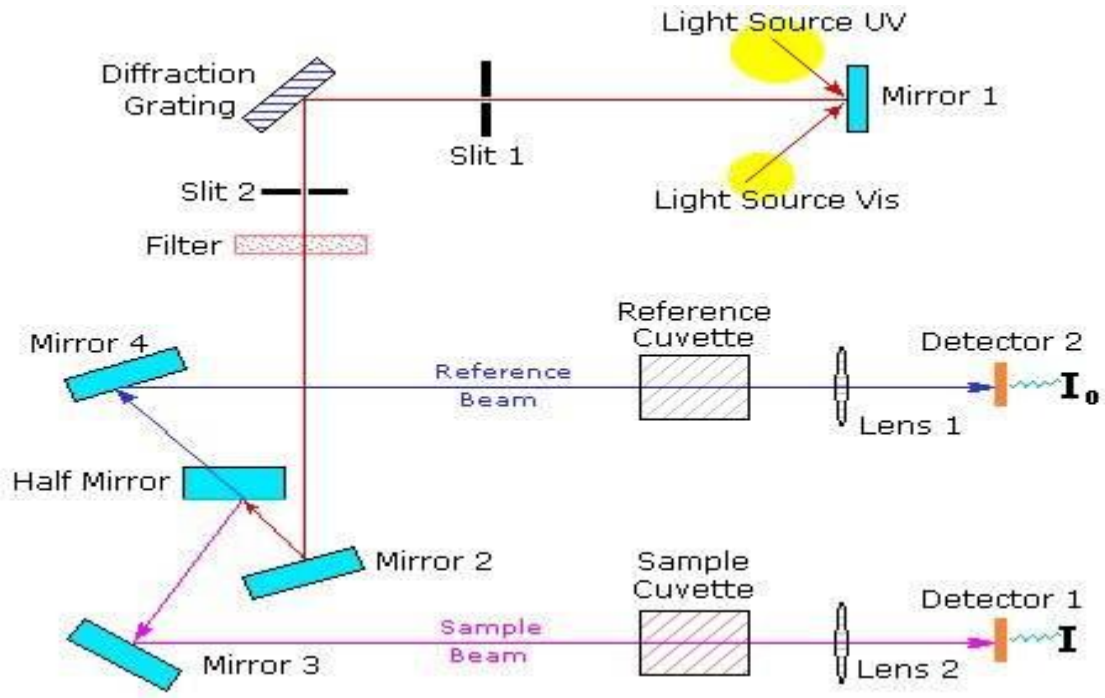

Schematics of a typical Double-Beam UV-Visible Spectrophotometer

The absorption of light is usually experimentally measured in terms of transmittance (T) or absorbance (A). Transmittance is defined as $T = I / I_0$, where I is the light intensity after it passes through the sample and Io is the initial light intensity. The relation between A and T is: A = -log{10}T = - log{10} {I \ I{0}}.

Modern absorption measurement instruments such as colorimeter and spectrophotometers can usually display the data as transmittance, %-transmittance, or absorbance. In a spectrophotometer, a whole series of wavelengths of light passes through a substance or its solution taken in a cell (sample cell) and through an identical container (reference cell) which only has the solvent in it. The intensity of the light entering the sample and that of the light exiting the sample are compared producing a suitable spectrum. In fact, light attenuation in an absorbance experiment occurs from many processes such as absorbance by the solvent, reflections from the interface between air and the sample, the sample and the cuvette, in addition to the chromophore. These factors are often removed by defining I_0 as the light passing through sample "blank" or reference sample ("baseline" correction). A sample blank or reference sample is the solvent and other substances, if any, excluding the chromophore substance. A variety of sample holders or sample cells are available. The choice of the sample cell

is based on a number of factors, such as the path length, shape, size, the transmission characteristics at the wavelength of interest, etc. The cell holding the sample or its blank should be transparent to the wavelength region to be recorded. A quartz or fused silica cuvette is chosen for better UV light transmission. Silicate glass cuvettes can be used for the use between 350 and 2000 nm wavelengths. The cells are generally rectangular with different pathlengths, ranging from 10 mm to 1 mm.

