Chapter 2

Materials and Experimental Techniques

Abstract

This chapter deals with the discussion about the structure, properties and utilities of the polymer which were used in the present work. Preparation of films of polymer blends and composites are discussed here. The specification of different characterization techniques, which have been used for the analysis of polymer blends/composites films, are also discussed in this chapter.

2.1. Introduction

This chapter describes a detailed account of the polymeric materials used for the present study, methods to prepare films of polymeric blends/composites and various techniques used for the analysis of polymer blends/composites films. Detailed descriptions of following are considered in this chapter.

- Materials: Properties
- Sample preparation
- Thickness measurement
- Fourier Transform Infra-Red (FTIR) Spectroscopy
- UV-Vis Spectroscopy
- RAMAN Spectroscopy
- Mechanical Properties
- Thermogravimetric Analysis(TGA)
- Scanning Electron Microscopy
- Differential Scanning Calorimeter

2.2. Materials

The Materials used in the present study are

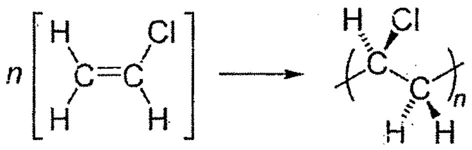
1. Polyvinyl Chloride (PVC)
2. Polymethyl methacrylate (PMMA)
3. Poly Acrylamide (PAM)
4. Polyvinyl Alcohol (PVA)
5. Polyethylene Oxide (PEO)

6. Titanium Dioxide (TiO_2)

2.2.1. Polyvinyl Chloride (PVC)

Polyvinyl Chloride (PVC) is the third widely produced plastic [1]. PVC is widely used because it is durable, cheap and easily worked. It has large number of properties, so can be used to make hundreds of products [2]. PVC's are relatively low cost, biological and chemical resistance and workability have resulted in it being used for a wide variety of applications. With the addition of impact modifiers and stabilizers, it has become a popular material for window and door frames. By adding plasticizers, it can become flexible enough to be used in cabling applications as a wire insulator. It has been used in many other applications.

PVC is also widely used vinyl member which is formed by the free radical polymerization of vinyl chloride monomer units as shown below.



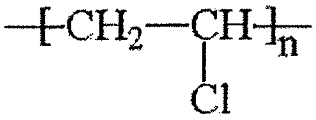
PVC consists of polar molecules which are attracted to each other by electrostatic attraction due to dipole-dipole interaction of a chlorine atom in one atom to a hydrogen atom in another atom. Due to this intermolecular interactions between polymer chain PVC is fairly strong thermoplastic materials.

PROPERTIES

- **Composition**

  $[-C_2H_3Cl-]_n$

❖ Structure of Polyvinyl chloride (PVC)



$$-\!\!\left[\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\right]_n\!\!-$$

❖ PHYSICAL PROPERTIES OF PVC

Physical properties of PVC are described below (**Table 2.1**).

Table 2.1 Physical properties of PVC

Property	**PVC**
Density [g/cm^3]	1.3–1.45
Thermal conductivity [W/(m·K)]	0.14–0.28
Yield strength [MPa]	31–60
Young's modulus [psi]	490,000
Surface resistivity [Ω]	10^{13}–10^{14}
Elongation at break (%)	20–40
Glass temperature (°C)	82 °C
Melting point (°C)	100–260
Specific heat (*c*) (kJ/(kg•K))	0.9

❖ Other Properties

- **Weathering stability**. PVC is resistant to aggressive environmental factors, therefore is the material of choice for roofing.
- **Versatility.** PVC can be flexible or rigid.
- **Fire protection.** PVC is a material resistant to ignition due to its chlorine content.
- **Longevity.** PVC products can last up to 100 years and even more.

- **Hygiene.** PVC is the material of choice for medical applications, particularly blood and plasma storage containers.
- **Energy recovery.** PVC has high thermal power; when utilized in incinerators PVC provides power and heat for homes and industries, and all that without any environmental impact
- **Barrier properties.** PVC can be made impervious to liquids, vapors and gases.
- **Eco-efficiency.** Only 43% of PVC's content comes from oil (57% comes from salt); it therefore contributes to the preservation of that highly valuable natural resource.
- **Recyclability.** PVC is very recyclable, more so than many other plastics.
- **Economical efficiency.** PVC is the cheapest of large-tonnage polymers providing many products with the best quality-price ratio.

2.2.2. Poly (methyl methacrylate) (PMMA)

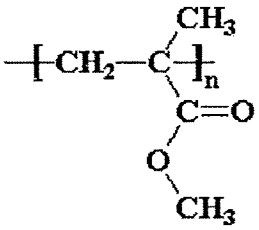
Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic which is the synthetic polymer of methyl methacrylate. PMMA is routinely produced by emulsion polymerization, solution polymerization, and bulk polymerization. It is commercially polymerized by free radical initiators such as peroxides and azo compounds in suspension or for more specialized applications such as for hard contact lenses. PMMA is an amorphous, transparent and colorless thermoplastic which is hard and stiff but brittle. PMMA is a strong and lightweight material. PMMA is often preferred because of its moderate properties, easy handling and processing, and having low cost, but behaves in a brittle manner when loaded. It has good abrasion and UV resistance and excellent optical clarity [3, 4].

PROPERTIES

- **Composition**

  $[-C_5H_8O_2-]_n$

- **Structure of Polymethyl methacrylate (PMMA)**



- **PHYSICAL PROPERTIES OF PMMA**

  Physical properties of PMMA are described below (**Table 2.2**).

Table 2.2 Physical properties of PMMA

Property	**PMMA**
Density [g/cm^3]	1.18
Thermal conductivity [W/(m·K)]	0.167-0.25
Young's modulus [MPa]	1800-3100
Glass temperature (°C)	85
Melting point (°C)	130–140
Specific heat (*c*) (kJ/(kg.K))	1.47

- **Application**
  - Optical instruments:

    Production of optical lenses, such as glasses, magnifying glass, various lenses.

  - Stationery and daily necessities:

    Making a variety of drawing tools, teaching model, specimen shield, lamps, all kinds of pens, buttons, hair clips, candy, soap box, household accessories.

- Construction areas:

  Indoor and outdoor lighting and non-lighting signal display, ceiling lighting, furniture, partition materials, solar energy collector housings etc.

- Other areas:

  Can be used as medical devices, such as additional limbs, dentures, medical optical basic raw material, aero-space equipment, light cover, surface cover plates, car and motorcycle windshields. PMMA finds major applications in automotive industry, as acrylic sheet for bathtubs, sign boards and as composites materials for kitchen sinks, basins and bathroom fixtures.

2.2.3. Polyacrylamide (PAM)

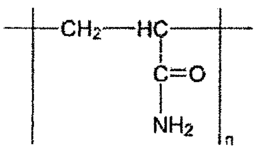
Polyacrylamide (PAM) is a polymer formed from acrylamide subunits. It can be synthesized as a simple linear-chain structure or cross-linked, typically using *N*,*N'*-methylenebisacrylamide. Polymers of acrylamide are well known for their hydrophilicity and inertness. PAM is well-known hydrophilic polymer and has been greatly used in the field of agriculture and biomedicine [5, 6]. It is water soluble polymer that's why Polyacrylamide-based polymers have received a great extent of utility in industry.

PROPERTIES

❖ **Composition**

$[-C_3H_5NO-]_n$

❖ **Structure of Polyacrylamide (PAM)**



$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{HC}}}- \right]_n$$

❖ PHYSICAL PROPERTIES OF PAM

Physical properties of PAM are described below (**Table 2.3**).

Table 2.3 Physical properties of PAM

Property	**PAM**
Density [g/cm^3]	1.5
Thermal conductivity [W/(m·°C)]	0.56
Glass temperature (°C)	160-170
Melting point (°C)	230–240

❖ Application

Polyacrylamide is not toxic. It is used to coagulate solids in a liquid like in water treatment plant, Enhanced Oil Recovery, used for horticultural and agricultural, to make Gro-Beast toys, which expand when placed in water, can be utilized as an additive in body-powder, used in molecular biology applications as a medium for electrophoresis of proteins and nucleic acids.

