# CHARACTERIZATION, ANALYSIS, AND PHYSICAL TESTING OF POLYMERS

# LABORATORY PRACTICAL WORKNOTE

**STUDENT NAME:**____________________________________________

**MATRICULATION NUMBER:**____________________________________

**ACADEMIC SESSION:** _______________________________________

**CLASS:**____________________________________________________

**DATE:** ____________________________________________________

***Compiled by:***

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**Points to remember while performing the experiment in a real laboratory:**

1. Always wear laboratory coat and gloves when you are in the laboratory. When you enter the laboratory, switch on the exhaust fan and make sure that all the chemicals and reagents required for the experiment are available. If it is not available, prepare the reagents using the components for reagent preparation.
2. Make sure you do not use an unknown reagent. Do not assume that all plastic containers contain water.
3. Cover-shoe or, preferably, safety boots should be put on to ensure safety of the feet.
4. Make sure to clean all your working apparatus with chromic acid and distilled water and ensure that all the apparatus are free from water droplets while performing the experiment.
5. Make sure to calibrate the electronic weighing balance before taking the measurements.
6. Ensure that the stop watch and hot air gun are working properly.
7. Clean all glass wares with soap and distilled water. Once the experiment is completed, recap the reagent bottles. Switch off the light, and exhaust fan before leaving the laboratory.
8. Discard the used gloves in a waste bin.

# EXPERIMENT 1

## Determination of Molecular Weight by Dilute Solution Viscometry
## Intrinsic Viscosity Measurements

**Practical Date:**______________________________________________

### Aim/Objectives

1. Determine the absolute viscosity of Polymer solutions of different concentrations
2. Determine the viscosity average molecular weight of a polymer.

### Theory

One of the most important parameters in molecular characterization is the determination of the average molecular weight of the polymer chain. One of the simplest and most widely used methods for molecular weight determination is dilute solution capillary viscometry. In this experiment, the molecular weight of a commercial polystyrene sample of industrial grade polymers will be determined. The background information for this laboratory session can be found in the references given below.

Viscosity is an internal property of a fluid that offers resistance to flow. It is due to the internal friction of molecules mainly depends on the nature & temperature of the liquid.

Many methods are available for measuring viscosity of polymer solution. The Ostwald method is a simple method for the measurement of viscosity, in which viscosity of liquid is measured by comparing the viscosity of an unknown liquid with that of liquid whose viscosity is known. In this method viscosity of liquid is measured by comparing the flow times of two liquids of equal volumes using same viscometer.

Consider two liquids are passing through a capillary of same viscometer. Then the coefficient of viscosity of liquid ($\eta_2$) is given by equation:

$$\eta_2 = \frac{\eta_1 \rho_2 t_2}{\rho_1 t_1}$$

Here, $t_1$ and $t_2$ are the time of flow of the liquids and $\rho_1$ and $\rho_2$ are the respective densities. And $\eta_1$ is the coefficient of viscosity of water.

For a given liquid $\eta$ has a specific value at the same temperature.

Various mixtures of two non-interacting liquids viscosities will lie among the viscosities of those pure components.

The time of flow of liquid depends on the viscosity and composition. In this method the flow times are measured for different known compositions and a graph is plot for time of flow and compositions. The unknown composition can be determined by plotting a graph for the time of flow and compositions.

The molecular weight of the polymer is measured by using viscometer and the molecular weight obtained by this technique is called viscosity average molecular weight. The molecular weight of the polymer solution is very high so the viscosity of polymer solution is very high compared to that of pure solvent.

From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below:

$$[\eta] = KM^{\alpha}$$

where, [η] is the intrinsic viscosity, *M* is Molecular weight, *K* and α are constants for a particular polymer solvent system.

If we know the *K* and α values for a given polymer solution the intrinsic viscosity and molecular weight can be calculate using the above equation.

**Materials Required**

1. Safety glasses for all group members at all times.
2. Ubbelohde viscometer
3. 5ml or 10 ml pipette and a plastic pipetter
4. Stopwatch
5. Ring stand and appropriate clamps
6. 25 ml volumetric flask
7. solvent (common PS solvents are Toluene and THF)
8. Polystyrene Sample

**Procedure**

1. In the Polymer Handbook find the section on Viscosity-Molecular Weight Relationships and look up the Mark-Houwink-Sakurada (MHS) parameters for polystyrene in a variety of solvents. Pick a "good" solvent for PS in which to conduct the experiment. How does one determine the "goodness" of solvent from the MHS parameters?
2. Once the solvent is chosen, calculate the starting concentration for the dilute solution viscometry experiments. Experiments should be conducted at four (4) decreasing concentrations:. These should be made by the successive dilution method directly in the viscometer if possible. This typically leads to less experimental error than making four separate solutions, especially when small sample weights are involved. What is the "drawback" to this method?