3.Apparatus: UV-VIS spectrophotometer, beakers, test tubes

4.Chemicals: Polymer solution of unknown concentration

5.Procedure:

- Turn on the instrument clicking on the power button and wait for 30 min for initialization of the instrument.
- Prepare the polymer solution in the required solvent.
- Using a micropipette collect appropriate quantity of solution from the beaker.
- Take a cuvette and pour the solution from the micropipette into the cuvette filling it about two-third of its volume.
- Open the spectrophotometer..
- Place the cuvette in the sample holder
- On the screen, enter the wavelength range of spectral scan. Here the wavelength range of incident light for the sample is chosen and the wavelength scan is run via the accompanied computer software. One can run the scan in absorbance (A) or transmittance (%T) mode.

- Click on the green 'Start' button on the measurement set-up screen to run the wavelength scan. Observe the wavelength scan. If the spectrophotometer is a single beam instrument, then first the sample blank or reference is taken in a cuvette and the wavelength scan is run followed by the sample. One has to subtract the reference data from the sample data for respective wavelengths.

- Click on Close button when spectral scan is complete. The scan data are stored in the computer. The instrument stores data and therefore asks for the Sample File name. One enters a file name to save the data.
- Repeat the measurement for another sample.
- Collect data by clicking on the Data tab.
- Plot the absorbance (or transmittance) of the sample vs. wavelength for the sample.
- Determine the wavelengths of maximum absorption for main peaks for the sample.

6.Result:

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Department of Plastics and Polymer Engineering

LABORATORY MANUAL

Academic year: 2019-20 **Part: I**

Course: Instrumental Analysis of Polymer **Course Coordinator: Ms. A.S.Dutta**

Experiment no.-6

1. Aim:To study thermal degradation of a polymer through TGA and DTG analysis.

2.Theory: Thermogravimetric Analysis measures the percent weight loss of a test sample while the sample is heated at a uniform rate in an appropriate environment. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability .
Thermogravimetric (TGA) analysis provides determination of endotherms, exotherms, weight loss on heating, cooling, and more. Materials analyzed by TGA include polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives and biological samples.

TGA materials analysis:

Thermogravimetric analysis uses heat to force reactions and physical changes in materials. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation. TGA records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature. Characteristic thermogravimetric curves are given for specific materials and chemical compounds due to unique sequence from physicochemical reactions occuring over specific temperature ranges and heating rates. These unique characteristics are related to the molecular structure of the sample.

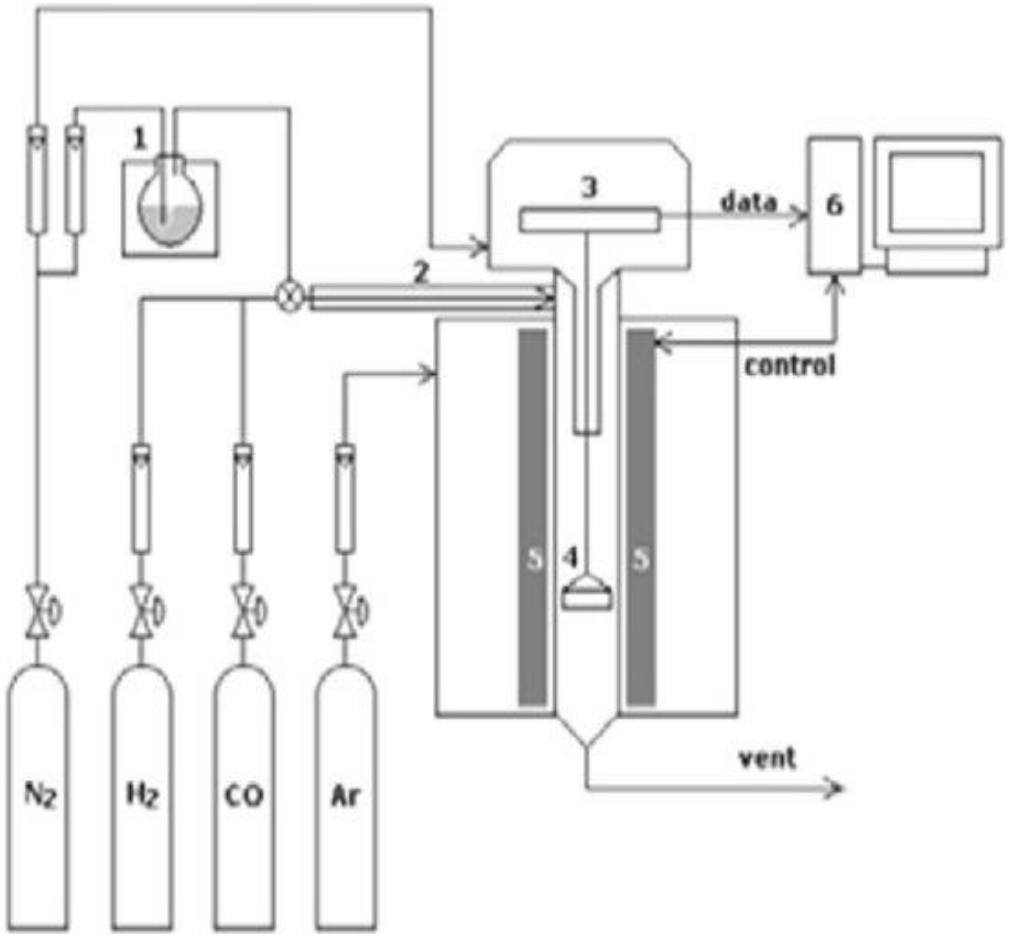
Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection.