2.2.4. Polyvinyl Alcohol (PVA)

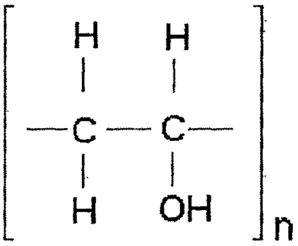
Polyvinyl alcohol is obtained by the direct hydrolysis of poly (vinyl acetate). PVA is a non-toxic, water soluble synthetic polymer that has been commercially produced on a large scale. It has a large number of hydroxyl groups which allows it to react with many types of functional groups. This advantage makes it suitable as biocompatible materials. Polyvinyl alcohol (PVA) has excellent film forming, emulsifying and adhesive properties [7]. It is also resistant to oil, grease and solvents. It is odorless and nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. The chemical resistance and physical properties of PVA have led to its broad industrial use. Chemically cross linked PVA have received increasing attention in biomedical and biochemical applications.

PROPERTIES

- **Composition**

  $[-C_2H_4O-]_n$

- **Structure of Polyvinyl Alcohol (PVA)**



$$\left[-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}- \right]_n$$

- **PHYSICAL PROPERTIES OF PVA**

  Physical properties of PVA are described below (**Table 2.4**).

Table 2.4 Physical properties of PVA

Property	PVA
Density [g/cm^3]	1.19-1.39
Thermal conductivity [W/(m·K)]	0.2
Refractive Index	1.54
Glass temperature (°C)	75-85
Melting point (°C)	180-190
Specific heat (*c*) (kJ/(kg.K))	1.67

- **Application**

  PVA has been widely utilized in diverse fields, ranging from thickening agent to controlled release systems [8]. It has been widely used as a basic material for a variety of biomedical applications [9]. PVA is useful as thickener and modifier, useful in water transfer printing process, as hard contact lens solution as a lubricant, used in the formation of polymer encapsulated nano beads, to making protective chemical-resistant gloves, for packaging purpose, as an additive for strength to concrete and cements.

2.2.5. Polyethylene Oxide (PEO)

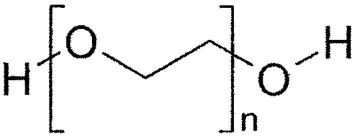
Polyethylene Oxide is a polyether compound with many applications from industrial manufacturing to medicine. PEO is synthetic polymer of ethylene oxide monomer. Polyethylene oxide is non-toxic, odorless, neutral, lubricating, nonvolatile and nonirritating and is used in a variety of pharmaceuticals and in medications as a solvent, dispensing agent, ointment and suppository bases [10].

PROPERTIES

- **Composition**

  $C_{2n}H_{4n+2}O_{n+1}$

- **Structure of Polyethylene Oxide (PEO)**



- **PHYSICAL PROPERTIES OF PEO**

  Physical properties of PEO are described below (**Table 2.5**).

Table 2.5 Physical properties of PEO

Property	PEO
Density [g/cm^3]	1.15-1.26
Thermal conductivity [W/(m·K)]	0.17
Refractive Index	1.45
Glass temperature (°C)	-67
Melting point (°C)	65-75

❖ Application

PEO has good chemical stability, both acid and alkali - resistant, corrosion-resistant. It is useful to enhance water dispersibility and water-based coatings, Anti dusting agent in agricultural formulations, Coupling agent, humectants, solvent and lubricant in cosmetics and personal care bases, Dye carrier in paints and inks, Low volatile, water soluble, and noncorrosive lubricant without staining residue in food and package process, Plasticizer to increase lubricity, Softener and antistatic agent for textiles.

2.2.6. Titanium Dioxide (TiO_2)

Titanium dioxide, also known as titanium (IV) oxide or Titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. Generally it comes in two different forms, rutile and anatase.

PROPERTIES

❖ Composition

TiO_2

❖ PHYSICAL PROPERTIES OF TiO_2

Physical properties of TiO_2 are described below **(Table 2.6)**.

Table 2.6 Physical properties of TiO_2

Property	TiO_2
Molar Mass [g/mol]	79.866
Density [g/cm^3]	4.23
Refractive Index	2.488
Melting point (°C)	1843

❖ Application

TiO_2 has a wide range of applications, from paint to sunscreen to food coloring. Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index. TiO_2 is useful in cosmetic and skin care products, as a UV absorber, as a photo catalyst.

2.3. Methods

2.3.1. Blend preparation

All the polymeric blends, studied here, are prepared by solution cast technique. All the polymer, dopant and solvent are purchased from local chemical supplier. Methods of preparation of all blends are described below.

i. **Preparation of PVC and PMMA blends**

The polymeric blends of PVC and PMMA were prepared in different weight proportion by solution cast technique. The weighed fractions of PVC and PMMA were dissolve in acetone plus toluene solution in 1:3 fraction at room temperature and stirred for approximately 24 hrs at different proportions starting from 90/10, 80/20, 70/30, 60/40, 50/50, 30/70. And the solution was cast on a clean and flat petty dish. Then petty dish is kept open at room temperature to evaporate the solvent. Then the films were lifted from the petty dish and used for further analysis and characterization.

ii. **Preparation of PAM and PVA blends**

The blend films were prepared by the solution casting method in three different weight percentages 30:70, 50:50 and 70:30 of PAM and PVA using distilled water as solvent at room temperature. The gel like solution was cast on a clean and flat Teflon dish. Then the dish is kept in bulb oven to evaporate the solvent. After drying the films, it's used for further analysis and characterization.

iii. Preparation of PAM and PEO blends

The blend films of PAM/PEO in three different weight proportions (30:70, 50:50 and 70:30) were prepared by the solution casting method using distilled water as solvent. After stirring for 12 hours at room temperature, we get homogenous gel like solution. Then solution was cast on a clean and flat Teflon dish to evaporate solution. After getting dry, the films are used for further analysis and characterization.

2.3.2. Composites Preparation

We have studied PMMA and TiO_2 composites here. These composites are also made by solution cast techniques in different weight proportion.

i. Preparation of PMMA and TiO_2 composites

The weighed fractions of PMMA and TiO_2 were dissolve in Tetra hydrofuran (THF) solution at room temperature and stirred for approximately 12 hrs for homogeneous solution at different weight percentage of TiO_2 starting from 0.01%, 0.03%,0.05%,etc. The solution was cast on a flat petty dish which is cleaned with acetone. The solution was allowed to spread uniformly in all direction in the petty dish. Then petty dish is kept open at room temperature to evaporate the solvent. Then the films were lifted from the petty dish for the experimental analysis.

2.3.3. Thickness Measurement

The thickness of the synthesized blends and composites are measured by a sensitive digital vernier caliper. Least count of the instrument is 0.001 mm. The thickness of all blends and composites films are measured at 5 different places, choose randomly, and then average of it is taken in the count. The obtained thickness is given in **Table 2.7**.

Table 2.7 Thickness of various polymers and its blends

Sr. No.	Polymer film	Thickness(mm)
1.	Pure PVC	0.23
	PVC+PMMA (90:10)	0.19
	PVC+PMMA (80:20)	0.18
	PVC+PMMA (70:30)	0.11
	PVC+PMMA (60:40)	0.26
	PVC+PMMA (50:50)	0.28
	PVC+PMMA (30:70)	0.27
	Pure PMMA	0.30
2.	Pure PAM	0.06
	PAM+PVA (70:30)	0.07
	PAM+PVA (50:50)	0.06
	PAM+PVA (30:70)	0.05
	Pure PVA	0.07
3.	Pure PAM	0.06
	PAM+PEO (70:30)	0.12
	PAM+PEO (50:50)	0.14
	PAM+PEO (30:70)	0.06
	Pure PEO	0.06
4.	Pure PMMA	0.31
	PMMA+ TiO_2 (0.03%)	0.25
	PMMA+ TiO_2 (0.1%)	0.15
	PMMA+ TiO_2 (0.3%)	0.17
	PMMA+ TiO_2 (0.5%)	0.42

2.4. Experimental Techniques and Instruments

The Pure and Blend samples were characterized with different characterization techniques to study the structural, physical, chemical, optical, thermal properties and surface morphology. Different characterization techniques with their working principle have been discussed as below.