   NOTE: Make certain to mix the diluted samples well in the viscometer and always run the new solution up through the capillary once before taking data.
3. Select Ubbelohde viscometer to do the experiment. Which viscometer are you using? What do you expect to be the difference?). The viscometer should first be rinsed thoroughly (including the capillary bore) with the solvent to be used before starting the experiment.
4. Flow Time Measurement
5. Follow the instructions below for performing a flow time measurement (a demonstration will be given). With reference to the diagram in the polymer handbook,
   a. Load 8 ml of solvent into tube 1 (reservoir B) using the pipette.
   b. Attach the pipette to the top tube 2 and cover the hole of tube 3 (sidearm) with your thumb.

c. With the sidearm firmly blocked, suck the solvent up into reservoirs A, C, and D (just past the upper mark). Remove the pipette from tube 2, then remove your finger from the sidearm.
   NOTE: You must remove the pipette BEFORE taking your finger off the sidearm!

d. Measure the flow time for the solution (solvent or polymer). The flow time of interest is the time for the meniscus to pass from the upper to lower marks on the capillary. Note: The choice of Viscometer # (capillary diameter) is made by the criteria of a solvent flow time greater than 60 sec. (minimum) and preferably 100 sec. Why must the solvent flow time be kept to this low value?
   NOTE: Repeat the measurements until you get flow times within 0.2 - 0.5 sec.
   If agreement is not obtained in 3-5 measurements, you may have to clean the viscometer and start over. Many times dust or other foreign material in the capillary is the cause for erratic results. Once at least three (3) consistent flow times have been obtained, go on to the next dilution.

e. Once the next dilution is done or the next solution is loaded in the viscometer allow it to equilibrate for 3-5 minutes, then run the new solution through the capillary at least two (2) times before taking your next set of readings.

f. When the experiment is complete, thoroughly clean the viscometer with solvent paying particular attention to the capillary. Run the solvent flow time one more time to check for consistency with the previous measurement. (Is the solvent flow time the same as at the start of the experiment? Why not and what do you do about it?) The viscometer should be stored with tubes 1, 2, and 3 covered to prevent contamination by foreign material.

Using the references provided for information, do the following for each material tested:

1) In the space provided, present a clean and neat table of your raw data, including solvent and polymer flow times, viscometer # and type, etc.
2) Calculate $\eta_{rel}$, $\eta_{sp}$, and $\eta_{inh}$ for each concentration of each solution.
3) On the same graph, plot $\eta_{sp}/c$ versus c and $\eta_{inh}$ versus c. Determine [η] as the common intercept at C=0 of the best straight lines through the data (Note: Use Engineering judgment in doing the curve fit – exclude "spurious" points that are obviously not following the observed trend.) Comment on your method of determining the "best" fit of the data. Explain any differences in the intercept obtained by the two techniques. Which is more reliable or more accurate?
4) Using the value of [η] measured; calculate the molecular weight of the sample.
5) If you had to choose another solvent for polystyrene, what would it be and why? What are the MHS parameters for your alternative polymer/solvent system?
   HINT: You need the Polymer Handbook or equivalent on-line resource to answer this question.

**Discussion Questions**

Briefly explain, give the relationship for, or define the following:

1) Define the following viscosity terms: relative viscosity; specific viscosity; reduced viscosity; inherent viscosity; intrinsic viscosity.

2) Mark-Houwink-Sakurada (MHS) Equation.
   a) Explain the significance of the various terms in the equation.

b) Is this a "universal" equation (i.e., for any polymer/solvent system)?
c) From a physical chemistry and practical viewpoint (not thermodynamics) discuss the terms "good" and "theta" solvent. Use sketches if necessary.
d) How do the MHS parameters depend on quality of solvent?
e) How would one determine experimentally (not from Polymer Handbook) the MHS parameters for a given polymer/solvent system?

3) Which molecular weight is determined by dilute solution capillary viscometry? Where would it fall in relation to $M_n$ and $M_w$ on a normal molecular weight distribution curve?

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor's Remark and Comments:**

# EXPERIMENT 2

## Swelling Test for Polymer by Solvent Absorption

**Practical Date:**_______________________________________________

### Objectives

1. To study and have an understanding of equilibrium swelling of polymers in solvent
2. To determine the density of rubber
3. To determine the swelling of rubber material

### Description of Experiment/Procedure

Circular specimens of diameter 20mm, is punched out from the vulcanized sheets. Thickness and diameter of the specimens are measure by means of a screw and vernier calipers, respectively. Specimens of known weight are immersed in the solvents (toluene and hexane) and oils like petrol, diesel, lubricating oil etc in diffusion test bottles and kept at room temperature. Samples are removed from the bottles at periodic intervals and the wet surfaces are quickly dry using tissue paper and weights of the specimen after swelling are determined at regular intervals until no further increase in solvent uptake is detected. Thickness and diameter of the specimen after equilibrium swelling are also measured.