A method known as hi-resolution TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that

the exact temperature at which a peak occurs can be more accurately identified. Several modern TGA devices can vent burnoff to an infrared spectrophotometer to analyze composition.

When used in combination with FTIR, Thermogravimetric Analysis / Infra-red spectroscopy (TGA/FTIR) is capable of detailed FTIR analysis of evolved gases produced from the TGA.

Schematic diagram of a thermal gravimetric analyzer (TGA) system for the reactivity test; 1 water reservoir and bubbler, 2 gas pre-heater, 3 electric balance, 4 sample basket, 5 heater, 6 personal computer:



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3.Procedure:

1.Turn on Nitrogen. (Verify flow. Flowmeter should read ~ 40/60. Do not adjust!)Open ball valves behind TGA. The one behind and to the left of the TGA is the combustion air; the pressure gauge should read approximately 5 PSI. The valve in back and to the right of the TGA is the purge air. This gauge should be set to

approximately 50 PSI.

2. Turn on TGA instrument and computer.

3. Turn on the TGA GAS SWITCHING ACCESSORY device, the power switch is in the rear. Set the operation switch to AUTO. Verify flow, flowmeter should read~ 40/60. Do not adjust! If flow is off consult lab personnel.

4. Run TA Instrument Control program.

5. Tare pan. ("Calibrate" Æ "Tare". Select tray no.1 and pan number.)

6. Set name, procedure, etc. (E.g. ambient to 875 °C @ 20 °C/min.)("View" Æ "Experiment View" Æ "Procedure"..."Editor")

7. Run. ("Control" Æ "Start" or click the green triangle on tool bar.)

8. Run TA Universal Analysis program.

9. Open the thermogram. ("File" Æ "Open" in C:\TA\Data\TGA\ folder.)

10. To analyze: macros – macro editor- step 5 – right click – modify step – browse to find your file directory (student data 2005-2006) then find your file. Unless you select you current file the analysis will be of the last file loaded in the analyze program not the current one being run. needed, do "Analyze" Æ "Weight Change"

11. Do "Analyze" Æ "Macro" Æ "TGA Weight Change Analysis". – over (May need to change the filename in the Macro by "Macro" Æ "Open" Æ "TGA Weight Change Analysis" then go to line 5. to change filename.)

12. Label Derivative Peaks. ("Analyze" Æ "Label At X,Y")

13. To undo "Edit" Æ "Delete Results" Æ ...

14. Save Analysis, filename.

15. Print Thermogram.

16. Unload sample, move furnace up – furnace switch on TGA - Clean pan.

17. Close programs. Turn off computer and instrument. Turn off Nitrogen.

4.Observation:

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Academic year: 2019-20 **Part: I**

Course: Instrumental Analysis of Polymer **Course Coordinator**: Ms. A.S.Dutta

Experiment no.- 7

1. Aim: Identification of polymer component by chromatography.

2. Theory:

Chromatographic separations of mixtures of various compounds are based on their distribution between a stationary and a mobile phase, which are present in a chromatographic column. The mobile phase moves across the column, in effect washing (eluting) compounds at a different rate. These differences are based in properties such as the boiling point, the polarity, the electric charge (for ionic compounds), the size of the molecule, and so forth. If at the column outlet there is a system for detecting and measuring the quantity of each component, then a quantitative determination of the separated components is achieved.