2.4.1. Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy has been a useful technique for materials analysis for over several years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms [11, 12].

The molecules are excited to a higher energy state when they absorb infrared radiation [13-15]. The absorption of infrared radiation is a quantized process. Only selected frequencies (energies) of infrared radiation will be absorbed by a molecule. In the absorption process, those frequencies of infrared radiation, which match the natural vibrational frequencies of the molecule, will be absorbed, and the energy absorbed will serve to increase the amplitude of the vibrational motions of the bonds in the molecule [16]. All bonds in a molecule are not capable of absorbing infrared radiation, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds which have a permanent dipole moment are capable of absorbing infrared radiation. The changing electrical dipole of the bond can then couple with the electromagnetic field of the incoming radiation. Every different type of bond has a different natural frequency of vibration. Since the same type of bond in two different compounds is in a slightly different environment, because each different compound is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification of every different kind of materials. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. (Nicolet Corporation) [17].

Fourier transform infrared spectroscopy is preferred methods of infrared spectral analysis for several reasons:

- It is a non-destructive technique
- It provides a precise measurement method which requires no external calibration
- It can increase speed, collecting a scan every second
- It can increase sensitivity
- It has greater optical throughput
- It is mechanically simple with only one moving part

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments, such as slow scanning process and measuring all of the infrared frequencies simultaneously, Which were overcome by developing optical device called an interferometer. The interferometer produces a signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly.

Interferometers produces interfering signal which is the combination of two beam signal which is called interferogram. But an analyst requires a frequency spectrum to make identification. Interferogram signal cannot be interpreted directly so decoding of the individual frequencies is required. This can be done by a technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis [17].

FTIR spectroscopy has been classified into two major areas: non-reflection techniques and reflection techniques. Attenuated Total Reflectance (ATR) spectroscopy is an internal reflection technique used in combination with FTIR. ATR spectroscopy is often considered as a technique to study the surface of different materials, such as thin films or opaque solids. The ATR technique requires an internal reflection element (IRE), such as the ATR crystal. The sample, which has lower refractive index, is in contact with the crystal. Thus an absorbing medium is in contact with a reflecting one. An incident beam enters the ATR crystal from one of the side faces and is totally reflected at the interface with the sample. The sample is able to absorb light in accordance with its spectrum through the penetration of an evanescent wave up to few microns and reflected back into the crystal. Some energy is removed from the reflected beam; it's called Attenuated Total Reflectance (ATR). The decrease in the reflected beam intensity results in an absorption spectrum. This spectrum can then be interpreted in terms of the physical and chemical structure and properties of the materials.

The normal instrumental process is as follows:

1. The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample.

2. The Interferometer: The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy are absorbed.

4. The Detector: The beam finally passes to the detector for final measurement. The detectors are designed to measure the special interferogram signal.

5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

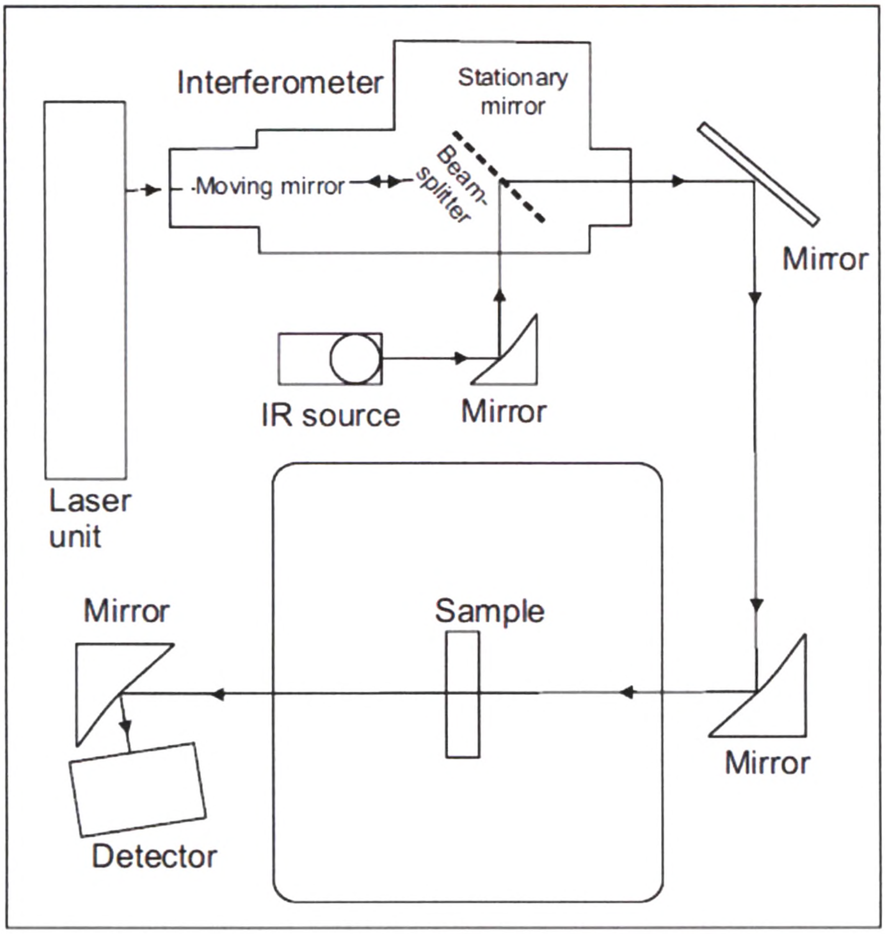


Figure 2.1 Schematic Diagram of an Infrared Spectrophotometer

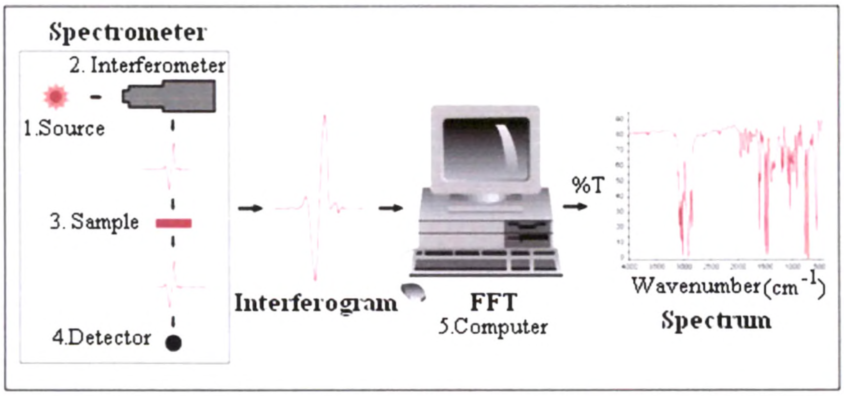


Figure 2.2 Analysis of IR spectroscopy data

Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the "percent transmittance." This technique results in a spectrum which has all of the instrumental characteristics removed and all spectral features which are present are strictly due to the sample.

The detectors employed are much more sensitive and the optical throughput is much higher. The sensitivity benefits enable identification of even the smallest of contaminants. These advantages, along with several others, make measurements made by FTIR extremely accurate and reproducible. Thus, it is a very reliable technique for positive identification of any sample. Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy.

2.4.2. UV- Vis Spectroscopy

Ultraviolet–visible spectroscopy or **ultraviolet-visible spectrophotometry** (**UV-Vis** or **UV/Vis**) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. Ultraviolet and visible spectrophotometry is the most preferable in laboratories. It concerned with the identification and measurement of organic and inorganic compounds. UV-Visible spectrometry used for its simplicity, versatility, speed, accuracy and cost-effectiveness.