The **mol % uptake of the solvent, Q**, for the polymer composite samples is determine using the equation:

$$Q = ((W_2-W_1/M_o) \times 100)/W_1$$

where, $W_1$ and $W_2$ are the weights of the specimen before and after swelling and Mo the molar mass of the solvent.

**Swelling index** is calculated by the equation:

$$\text{Swelling index\%} = (W_2-W_1)/W_1 \times 100$$

where, $W_1$ and $W_2$ are the initial and final (swollen) weights of the sample.

**Swelling coefficient**: it is an index of the ability with which the sample swells and is determined by the equation:

$$\text{Swelling coefficient, } U, = (A/m) \times (1/d)$$

where, A is the weight of the solvent sorbed at equlirium swelling, m, the mass of the sample before swelling and d, the density of the solvent used

**Polymer-fibre interactions:** the extent of interaction between polymer and fibre can be analyzed using Kraus equation which is given by:

$$V_m/V_{ef} = 1 - m[f/1-f]$$

where, $V_m$ and $V_{ef}$ are the volume fraction of polymer in the gum Vulcanizate and in fibre filled swollen sample, respectively, f, the volume fraction of fibre and m, the fibre polymer interaction parameter

**Volume Fraction of polymer** in the swollen sample, Vef, is calculated by the experission:

$V_{ef} = [(D-FT)/(d_t)]/[(D-FT)/(d_t)]+[A_o/d_s)]$

Where $d_t$ and $d_s$ are the densities of the polymer and solvent, D the deswollen weight of the test specimen (dry weight), F, the weight fraction of the insoluble components, T, the weight of the specimen and A, the weight of the absorb solvent corrected for swelling increment respectively.

**Crosslink Density**, Ve = 2C/Rt
where, 2C, = 1000 gm/cm$^2$ . The term C is defined as the Gaussian term in Flory's equation, R, Ryberg constant, T the temperature

### (1) Determination of density of rubber

Cut the rubber sample into small pieces (≈ 5 mm), and place them in a 100 ml beaker. Pour into it 25 ml of glycerol. Using a burette, gradually add methanol into the beaker, with occassional shaking, until the rubber pieces remain suspended in the methanol/glyecerol mixture. At this instance, the densities of the rubber and the solution mixture are the same. Detremine the density of the mixture using a SG bottle.

### (2) Determination of the swelling of the rubber sample

Cut about 3 cm of the rubber sample and **accurately** determine its weight. Place the sample in a conical flask containing 25 ml toluene. Stopper the flask and place it in a dark corner of a cupboard for at least 12 hours. Take the rubber out and place it on a wire mesh for 5 seconds. Transfer the rubber to a weighing bottle of known weight, close it, and determine the weight of the rubber.

### Analysis of Data

The ratio of the volume of solvent trapped in the rubber sample is,

$$Q_m = (W_g - W/d^1)/(W/d)$$

where *Wg* is the weight of swollen rubber, *W* the initial weight of rubber, *d'* the density of toluene (0.867 g.ml$^{-1}$) and *d* the density of rubber. The volume fraction of rubber in the swollen sample is,

$$V_2 = 1/1 + Q_m$$

The molecular weight $M_c$ can then be calculated from the following equation,

$$M_c = -dV_oV_2^{1/3}/(in1 - V_2) + V_2 + \mu V_2^2$$

where, $V_o$ is the molar volume of toluene (mol. wt / density), and μ the interactive constant between natural rubber and toluene (= 0.42).

### Determination of the density of rubber

1. Cut a portion of the rubber sample (~10 cm) and determine its ACCURATE weight.
2. Fill a 5 ml. measuring cylinder with distilled water to its 3.00 ± 0.05 ml.
3. Cut the rubber into smaller pieces and put them into the measuring cylinder. [Make sure there are no **AIR BUBBLES** on the rubber samples].
4. Accurately read the new water level in the flask.

5. Determine the volume (V) of the rubber.
6. Calculate the density of the rubber.

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor’s Remark and Comments:**

# EXPERIMENT 3

## Molecular Weight Determination by End Group Analysis

**Practical Date: ________________________________________________________**

### Aim/Objective

To determine the number average molecular weight of a polymer material by End group analysis method.