Types of chromatography:

- **Liquid Chromatography** – It separates liquid samples with a liquid solvent (mobile phase) and a column composed of solid beads (stationary phase).
- **Gas Chromatography**–The organic compounds areseparated due to differences in their partitioning behavior between the mobile gas phase and thestationary phase in the column.
- **Paper Chromatography**– Itseparates dried liquid samples with a liquid solvent (mobile phase) and a paper strip (stationary phase).The certain solvent are used to separate a mixture ex: water, alcohol. With capillary action the solvent will move up to filter paper. Movement of a solvent will bring together component that are separated from the mixture. Every component that are separated will move to several velocity
- **Thin-Layer Chromatography** – In TLC, components of the mixture are partitioned between an adsorbent (the stationary phase, usually silica gel, SiO_2) and a solvent (themobile phase) which flows through the adsorbent.
- **Ion Exchange Chromatography**-Different affinity of the different components to stationary phase causes the separation.

- **High Pressure Liquid Chromatography**- It relies on pumps to pass a pressurized liquid solvent containing sample mixer through a column filled with a solid absorbent material. Each component in this sample interacts slightly differently with the absorbent material, causing different flow rate for the different components and a leading to the separation of the component as they flow out the column.
- **Gel Permeation Chromatography**-GPC is a type of size exclusion chromatograph, that separate analytes on the basis of size. GPC separate based on the size and hydrodynamic volume of the analytes. Separation occurs via the use of porous bids packed in a column.

  In this practical we are concentration on Gel Permeation Chromatography

Gas Chromatography/Mass Spectrometry (GC/MS)

Gas chromatography is a term used to describe the group of analytical separation techniques used to analyze volatile substances in the gas phase. In gas chromatography, the components of a sample are dissolved in a solvent and vaporized in order to separate the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyte through the heated column. Gas chromatography is one of the sole forms of chromatography that does not utilize the mobile phase for interacting with the analyte. The stationary phase is either a solid adsorbant, termed gas-solid chromatography (GSC), or a liquid on an inert support, termed gas-liquid chromatography (GLC).

Instrumentation

Sample Injection

A sample port is necessary for introducing the sample at the head of the column. Modern injection techniques often employ the use of heated sample ports through which the sample can be injected and vaporized in a near simultaneous fashion. A calibrated microsyringe is used to deliver a sample volume in the range of a few microliters through a rubber septum and into the vaporization chamber. Most separations require only a small fraction of the initial sample volume and a sample splitter is used to direct excess sample to waste. Commercial gas chromatographs often allow for both split and splitless injections when alternating between packed columns and capillary columns. The vaporization chamber is typically heated 50 °C above the lowest boiling point of the sample and subsequently mixed with the carrier gas to transport the sample into the column.

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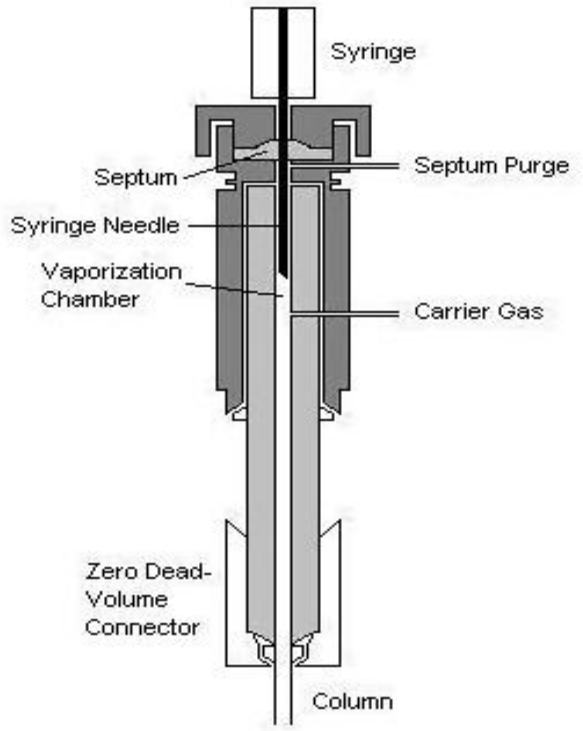


Carrier Gas

The carrier gas plays an important role, and varies in the GC used. Carrier gas must be dry, free of oxygen and chemically inert mobile-phase employed in gas chromatography. Helium is most commonly used because it is safer than, but comprable to hydrogen in efficiency, has a larger range of flow rates and is compatible with many detectors. Nitrogen, argon, and hydrogen are also used depending upon the desired performance and the detector being used.