The Origin of the Absorption

Valence electrons can generally be found in one of three types of electron orbital:

1. Single bond (σ bonding orbitals)

2. Double or triple bonds (π bonding orbitals)

3. Non-bonding orbitals (lone pair electrons)

Sigma bonding orbital tend to be lower in energy than π bonding orbital, which in turn are lower in energy than non-bonding orbital. When electromagnetic radiation of the correct frequency is absorbed, a transition occurs from one of these orbitals to an empty orbital, usually an anti-bonding orbital like σ* or π* (**Figure 2.3**).

1. The exact energy differences between the orbital depend on the atoms present and the nature of the bonding system. Most of the transitions from bonding orbital involve only π→π*, n→σ* and n→π* transitions [18].

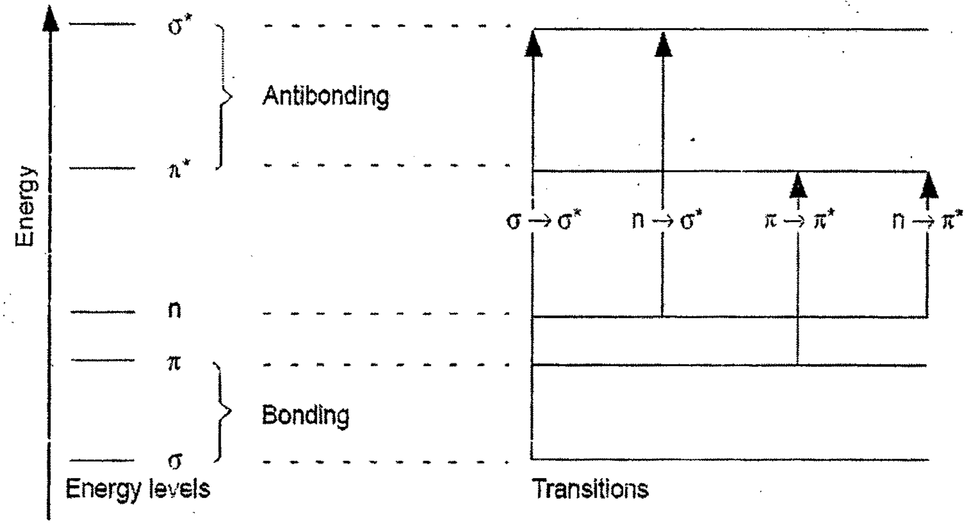


Figure 2.3 Different molecular orbital transitions

Instrumentation

The minimum requirements of an instrument to study absorption spectra (spectrophotometer) are shown in **Figure 2.4**.

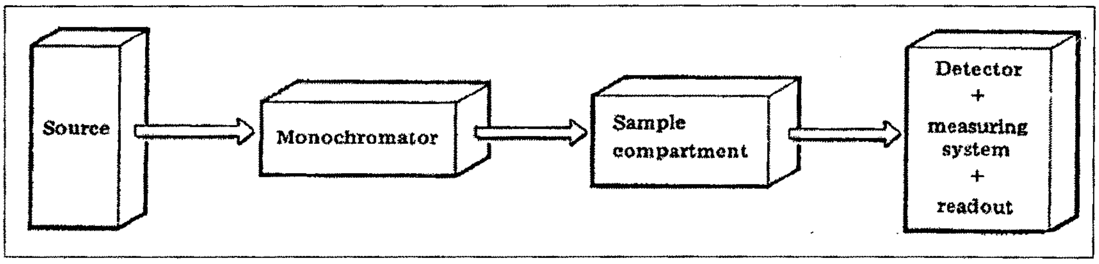


Figure 2.4 Essential elements of UV-Vis Spectrophotometer

1. A source of radiation of appropriate wavelengths.
2. A means of isolating light of a single wavelength and getting it to the sample compartment -monochromator and optical geometry.
3. A means of introducing the test sample into the light beam - sample handling.
4. A means of detecting and measuring the light intensity.

Source

Source should be stable during the measurement period, i.e. that the intensity of emitted radiation should not fluctuate, and that there should be enough intensity over large wavelength region. No single lamp provides radiation across the whole of the range required, so two are used. Ultraviolet light is generally derived from a deuterium arc that provides emission of high intensity and visible light is normally supplied by a tungsten lamp or tungsten-halogen lamp. Recently, xenon lamp sources have been introduced, and these cover the UV and visible range.

Monochromator

The function of a monochromator is to produce a beam of monochromatic (single wavelength) radiation that can be selected from a wide range of wavelengths. The radiation is separated according to its frequency/wavelength by a monochromator followed by a narrow slit. The slit ensures that the radiation is of a very narrow waveband i.e. it is monochromatic. Two basic methods of wavelength selection may be noted, filters and a dispersing system (e.g. a prism or diffraction grating).

Detectors

Detection of the radiation passing through the sample or reference cell can be achieved by detectors. The four principal types of detectors found in spectrophotometers are the photoconductive cell, the photomultiplier, the silicon diode and the diode array. A photomultiplier or a photodiode converts photons of radiation into tiny electrical currents and a semiconducting cell emits electrons when radiation is incident on it.

Measuring Systems

A spectrophotometer ends with the provision of a signal (normally an electrical voltage) that is proportional to the absorption by a sample at a given wavelength. The signal handling and measuring systems can be as simple as an amplifier and a meter or as elaborate as a personal computer and printer, depending on the application.

Traditionally, the preferred technique was double-beam geometry in the sample handling area (**Figure 2.5**). Double-beam operation is achieved by a time-sharing system in which the light path is directed (by rotating sectional mirror or similar device) alternately through the sample and the reference cell. Modern instruments are self-calibrating, though the accuracy of the calibration can be checked if necessary. Wavelength checks are made by passing the sample beam through glass samples (containing holmium oxide) that have precise absorption peaks, and the absorption is calibrated by passing the sample beam through either a series of filters, each with a specific and known absorption, or a series of standard solutions.

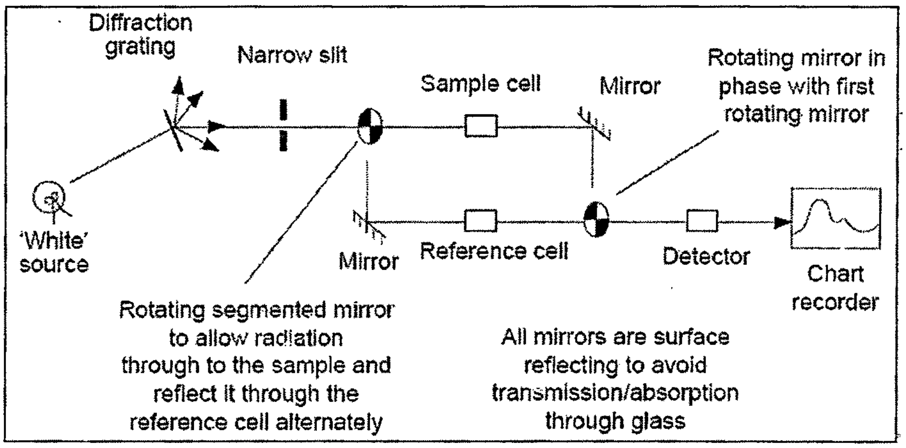


Figure 2.5 Schematic Diagram of UV-Vis Spectrophotometer

Beer-Lambert law

The method is most often used in a quantitative way to determine concentrations of an absorbing species, using the Beer-Lambert law [19]:

$$A = \log_{10}(I_0/I) = \epsilon . c . L$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the path length through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptivity or extinction coefficient. In the range of wavelengths where a sharp increase of absorption appears in the substance, the Tauc relation for dependence of absorbance on wavelength or light photon energy applies [20].

The absorption (A) and transmission (T) of samples were carried out by UV-Vis spectrometer. The absorption coefficient was determined from the UV-Vis spectra using the formula:

$$\alpha = A/d \qquad \ldots(2)$$

Where A is the absorbance and d is the thickness of the film. When a band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [21, 22].

$$\alpha h\nu = B\left(h\nu - E_g\right)^x \qquad \ldots (3)$$

Where α is the absorption coefficient of the substance, E_g is the substance optical gap, h is plank's constant, ν is a corresponding frequency x is the parameter that gives the type of electron transition and factor B depends on the transition probability and can be assumed to be constant within the optical frequency range [23]. The band gap (E_g) depends on many parameters, e.g. on crystalline materials, on their anisotropy, temperature, pressure, on effect of external electric and magnetic forces [24]. As explained Tauc [25], approximate absorption edges and optical activation energies can be calculated from the absorption spectra using equation (3).