### Description of Experiment/Procedure

In order to titrate the samples that were prepared in the previous lab period, they first must be dissolved in an appropriate solvent. The solvent for these Nylon samples will be phenol. This is a good solvent for the polymer but phenol readily oxidizes in air and discolors making it virtually impossible to detect the endpoint during the titration. To avoid this problem, use a fresh, unopened bottle of phenol or distill the phenol prior to use. Also, since the phenol must be heated to dissolve the polymer samples, be sure to do this under a nitrogen atmosphere. The titration does not have to be performed under nitrogen since the phenol is then at room temperature. However, it is necessary to dissolve the samples and do the titration during the same lab period.

1. Place 35 g of phenol and 15 g (19 mL) of methanol into each of five 19/22 100 mL round bottom flasks.
2. Equip one of the flasks with a stir bar, condenser, and nitrogen inlet. It may be necessary to gently warm the flask in order to melt the phenol. Add 1.5-2 g (accurately weighed) of the first polymer sample (ground-up) to the solution in the flask. Purge the flask with nitrogen and then maintain it under a positive pressure of nitrogen. Heat the mixture at the reflux temperature until the polymer is completely dissolved. Remove the heat and allow the flask to cool to room temperature. It may be helpful to have a second condenser available so that the second sample can be prepared while the first is cooling.
3. While the first sample is dissolving, fill a 10 mL microburette (0.01 mL graduations) with standardized 0.1 N HCl. Preparing a standard for detecting the end-point: Dissolve about 100 mg (accurately weighed) of the monomer in one of the flasks containing phenol and methanol.
4. Add 4 drops of thymol blue indicator to the flask. Knowing the molecular weight of the monomer, the milligrams of monomer that were added to the flask, and the normality of the acid, calculate the expected amount of titrant that will be needed to reach the end-point (assume a 1:1 stoichiometry, that is, one molecule of monomer or polymer for each molecule of HCl).
5. Then titrate to a pink end-point. Use this end-point for comparison when the polymer samples are analyzed.
6. To titrate the polymer samples, add 4 drops of thymol blue indicator to the flask and titrate with 0.1 N HCl to a pink end-point. Add the HCl slowly to the polymer samples, since the concentration of end-groups may be quite low and the end-point can be easily missed.

7. Repeat step 4 for each of the polymer samples.
8. Calculate $M_n$ (g/mole) and $D_P$ for each of the polymer samples. Obtain the second-order rate constant from the slope of a plot of $D_P$ vs C.

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor's Remark and Comments:**

# EXPERIMENT 4

## Determination of Compression Set of a Polymer Material

**Practical Date:**________________________________________________________

### Aim/Objective

To determine the compression set values of a set of test piece of a polymer material

### Theory

The compression set (ASTM D395) of a material is the permanent deformation remaining when a force (that was applied to it) is removed. The term is normally applied to soft materials such as elastomers.

Compression set is defined as the percentage of original specimen thickness after the specimen has been left in normal conditions for 30 minutes (therefore $C_A$, the compression set is given by $C_A = [(t_o - t_i)/t_o] * 100$ where $t_o$ is the original specimen thickness and $t_i$ is the specimen thickness after testing)

### Procedure

The test procedure is as follows:

1. Rubber specimens are measured to determine their height.
2. Spacers measuring 75% of the specimen height are installed.
3. The plates are tightened down to ensure the fixture plates are in complete contact with the spacers.
4. The fixture containing the compressed specimens is put into a temperature chamber for a prescribed time at a certain temperature.
5. The specimens are removed from the fixture and, after 30 minutes, their heights are measured. Results are computed and expressed as a percentage. Zero compression set means that the test specimen completely returned to its original height. One hundred percent compression **set** means that the test specimen remained in the deformed position and did not recover at all when removed from the fixture. Record the results of the test piece samples provided. Calculate their compression set values using the formula provided.

**Precautions:** Record the necessary precautions you took in course of the work

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**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor’s Remark and Comments:**

# EXPERIMENT 5

## Determination of Flexural Properties of a Polymer Material

**Practical Date:**______________________________________________________

### Aim/Objectives

1. To study the principles of bend testing, practice their testing skills and interpreting the experimental results of the provided materials when failed under three-point bending.
2. To investigate responses of metals when subjected to bending
3. To determine parameters such as bend strength, yield strength in bending and elastic modulus.
4. To interpret the obtained test data and select appropriate engineering materials for their intended uses in order to prevent creep failures.

### Theory

Flexural strength, also known as modulus of rupture, bend strength, or fracture strength, a mechanical parameter for brittle material, is defined as a material's ability to resist deformation under load. The transverse bending test is most frequently employed, in which a specimen having either a circular or rectangular cross-section is bent until fracture or yielding using a three point flexural test technique. The flexural strength represents the highest stress experienced within the material at its moment of rupture. It is measured in terms of stress, here given the symbol $\sigma$.