Column Oven

The thermostatted oven serves to control the temperature of the column within a few tenths of a degree to conduct precise work. The oven can be operated in two manners: isothermal programming or temperature programming. In isothermal programming, the temperature of the column is held constant throughout the entire

separation. The optimum column temperature for isothermal operation is about the middle point of the boiling range of the sample. However, isothermal programming works best only if the boiling point range of the sample is narrow. If a low isothermal column temperature is used with a wide boiling point range, the low boiling fractions are well resolved but the high boiling fractions are slow to elute with extensive band broadening. If the temperature is increased closer to the boiling points of the higher boiling components, the higher boiling components elute as sharp peaks but the lower boiling components elute so quickly there is no separation.

Open Tubular Columns and Packed Columns

Open tubular columns, which are also known as capillary columns, come in two basic forms. The first is a wall-coated open tubular (WCOT) column and the second type is a support-coated open tubular (SCOT) column. WCOT columns are capillary tubes that have a thin later of the stationary phase coated along the column walls. In SCOT columns, the column walls are first coated with a thin layer (about 30 micrometers thick) of adsorbant solid, such as diatomaceous earth, a material which consists of single-celled, sea-plant skeletons. The adsorbant solid is then treated with the liquid stationary phase. While SCOT columns are capable of holding a greater volume of stationary phase than a WCOT column due to its greater sample capacity, WCOT columns still have greater column efficiencies.

Most modern WCOT columns are made of glass, but T316 stainless steel, aluminum, copper and plastics have also been used. Each material has its own relative merits depending upon the application. Glass WCOT columns have the distinct advantage of chemical etching, which is usually achieved by gaseous or concentrated hydrochloric acid treatment. The etching process gives the glass a rough surface and allows the bonded stationary phase to adhere more tightly to the column surface.

Detection Systems

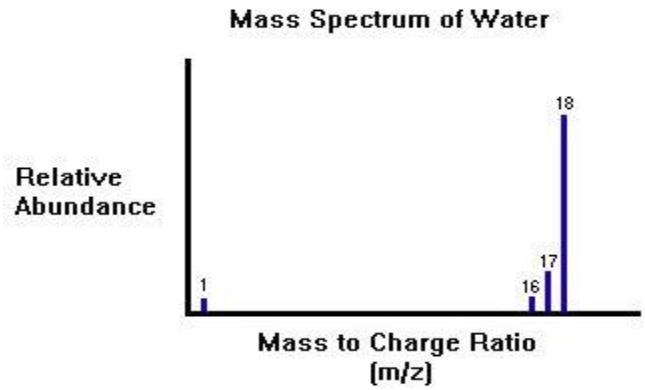
The detector is the device located at the end of the column which provides a quantitative measurement of the components of the mixture as they elute in combination with the carrier gas. In theory, any property of the gaseous mixture that is different from the carrier gas can be used as a detection method. These detection properties fall into two categories: bulk properties and specific properties. Bulk properties, which are also known as general properties, are properties that both the carrier gas and analyte possess but to different degrees. Specific properties, such as detectors that measure nitrogen-phosphorous content, have limited applications but compensate for this by their increased sensitivity.

Each detector has two main parts that when used together they serve as transducers to convert the detected property changes into an electrical signal that is recorded as a chromatogram. The first part of the detector is the sensor which is placed as close the the column exit as possible in order to optimize detection. The second is the electronic equipment used to digitize the analog signal so that a computer may analyze the acquired chromatogram. The sooner the analog signal is converted into a digital signal, the greater the signal-to-noise ratio becomes, as analog signal are easily susceptible to many types of interferences.