The study of optical absorption gives information about the band structure of solids. Insulators/semiconductors are generally classified into two types: (1) direct band gap and (2) indirect band gap. In direct band gap semiconductors, the top of the valence band and the bottom of the conduction band both lie at the same position, zero crystal momentum (wave vector). If the bottom of the conduction band does not correspond to zero crystal momentum, then it is called an indirect band gap semiconductor. In indirect band gap materials, transition from valence to conduction band should always be associated with absorption of a phonon of the right magnitude of crystal momentum [26].

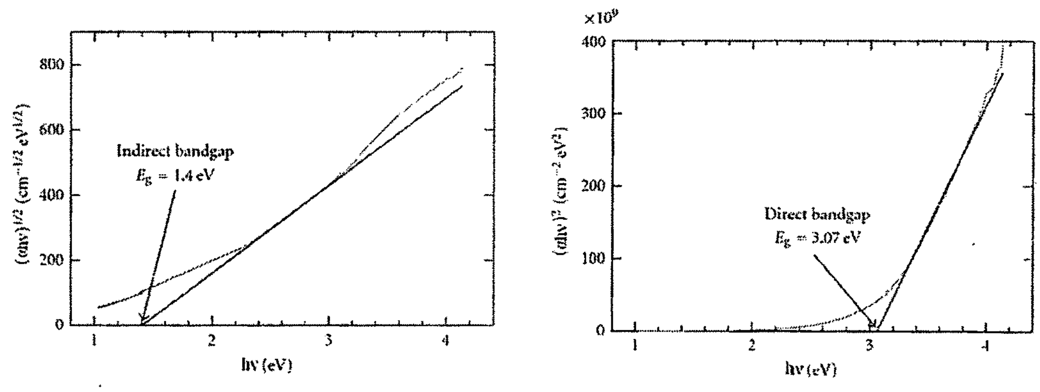


Figure 2.6 **Tauc's plot of Indirect and Direct energy band gap**

Optical absorption studies on pure and doped films were carried out to determine the optical constants such as optical band gap (E_g) and the position of the fundamental band edge. According to Shahada *et al* [27], it was observed that two distinct linear relations were found, corresponding to different inter band absorption processes. The lower energy range of $x = 2$ is typical of an indirect allowed transition. The indirect optical energy gap can be obtained from the plot of $(\alpha h v)^{1/2}$ versus hv, while the direct energy gap, $x = 1/2$, can be obtained from the plot of $(\alpha h v)^2$ versus hv, is believed to be appropriate for the higher energy absorption (use equation 3). The intercept on the energy axis on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of the band gap as shown in **Figure 2.6.**

2.4.3. RAMAN Spectroscopy

Introduction

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light. Raman spectroscopy [28-33] provides the ability to study the interactions of the vibrational and rotational energies of atoms or groups of atoms within molecules. The excitation energy causes a change in the induced dipole moment, or polarisability, of the molecule. Laser sources and the excitation wavelengths for Raman spectroscopy may range from the ultraviolet (UV) to the near infrared (NIR) and the resultant spectral pattern is interpreted similarly to the infrared spectrum of the molecule. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectra result from vibrational motions that cause a change in a source-induced molecular dipole moment. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

The Raman effect is based on molecular deformations in electric field E determined by molecular polarizability, α. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency ν_m. When the polarization in the molecules couples to a vibrational state that is higher in energy than the state they started in, then the original photon and the scattered photon differ in energy by the amount required to vibrationally excite the molecule. The Raman effect corresponds to the absorption and subsequent emission of a photon via an intermediate quantum state of a material.

Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency ν_0 excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (**Figure 2.7**):

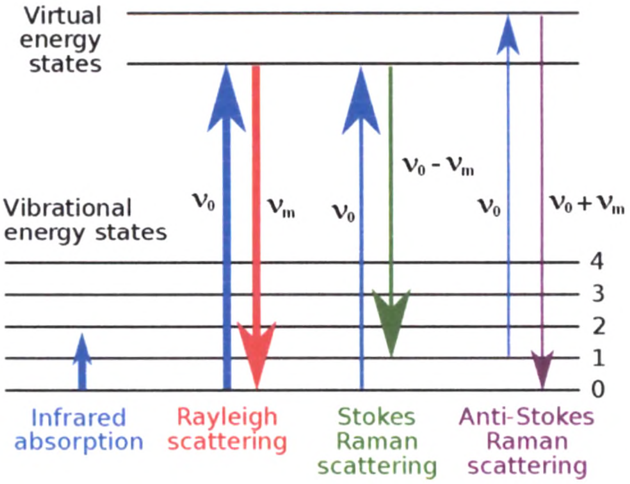


Figure 2.7 Energy level diagram of the states involved in Raman signal.

1. A molecule with no Raman-active modes absorbs a photon with the frequency ν_0. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency ν_0 as an excitation source. This type if interaction is called an elastic **Rayleigh scattering**.

2. A photon with frequency ν_0 is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman-active mode with frequency ν_m and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency, or just "**Stokes**".

3. A photon with frequency ν_0 is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti- Stokes frequency, or just "**Anti-Stokes**".

About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $\nu_0 \pm \nu_m$. Spontaneous Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering. Instruments such as notch filters, tunable filters, laser stop apertures, double and triple spectrometric systems are used to reduce Rayleigh scattering and obtain high-quality Raman spectra.

Instrumentation

A Raman system typically consists of four major components (**Figure 2.8**):

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer). ,
4. Detector (Photodiode array or CCD).

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak the main difficulty of Raman spectroscopy is separating it from the intense Rayleigh scattering. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line. People use commercially available interference (notch) filters which cut-off spectral range of the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency Raman modes in the range below 100 cm^{-1}.

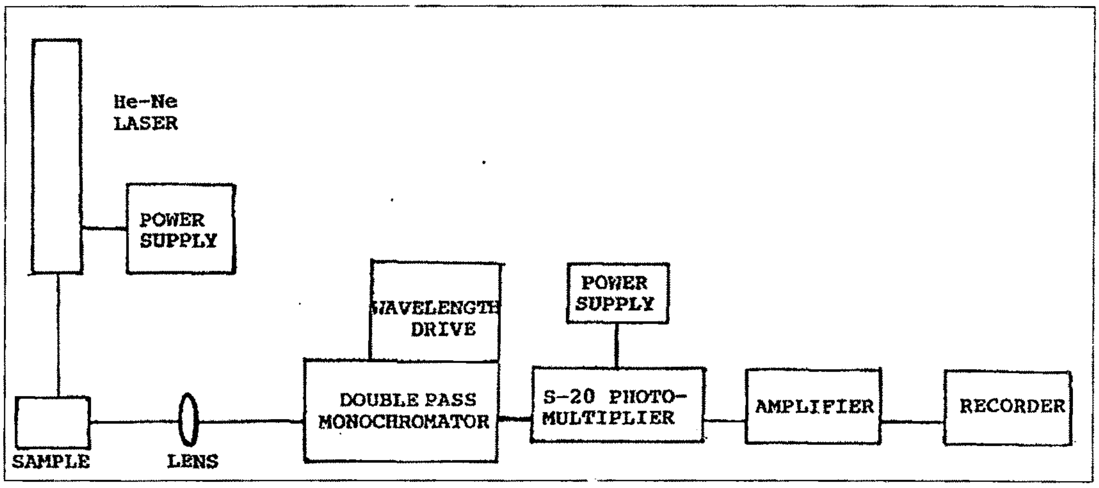


Figure 2.8 Scheme of Raman Spectrometer

Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure than the ruled one. In such systems Raman-active modes with frequencies as low as 3-5 cm^{-1} can be efficiently detected. Nowadays, more and more often researchers use multi-channel detectors like Photodiode Arrays (PDA) or a Charge-Coupled Devices (CCD) to detect the Raman scattered light. In many cases CCD is becoming the detector of choice for Raman spectroscopy.

Ways to improve Raman signal intensity

Raman signal is normally quite weak and people are constantly improving Raman spectroscopy techniques. Many different ways of sample preparation, sample illumination or scattered light detection were invented to enhance intensity of Raman signal. Some of techniques are shown below.

Stimulated Raman (SR)

Coherent Anti-Stokes Raman (CARS)

Resonance Raman (RR)

Surface-Enhanced Raman Spectroscopy (SERS)

Surface-Enhanced Resonance Raman Spectroscopy (SERRS)

2.4.4. Mechanical Testing Facility

The LR30K advanced materials testing machine incorporates an extensive range of features making it ideal for performing complex as well as routine testing applications up to 30 kN.

Lloyd LR30K is a versatile instrument can be used for many types of tests. Possible tests are given below:

1. Load-elongation from zero loads to breaking load
2. Percentage elongation above and below the yield point.
3. Tearing test
4. Compression test
5. Adhesion test etc.

Lloyd Testing machine has the following basic components

- Load frame – It is usually consisting of two strong supports for the machine.
- Load cell - A force transducer or other means of measuring the load is required.
- Cross head - A movable cross head is controlled to move up or down. Usually this is a constant rate of extension. Machines can program the crosshead speed.
- Means of measuring extension or deformation- It is a measure of the response of the test specimen to the movement of the cross head.

- Output device - A means of providing the test result is needed. Machine has a computer interface for analysis and printing.

The specimen is placed in the machine between the grips. It can automatically record the change in gauge length during the test. Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, proportional limit, and reduction in area, tensile strength, yield point, yield strength and other tensile properties. The main product of a tensile test is a load versus elongation curve which is then converted into a stress versus strain curve. A typical engineering stress-strain curve is shown below **Figure 2.9**[34].

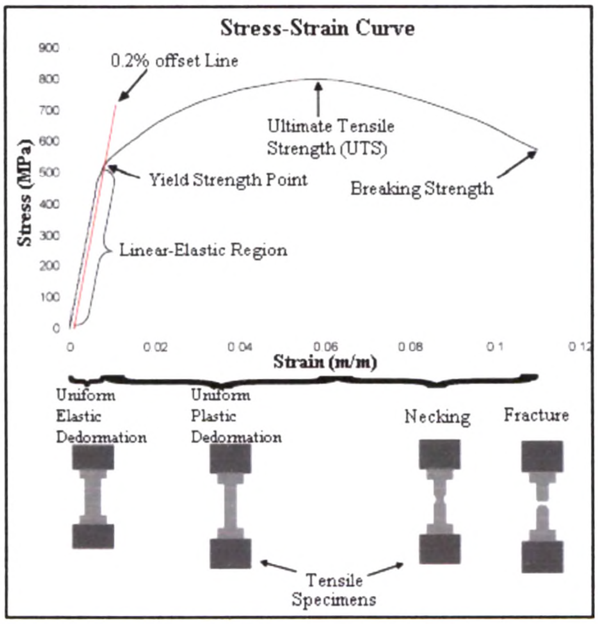


Figure 2.9 A typical stress versus strain curve

The machine itself can record the displacement between its cross heads on which the specimen is held and it gives stress versus strain curve (**Figure 2.9**). And software automatically derived different mechanical properties from that data.

Linear-Elastic Region

As shown in the curve, the stress and strain initially increase with a linear relationship. This is the linear-elastic portion of the curve and it indicates that no plastic deformation has occurred. In this region of the curve, when the stress is reduced, the material will return to its original shape. In this linear region, the line obeys the relationship defined as ***Hooke's Law*** where the ratio of stress to strain is a constant. The slope of the line in this region where stress is proportional to strain is constant and is called the ***Young's modulus***. ***Elastic limit*** is the greatest stress, the material can withstand without any measurable permanent strain remaining on the complete release of load.

Yield Point

At some point, the stress-strain curve deviates from the straight-line relationship. From this point on in the tensile test, some permanent deformation occurs in the specimen and the material is said to react plastically to any further increase in load or stress. The material will not return to its original condition when the load is removed. To determine the yield strength using this offset, the point is found on the strain axis (x-axis) of 0.002, and then a line parallel to the stress-strain line is drawn. This line will intersect the stress-strain line slightly after it begins to curve, and that intersection is defined as the yield strength with a 0.2% offset. Knowledge of the yield point is very crucial when designing a material as it generally represents an upper limit of the load that can be applied to material.

Ultimate Tensile Strength

The ultimate tensile strength (UTS) is the maximum engineering stress level reached in a tension test. The strength of a material is its ability to withstand external forces without breaking.

Breaking load

Load at which specimen breaks is called breaking load. It is expressed in grams weight.

2.4.5. Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimetry (DSC) is a technique in which the heat flow rate difference into a substance and a reference is measured as a function of temperature while the substance and reference are subjected to a controlled temperature program. DSC uses the temperature difference developed between the sample, and a reference for calculation of the heat flow. An exotherm indicates heat flowing out of the sample, while an endotherm indicates heat flowing in.

Two types of DSC systems are commonly in use:

Power-compensation DSC:

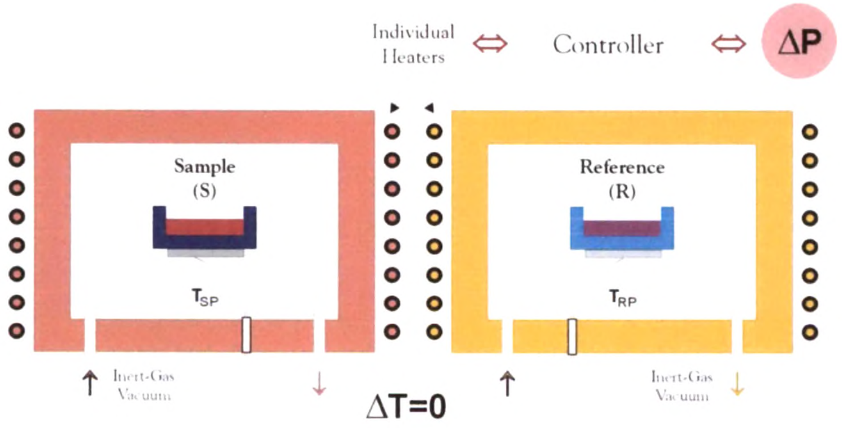


Figure 2.10 Cross section of Power-compensation DSC

In power compensation DSC (**Figure 2.10**), the specimen and reference temperatures are controlled independently using separate furnaces. The temperature difference between the sample and reference is maintained to zero by varying the power input to the two furnaces. This energy is then a measure of the enthalpy or heat capacity changes in the test specimen S relative to the reference R.

Heat-flux DSC:

In Heat flux DSC (**Figure 2.11**), the test specimen S and reference material R (usually an empty sample pan + lid) are enclosed in the same furnace together with a metallic block with high thermal conductivity that ensures a good heat-flow path between S and R. The enthalpy or heat capacity changes in the specimen S lead to temperature differences relative to R. This results in a certain heat-flow between S and R. The temperature difference ΔT between S and R is recorded and further related to the enthalpy change in the specimen using calibration experiments.

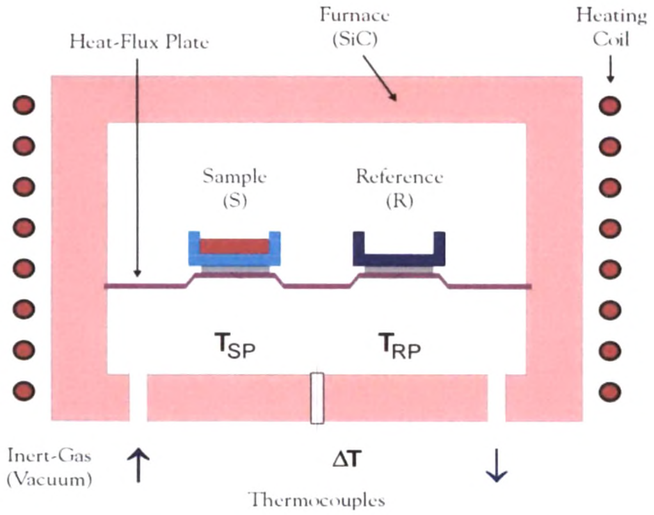


Figure 2.11 Cross section of main components of a typical heat-flux DSC cell.

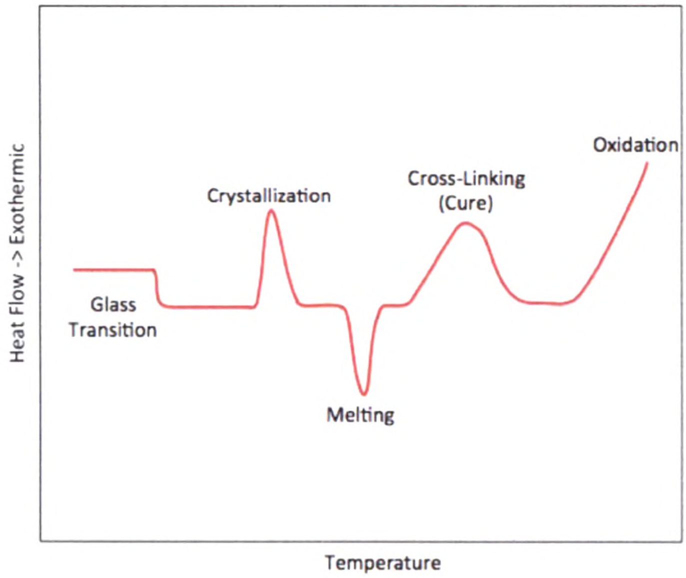


Figure 2.12 A typical DSC curve for polymer

Measuring principle of DSC is to compare the rate of heat flow to the sample and to reference which are heated or cooled at the same rate. Changes in the sample that is associated with absorption or evolution of heat cause a change in the differential heat flow which is then recorded as a peak. The area under the peak is directly proportional to the enthalpic change and its direction indicates whether the thermal event is endothermic or exothermic. The plot heat flow versus temperature (**Figure 2.12**) gives information about glass transition temperature, crystallization, melting temperature, cross-linking and oxidation process of the materials. Glass transition temperature, crystallization and melting temperature are described as below.

Glass Transition Temperature:

When we heat the polymer, after certain temperature, behavior of the graph changed suddenly pointing downward, which indicates endothermic reaction taken place. The glass transition (T_g) is the temperature assigned to a region above which materials are fluid or rubbery and below which they are immobile and rigid [35].

Crystallization Temperature:

When we heated above T_g, at a particular temperature Polymer will have gained enough energy to move into order arrangement called crystalline state. When polymers fall into this state they gives of energy, so we get a peak in DSC heat flow versus temperature plot. *Crystallization* is a process in which polymer from the amorphous state is transformed into the crystalline state from either solution or the melt and at which temperature crystallization occurs is called polymer crystallization temperature T_c [36].

Melting Temperature:

If polymer further heated after T_c, It will reach another thermal transition, called melting. It is the transition from the crystalline state to the melt. Melting is a transition with an increase of disorder of the system. When polymer reached melting temperature T_m, polymer chains come out of their order arrangement and become free to move around [37].

2.4.6. Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) or thermo-gravimetry (TG) is a technique where the mass of a polymer is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere [38]. TGA gives weight loss curve with respect to different temperature.

The basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample, and a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time. Sample is heated under the different gas environment. Basically nitrogen gas is used in TGA.

TGA Instrumentation

The essential components of the TGA instrument, are an analytical microbalance, furnace, temperature programmer, sample holder, an enclosure for establishing the required atmosphere, and a means of recording and displaying the data. Typical arrangements of the components for TGA are shown in the **Figure 2.13**.

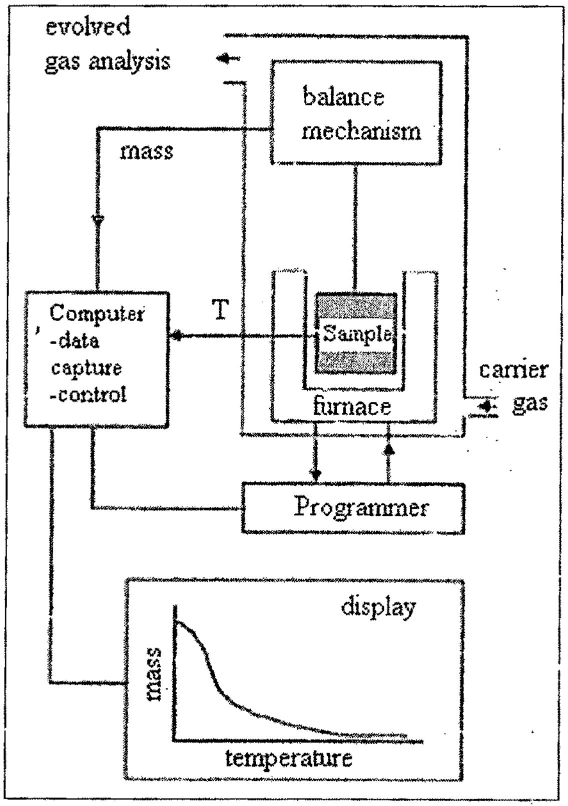


Figure 2.13 Scheme of Thermal gravimetric analysis

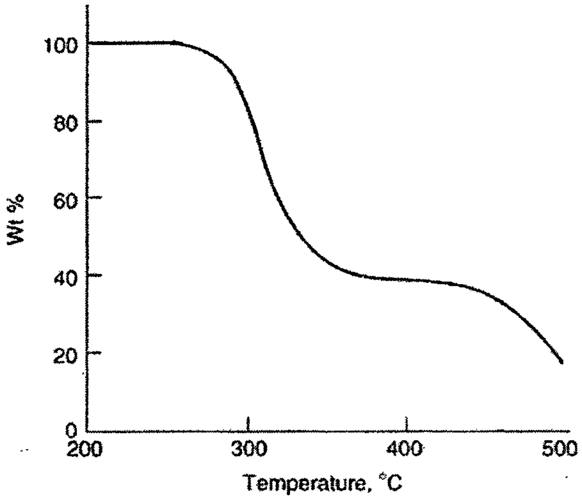


Figure 2.14 **A typical thermal degradation TGA curve**

There are three ways in which a polymer degrades: random scission, systematic chain scission or the combination of two. Random scission along the chain produces radicals or other reactive species. These reactive species continue to break down into progressively smaller species, which become volatile and are lost or they may attack other polymer chains leading to cross-linked polymers, which are less prone to degradation and ultimately lead to high temperature residue referred to as a char [39]. A generalized degradation plot of polymer is shown in the **Figure 2.14.**

TGA measurements record only the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking. In TGA measurement one should take care of materials, sample weight and heating rate.

TGA is commonly used to determine characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are (1) materials characterization through analysis of characteristic decomposition patterns, (2) studies of degradation mechanisms and reaction kinetics, (3) determination of organic content in a sample, and (4) determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis.[Wikipedia]

2.4.7. Scanning Electron Microscopy (SEM)

Microscopy is the study of the fine structure and morphology of objects with the use of microscope [40, 41]. Microscopes range from optical microscopes to transmission electron microscopes, which resolve details on micrometer level to nanometer level. In microscopy resolution and contrast are key parameter.

The scanning electron microscope (SEM) is capable of producing high resolution image of sample surface. SEM images have a three dimensional appearance and are useful for judging the surface structure of sample. SEM forms an image by scanning a probe, a focused electron beam, across the specimen [42].

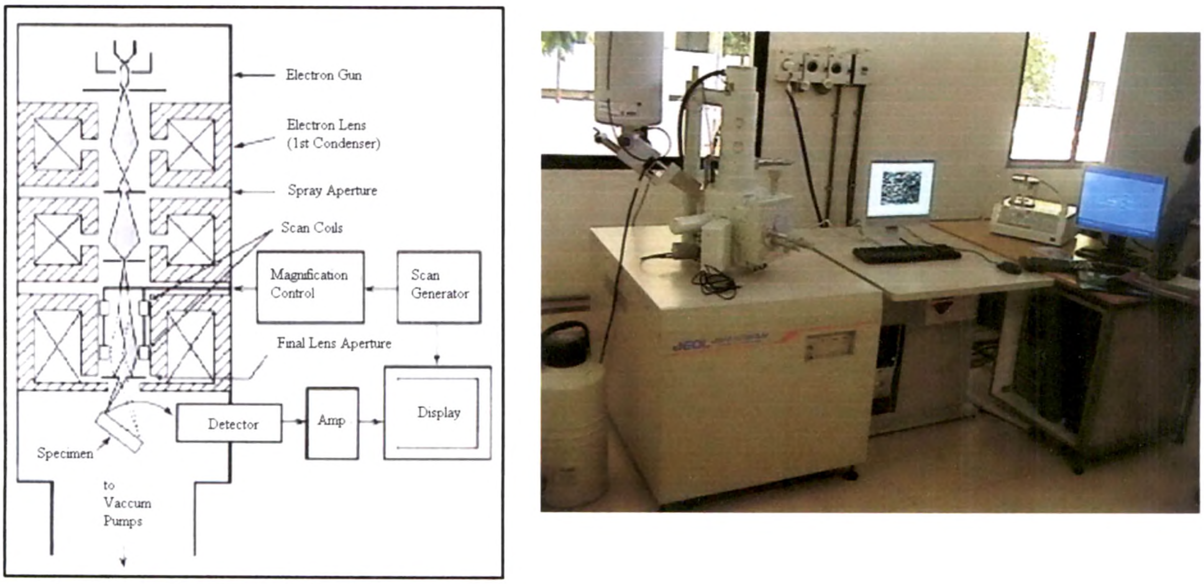


Figure 2.15 Cross section and lab image of Scanning electron microscope

The SEM consists of electron column which containing the lens system, a specimen chamber, detectors as well as imaging and recording units as shown in **Figure 2.15**. Different parts of SEM are described below:

Electron gun: located at the top of the column where free electrons are generated by emission from a tungsten filament.

Condenser lenses: after electron beam passes the anode two condenser lenses converges the beam and make pass through a focal point.

Apertures: the function of apertures is to reduce and exclude extra electrons in the lenses and also to determine the spot size of beam at specimen which is very important to determine resolution and depth of field [43, 44].

Scanning system: images are formed by scanning the electron beam across the specimen using deflection coils inside the objective lens [44].

Specimen chamber: at the end, the specimen stage and controls are located. The secondary electrons from the specimen are attracted to detectors by positive charge.

Modern SEM mostly uses a PC to control the electron beam, to select the signals and to record and store the digital images [45]. Microscope column and the specimen chamber are evacuated using high vacuum pumps at a pressure of at least 5 x 10^{-5} Torr, which is necessary to allowing the beam electrons to travel from the cathode to the specimen with little interaction with the residual gas molecules.

Sample Preparation: As SEM utilizes vacuum conditions, special preparation must be done to the sample. All metal are conductive and require no preparation before being used. While non-metal samples are non conductive so they needs to be made conductive by covering the samples with a thin layer of conductive material. This is done by a using a device called "sputter coater".

Now when electrons are coming from source, they can be controlled by field emission. The probe size is reduced by demagnification of the filament image using two electromagnetic lenses and then focusing onto the specimen surface by using an objective lens. The probe is scanned on the specimen surface by two set of scanning coils, controlled by the same scan generator used to observe the image. The signal is detected by a low noise scintillation-photomultiplier-amplifier system and modulates the display signal. Once the probe is focused and corrected for astigmatism, the magnification can be changed by changing the size of the scanned area without refocusing [46].

2.5. Experiment specification detail

2.5.1. Fourier Transform Infrared Spectroscopy

The FTIR spectra of all polymer blend samples have been recorded on a JASCO- FTIR-4100 Spectrometer. between 4000 cm^{-1} and 600 cm^{-1} in the ATR mode.

2.5.2. UV-Vis Spectroscopy

The absorption spectra and transmission spectra of samples were taken in the range of 200-800 nm using Perkin-Elmer Lambda 25 UV-VIS spectrophotometer.

2.5.3. FT-RAMAN Spectroscopy

Fourier Transform Raman spectra of pure and blend polymers were obtained with a Bruker RAM II Vertex-70 FTIR spectrometer equipped with FRA106 Raman module. Spectral resolution was 4 cm^{-1}. The samples were excited with λ = 1064 nm by diode laser pumped Nd:YAG solid state laser with maximum output power 150 mW.

2.5.4. Mechanical Analysis

Mechanical properties of all polymer blend samples of PVC/PMMA have been reported in this study. These measurements were made on Lloyds LR30 K instrument with a crosshead speed of 10 mm/min and a gauge length of 10 mm. The measurements were repeated for five times and their mean value is reported here. All testing were carried out at room temperature. Pores or nicks free samples were used for measurements. Access to this instrument was available at Textile Engineering Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara, for this work.

2.5.5. Differential Scanning Calorimeter

For the DSC measurements SII Exstar-6000, operating in dynamic mode (heating rate=10 °C/min) in N_2 gas environment, was employed. Samples in appropriate amount were placed in sealed aluminum pans. Prior to use the calorimeter was calibrated with metal standards; an empty aluminum pan being used as a reference.

2.5.6. Thermal Gravimetric Analysis

Thermo-gravimetric (TG) and DTG measurements were made on EX STAR TGA instrument with heating rate 10°C/min under nitrogen atmosphere. The samples were taken 5–10 mg in an aluminum pan.

2.5.7. Scanning Electron Microscopy

For present work, Scanning Electron Microscopy Model: JEOL make Scanning Electron Microscope, model number JSM 6380LV at ERDA, Vadodara have been used. The working distance (WD, sample distance from objective lens) is varied from 15 mm to 20 mm as per resolution of the images. The spot size is also varied from 30 to 60 nm. The accelerating voltage is fixed at 20 kV and filament current is kept nearly 85 μA to 100 μA to conduct morphological analysis. Inside the SEM chamber, the vacuum is created less than 10^{-7} torrs (within 5 minutes) for minimizing impurities and viewing the sharp surfaces of the sample. The magnifications of the images are varied as per the image clarity.

2.6. References

1. W. V. Titow. PVC technology. Springer. pp. 6–. ISBN 978-0-85334-249-6, 31st December 1984.
2. Chanda, Manas; Roy, Salil K. Plastics technology handbook. CRC Press. pp. 1–6. ISBN 978-0-8493-7039-7, 2006.
3. Joel R. Fried, Polymer Science and Technology, Prentice hall of India Private Limited, New Delhi, 2000.
4. V. R. Govariker, N. V. Viswanathan and Jaydev Sreedher, Polymer Science, New age International (P) Ltd., Publishers Edition 1, 1996.
5. Lopatin VV, Askadskii AA, Peregudov AS, Vasilev VG, J Appl Polym Sci 96:1043–1058, 2005.
6. Durmaz S, Okay O, Polym Bull 46:409–418, 2001.
7. Chan LW, Hao JS, Heng PWS, Chem Pharm Bull 47(10):1412–1416, 1999.
8. Morita, R., R. Honda and Y. Takahashi, Journal of Controlled Release, 90(1): 109-117, 2000.
9. Gutzler R, Smulders M, Lange RFM. Macromol Symp 225:81–93, 2005.
10. Smolinske, Susan C. Handbook of Food, Drug, and Cosmetic Excipients. Boca Raton: CRC Press. p. 287. ISBN 0-8493-3585-X, 1992.
11. B. P. Straughan and S. Walker, editors, Spectroscopy, volume 2, John Wiley and Sons, 1976.
12. A. H. Fawcett, editor, Polymer spectroscopy, John Wiley and Sons, 1996.
13. D. L. Pavia, G. M. Lampman and J. George S. Kriz, "Introduction to Spectroscopy", W.B Saunders Company, p.13, 1979.