For a rectangular sample, the resulting stress under an axial force is given by the following formula:

$$\sigma = \frac{F}{bd}$$

This stress is not the true stress, since the cross section of the sample is considered to be invariable (engineering stress).

- $F$ is the axial load (force) at the fracture point
- *b* is width
- *d* is the depth or thickness of the material

The resulting stress for a rectangular sample under a load in a three-point bending setup is given by the formula below.

The equation of these two stresses (failure) yields:

$$\sigma = \frac{3FL}{2bd^2}$$

Usually, L (length of the support span) is much bigger than d, so the fraction $\frac{3L}{2d}$ is bigger than one

For a rectangular sample under a load in a three-point bending setup:

$$\sigma = \frac{3FL}{2bd^2}$$

- $F$ is the load (force) at the fracture point (N)
- $L$ is the length of the support span
- $b$ is width
- $d$ is thickness

For a rectangular sample under a load in a four-point bending setup where the loading span is one-third of the support span:

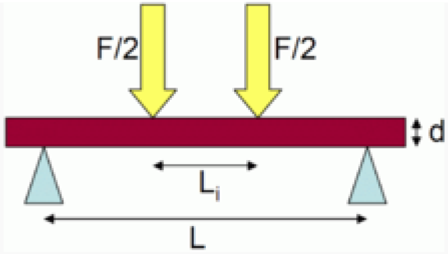
$$\sigma = \frac{FL}{bd^2}$$

- $F$ is the load (force) at the fracture point
- $L$ is the length of the support (outer) span
- $b$ is width
- $d$ is thickness

For the 4 pt bend setup, if the loading span is 1/2 of the support span (i.e. $L_i = 1/2\ L$ in:

$$\sigma = \frac{3FL}{4bd^2}$$

If the loading span is neither 1/3 nor 1/2 the support span for the 4 pt bend setup:



Beam under 4 point bending

$$\sigma = \frac{3F(L - L_i)}{2bd^2}$$

where, $L_i$ is the length of the loading (inner) span

**Materials Required**

1. Bend specimens
2. Micrometer or vernia caliper
3. Permanent pen
4. Universal testing machine

**Procedure**

1. Measure the width and thickness of the specimen including the span length in the table provided for the calculation of the stress and elastic modulus. Mark on the locations where the load will be applied under three-point bending.
2. Bend testing is carried out using a universal testing machine until failure takes place. Construct the load-extension or load-deflection curve if the dial gauge is used.
3. Calculate the bend strength, yield strength and elastic modulus of the specimen
4. Describe the failure under bending and sketch the fracture surfaces in the table provided.
5. Discuss the obtained experimental results and give conclusions.

**Question**

Give three examples of engineering applications which involve bending properties of the materials.

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

## Record of Experimental Results

**Instructor’s Remark and Comments:**

# EXPERIMENT 6

## Flame Test of Polymer Materials

**Practical Date:**________________________________________________

### Aim/Objectives

1. To identify polymers using flame/heating test
2. To classify polymers based on their heating behaviours

### Materials Required

1. Five polymer test samples
2. Stainless steel spatula
3. Bunsen burner

### Procedure

1. Place a small piece (0.1 g) of the test sample on a well cleaned glass or stainless steel spatula, previously heated to remove any traces of combustible or volatile materials.
2. Warm gently over a small colourless Bunsen flame, avoiding ignition till it begins to fume.
3. Move the sample to the hottest zone of the Bunsen flame
4. Repeat the same procedure for other test samples.
5. Present your observations/results in tabular form as shown below:

| S/N | Polymer Sample | Flame Colour | Odour | Thermoplastic/ Thermoset | Self-extinguishing/ Non-self-extinguishing | Nature of the residue |
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**Precautions:** Record the necessary precautions you took in course of the work

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**Experimental Observation:** Record your observations in the course of the experiment

## Record of Experimental Results

**Instructor’s Remark and Comments:**

# EXPERIMENT 7

## Sodium Fusion Test (Lassaigne Test)

**Practical Date**:_______________________________________________________

**Aim/Objectives**

1. To prepare sodium fusion filtrate
2. To confirm the presence of elemental nitrogen, sulphur and halogens in polymer materials

**Theory**

The number of elements, which can occur in an unknown sample of a rubber-like material, is quite large, because of the various substances that are used as compounding and vulcanizing ingredients. For the purpose of identifying the polymer present, only a limited number of the elements occur as part of the polymer and of these, fewer still have diagnostic significance e.g. N, F, S, Cl and Br. Although silicon could be found in silicone rubber, but, unfortunately, silicon-containing filler (silica and silicates) are in very common use in all rubbers and the presence of silicon is therefore significant.

The sodium fusion test is used in elemental analysis for the qualitative determination of elemental halogens, nitrogen and sulphur in a sample. It was developed by J.L. Lassaigne. The test involves heating the sample strongly with clean sodium metals, fusing it with the sample. The 'fused' sample is plunged into water, and the usual qualitative tests are performed on the resultant solution for the respective possible constituents.

When an organic compound is heated strongly with sodium, any halogens, nitrogen, and sulphur will be converted into inorganic sodium salts such as sodium halide (for halides), sodium cyanide (for nitrogen), sodium sulphide (for sulphur) and sodium thiocyanate (for sulphur and nitrogen).

**Materials Required**

1. Polymer sample
2. Sodium metal
3. Fusion tube
4. Ferrous sulphate
5. Dilute $H_2SO_4$
6. Dilute solution of sodium nitro-prusside
7. Carbon tetrachloride
8. Chlorine water
9. 2N nitric acid
10. Stop watch
11. Wire guaze

**Procedure**

1. Place a piece of clean sodium metal in a fusion tube
2. Add 50 mg of the sample to it.

3. Gently heat the tube at first allowing any distillate formed to drop back onto the molten sodium.
4. When charring begins, heat of the bottom the tube to dull redness for about 3 min.
5. Plunge the tube, while still hot, into a clean dish containing cold distilled water (6 ml) with the tube covered with a clean wire guaze.
6. Use the 'fusion' filtrate (clear and colourless) to confirm the presence of nitrogen, sulphur or the halogens in the sample.

**Nitrogen**

1. Add 0.2 g of powdered ferrous sulphate crystal to 2 ml portion of the 'fusion' filtrate. Boil the mixture for 30s, followed by cooling
2. Acidify the mixture with dil. $H_2SO_4$ dropwise.
   N.B: The formation of bluish-green (Prussian blue) precipitate indicates the presence of nitrogen.

**Sulphur**

1. Add a few drop of cold, freshly prepared dil. solution of sodium nitro-prusside to 2 ml portion of fusion filtrate.
   N.B: Production of rich purple colour indicates that the original substance contains sulphur.

**Halogens**

1. 1 ml of the 'fusion' filtrate is acidified with 2N nitric acid. Cool and add aqueous silver nitrate (1 ml) and compare with the blank.
   N.B: The formation of a heavy, white or yellow precipitate of silver halide indicates halogen.
2. To confirm the presence of the halogens one by one, add few drops of freshly prepared chlorine water and carbon tetrachloride (1 ml) to the filtrate and shake.
   N.B: Colourless layer of carbon tetrachloride indicates chlorine; brown layer indicates bromine; and violet layer indicates iodine

**Precautions:** Record the necessary precautions you took in course of the work

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**Experimental Observation:** Record your observations in the course of the experiment

## Record of Experimental Results

**Instructor’s Remark and Comments:**

# EXPERIMENT 8
## Infra-Red Spectrophotometric Determination of Polymers

**Practical Date**:________________________________________________________

### Aim/Objectives
1. To understand the operational principle of FTIR spectrophotometer
2. To analyse polymer samples with FTIR spectrophotometer
3. To differentiate between unmodified (native) and modified polymer

### Theory
Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It can be used to identify compounds or investigate sample composition.

The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

The Infrared Spectrometer provides data over the range from 4000 to 400 $cm^{-1}$ with the main instrument bench and a somewhat narrower range of analysis (4000 to approximately 650 $cm^{-1}$) when an attenuated total reflectance accessory is used.

Fourier Transforms Infra-Red (FTIR) Spectroscopy is a newer IR technique, which utilizes a single beam of un-dispersed light and has the instrument components similar to the previous one. In FTIR, the un-dispersed light beam is passed through the sample and the absorbances at all wavelengths are received at the detector simultaneously. A computerized mathematical manipulation (known as “Fourier Transform”) is performed on this data, to obtain absorption data for each and every wavelength. To perform this type of calculations interference of light pattern is required for which the FTIR instrumentation contains two mirrors, one fixed and one moveable with a beam splitter in between them. Before scanning the sample a reference or a blank scanning is required.

### Materials Required
1. Native starch sample
2. Acetylated starch sample
3. KBr pellet
4. Desiccator
5. Oven
6. Mortar and pestle
7. Hydraulic laboratory press
8. Stopwatch
9. FTIR Spectrophotometer (Shimadzu FTIR-8400S)

**Preparation of KBr Pellet**

10. Dry IR-grade KBr in a drying oven for at least 1 hour.
11. Allow the KBr to cool in a desiccator.
12. Weigh out 300 mg and place in a marble mortar and pestle and grind to fully powder it.
13. Carefully weigh 3 mg of the finely ground solid sample and place in the marble mortar and pestle with the KBr.
14. Grind for 60 seconds to thoroughly mix.
15. Place the KBr-compound mixture into an evacuable die on a hydraulic laboratory press. Press in vacuo at 15,000 pounds of pressure for 6 minutes.
16. Release the pressure, remove the die from the press, disassemble the die, and remove the KBr pellet.
17. Place the KBr pellet in a pellet holder and put it into the sample beam of an IR.

**Operation of Software**

1. Turn on the FTIR by pressing On/Off button which is in front of the Instrument.
2. Click on the FTIR icon and press OK
3. Select transmittance (%) mode:
4. Select resolution of 4 or 8
5. Select range from 4000 cm-1 to 500 cm-1
6. Select number of scans between 1 and 4000
7. Execute background scan with an empty sample holder
8. Place the KBr pellet in a pellet holder and put it into the sample beam of an IR
9. Click sample start
10. Save the spectrum by pressing CTRL+S and enter a file name
11. Display the peaks

**Discussion Question**

1. Identify the different peaks of the spectra for unmodified and modified starch samples
2. Give the schematic or pictorial diagram of a typical FTIR spectrophotometer
3. Highlight the strengths and weaknesses of FTIR spectroscopy as a method for polymer analysis

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

## Record of Experimental Results

**Instructor’s Remark and Comments:**

# ASSIGNMENT #1

**Date:** ____________________________________________________

**Q1.** With the aid of schematic diagrams show the improvement of FTIR spectrophotometer on dispersive IR spectrometer

**Q2.** Highlight the significance of IR spectroscopy in analyzing polymers

**Q3.** Give the schematic diagram of a typical Differential Scanning Calorimeter (DCS). Highlight its applications in polymer processing and analysis

**Instructor's Remark and Comments:**

# ASSIGNMENT #2

**Date:** ____________________________________________________________

**Q1.** Give the schematic diagram of Scanning Electron Microscopy (SEM). Indicate its strengths and weaknesses in polymer analysis

**Q2.** With the aid of a schematic diagram, show the features of a Transmission Electron Microscope

**Q3.** Outline the applications of UV-Visible Spectrophotometer

**Instructor's Remark and Comments:**

# EXPERIMENT 9

## Determination of Dirt Content

**Practical Date:**____________________________________________________

### Aim/Objectives

1. To identify the presence of dirts in polymer materials
2. To analyse the significance of dirts to the service life and performance of polymer products

### Theory

Dirt content is a measure of insoluble impurities such as wood, bark, sand and earth. Excess of dirt content leads to premature mechanical failure of natural rubber products in service life.

### Materials Required

1. Mineral turpentine (high aromatic white spirit, bp. 155-196 $^{o}$C)
2. Xylene mercaptan
3. n-hexane
4. Conical flask (500 ml)
5. Thermometer
6. Stainless steel sieve onto which a phosphor-bronze gauze (ASTM No. 325 mesh) of 44 side-square aperture is soldered
7. Sieve holder
8. Oil bath
9. Weighing balance
10. Drying oven
11. Ultrasonic bath
12. Two-roll mixing mill (150 x 300 mm)

### Procedure

1. Pass about 20 g of the homogenized rubber through the cold mill (nip setting 0.33 mm)
2. Weigh 10 g as a test portion and place in 500 ml conical flask, containing 250 ml mineral turpentine and 1 ml xylene mercaptan.
3. Place the flask and its content in the oil bath and heat to about 135 $^{o}$C for 4 h.
4. Stir the mixture occasionally to assist its dissolution
5. Filter the hot solution through a previously weighed, clean and dry sieve
6. Wash the dirt in the sieve with a jet of warm mineral turpentine
7. Complete the washing by rinsing with n-hexane
8. Dry the sieve with dirt in an oven at 90 – 100 $^{o}$C for 30 min, followed by cooling in a desiccator, and re-weighing to the nearest 0.1 mg
9. Express the dirt content as percentage of the test portion as follows:

$$\%\ \text{Dirt} = \frac{\text{Weight of dirt}}{\text{Weight of test portion}} \times 100$$

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor’s Remark and Comments:**

# EXPERIMENT 10

## Determination of Volatile Matter

**Practical Date:**_______________________________________________________

### Theory

Specification limit of 0.8 % for the parameter is aimed at reducing the incidence of wet rubber. Excessive moisture content in rubber would lead to difficulties in the dispersion of fillers thereby causing high product rejection rate.

### Material Required

1. Laboratory mill (150 x 300 mm)
2. Polythene bags
3. Weighing balance
4. Watch glasses
5. Aluminium trays
6. Clips
7. Drying oven

### Procedure

1. Wrap the polymer sample (20 g) in an air-tight polythene bag
2. Equilibrate the sample in an air-conditioned room for 30 min
3. Weigh out a test-portion of 10.00 – 10.20 g
4. Place the test-piece on a watch glass and dry in an oven at $100 \pm 3\ ^{o}C$ for 4 h
5. Remove the test-piece from the oven and insert in a polythene bag
6. Seal the bag and place it on one aluminium tray and cool for 30 min in an air-conditioned room
7. Remove the test-piece and weigh
8. Express the volatile matter as follows:

$$\%\ \text{Volatile Matter} = \frac{A - B}{A} \times 100$$

where, A = weight of the test-portion before drying and B = weight of the test-portion after drying

**Precautions:** Record the necessary precautions you took in course of the work

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**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor’s Remark and Comments:**

# EXPERIMENT 11
## Determination of Ash Content

**Practical Date:**____________________________________________________

### Aim/Objective
1. To appraise the significance of trace elements to the life span of polymers

### Theory
The ash content of represents a minimal figure for the amount of mineral present in a compound. Just like other constituents of NR latex, its ash content is variable. Some of the trace elements retained in the rubber, such as copper, manganese and iron are known to promote the oxidative degradation of rubber, resulting in reduction of Plasticity Retention Index (PRI). Thus, a low ash content is desirable for raw rubber.

### Materials Required
1. Silica crucible
2. Muffle furnace
3. Whatman No. 542 or No. 40 ashless filter paper

### Procedure
1. Weigh 5.0 g of the polymer sample
2. Wrap it in an ashless filter paper
3. Place the wrapped sample in a pre-weighed and pre-ignited crucible
4. Introduce the crucible with the content into a muffle furnace controlled at 550±20 $^{o}$C for 5 h
5. Remove the crucible and cool in a desiccator
6. Weigh the crucible with the content
7. Express ash content as follows:

$$\%\ \text{Ash Content} = \frac{\text{Weight of ash}}{\text{Weight of test} - \text{piece}} \times 100$$

### Questions
1. What are trace elements?
2. What do you understand by the term ‘ashless filter paper’?
3. What is the relationship between the ash content and Plasticity Retention Index (PRI) of a polymer sample?

**Precautions:** Record the necessary precautions you took in course of the work

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**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor's Remark and Comments:**

# EXPERIMENT 12

## Determination of Plasticity Retention Index

**Practical Date:**____________________________________________________

### Aim/Objective

1. To appraise the classification, grading and quality assessment of polymers using their plasticity retention indexes

### Theory

The Plasticity Retention Index (PRI) is a measure of the resistance of raw rubber to oxidation breakdown at temperature above 100 $^{o}$C, applied mainly to natural rubber. Natural rubber, if properly prepare, is well protected against oxidation. The high level of natural protection may, however, be reduced by excessive washing, excessive heat during drying, exposure to sunlight or contamination with pro-oxidant substance (mainly metals such as copper, manganese, iron, etc).
The degree of resistance to oxidation has an important bearing in processing and performance of the rubber in service. It has been adopted as a method of classifying, grading and qualitatively assessing the quality of raw rubber.

### Materials Required

1. Test-piece
2. Aluminium foil
3. Parallel Plate Plastimeter
4. Oven
5. Aluminium tray

### Procedure

1. Wrap the test-piece with a piece of aluminium foil to prevent the test-piece from sticking to the anvils of micrometer guage of the plastimeter
2. Place the sample in the test chamber, pre-heated for 10 s
3. Read the plasticity number of the unaged test-piece with the dial micrometer guage of the plastimeter
4. Place the test-piece in an oven controlled at an ageing temperature of 140±0.2 $^{o}$C for 20 min
5. Read the plasticity number of the aged test-piece with the dial micrometer guage of the plastimeter
6. Express Plasticity Retention Index as follows:

$$\text{PRI} = \frac{\text{Plasticity Number of Aged Sample}}{\text{Plasticity Number of Unaged Sample}} \times 100$$

### Questions

4. What is the significance of PRI to processing and service performance of a polymer material?

5. Determine PRI at 120 $^{o}$C and 160 $^{o}$C. Compare your results with PRI at 140 $^{o}$C. What is the effect of temperature on PRI?

**Precautions:** Record the necessary precautions you took in course of the work

**Experimental Observation:** Record your observations in the course of the experiment

**Record of Experimental Results**

**Instructor’s Remark and Comments:**