Mass Spectrometry Detectors

Mass Spectrometer (MS) detectors are most powerful of all gas chromatography detectors. In a GC/MS system, the mass spectrometer scans the masses continuously throughout the separation. When the sample exits the chromatography column, it is passed through a transfer line into the inlet of the mass spectrometer . The sample is then ionized and fragmented, typically by an electron-impact ion source. During this process, the sample is bombarded by energetic electrons which ionize the molecule by causing them to lose an electron due to electrostatic repulsion. Further bombardment causes the ions to fragment. The ions are then passed into a mass analyzer where the ions are sorted according to their m/z value, or mass-to-charge ratio. Most ions are only singly charged.

The Chromatogram will point out the retention times and the mass spectrometer will use the peaks to determine what kind of molecules are exist in the mixture. The figure below represents a typical mass spectrum of water with the absorption peaks at the appropriate m/z ratios.



Mass Spectrum of Water

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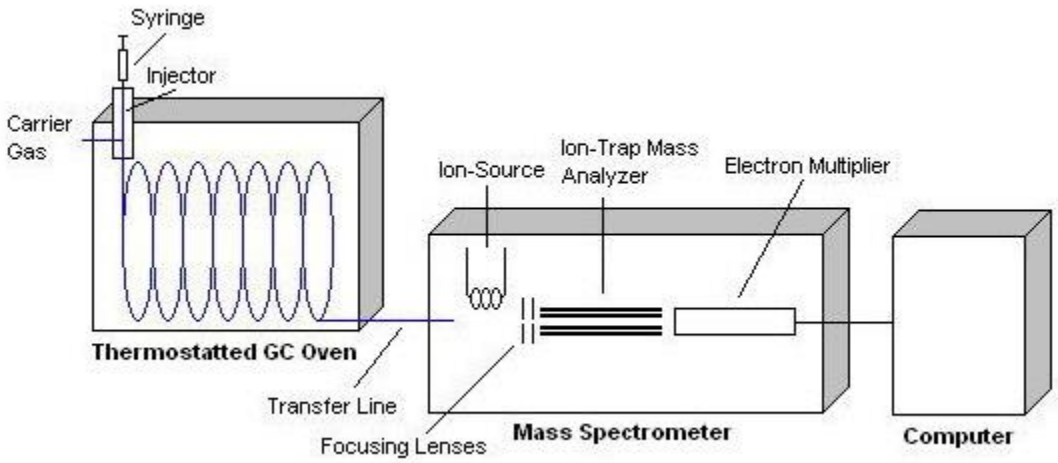

Schematic diagram of the GC/MS system

Procedure

Sample Gas Injection:

1) Click on Data Acquisition in the upper left to start the process
2) Click Sample Login to input sample specific information
3) Input your sample name, file name, and choose a tuning file (See Tuning for more information)
    a. Ensure to click the folder near the file name to send the file to the correct directory as it will default to the last user's file location
    b. Vial number and injection volume can be ignored for gas injections
4) Click okay and then click the file open icon in the upper left and choose your method file (See Method for more information)
5) Click download in the middle left side of the screen to send the initial parameters to the instrument.
6) Wait for both the GC and MS indicators in the upper right to be green (and the loud fans turn off inside the instrument for consistency) and then manually inject your gas sample into the back port (line 2) of the instrument while pressing the green start button on the GC
    a. Ensure to be consistent with each run, you can inject and then press the button, or press the button while injecting, or press the button and inject, etc.

7) Data will be outputted as the instrument acquires it. By clicking on the Snapshot icon in the lower left, it I possible to analyze the current data that has been generated but not in real time.

Sample Liquid Injection:

1) Click on Data Acquisition in the upper left to start the process
2) Click Sample Login to input sample specific information
3) Input your sample name, file name, and choose a tuning file (See Tuning for more information)
    a. Ensure to click the folder near file name to send the file to the correct directory as it will default the last user's file location
    b. Vial number and injection volume corresponds to the auto sampler rotunda. Standard injection volumes are 1 or 2 microliters.
4) Click okay and then click the file open icon in the upper left and choose your method file (See Method for more information)
5) Place your samples in the correct location on the auto sampler rotunda and ensure the auto sampler unit has the correct washes and waste containers placed along the auto sampler compartment (see the full guide for more information)
6) Click download to send the initial parameters to the instrument.
7) The auto sampler will automatically inject when the instrument is ready, meaning once you hit download the instrument will begin the process. Ensure everything is ready before you do so.
8) Data will be outputted as the instrument acquires it. By clicking on the Snapshot icon in the lower left, it is possible to analyze the current data that has been generated but not in real time.

Result: