

Importance of Characterisation Techniques in Applied Material

Deepali Maidh¹ and Bashir Ahmed²

¹Research Scholar JJT University Jhunjhunu, Rajasthan

²Department of Physics, Govt. Degree College Rajouri (J&K)-185131

E-mail: ¹drbashirmed90@gmail.com, ²dgbmaidh786@gmail.com

Abstract—With the growing interest in the field of space science, the study of the constituents of space and effect of space radiation on the structural materials and electronic components of space ships, has assumed a great importance. Radiation damage to structural materials in nuclear technology is already a significant factor in assessing the economic viability of the breeder reactor in it promises to play an even more significant role in the space technology. Polymer is one of the important classes of space materials in addition of various metals, alloys and ceramics. On account of successful developments in the physics and chemistry of polymers during last three decades, they have achieved the highest production status as compared to conventional materials like metals and ceramics etc. In addition to this, their economical superiority, vast spectra of physical properties, wide nature of mechanical parameters, flexibility, lightness, optical transparency, easy processing etc. also help polymer industry in highest growth rate among others.

As space material, they are analysed by using the various techniques like XRD, UV-VIS Spectroscopy, FTIR SEM, IR Electrical analysis, Magnetic Resonance etc.

Keywords: Techniques: Magnetic Resonance, XRD, UV-VIS Spectroscopy, FTIR SEM, IR, Electrical analysis.

1. INTRODUCTION

The smart materials such as metals, semiconductors, organic and inorganic particles, fiber, ceramics etc. Polymer has the advantage over the other conventional materials due to due to lightness, resistance to corrosion, low-cost production, and ease of processing. Further, improvement of their performance is intensely investigated. Polymers have existed in nature since life began in the form such as DNA, RNA and proteins, which play crucial roles in plants and animals life. From the early times, man has exploited naturally occurring polymers and used them as clothing, decoration, shelter, tools, weapons, writing materials, etc. However, the origin of today's polymer industry actually took place in the nineteenth century when important discoveries were made concerning the modifications of certain natural polymers.

The ancient Mayan civilization in Central America towards the end of 15th century for the first time used polymers as their children were found playing with balls made of rubber

extracted from local trees. In 1820, Thomas Hancock discovered that when masticated (i.e. subjected repeatedly to high shear forces); natural rubber behaves more like fluids making it easier to blend with additives and to mould. In 1839, Charles Goodyear discovered vulcanization by combining natural rubber with sulfur when heated them to 270°Fahrenheit. Vulcanized rubber is a polymeric substance and is much more durable than its natural counterpart. Its most common use today is in automobile tires. Cellulose nitrate, also called nitrocellulose or gun cotton was first used by Kodak as a film base in photography became prominent after Christian Schonbein prepared it in 1846. He was quick to recognize the commercial value of the material as an explosive, and within a year gun cotton was manufactured. However, more development of the polymer industry took place when cellulose nitrate was found to be a hard elastic material soluble in organic solvents and could be moulded into different shapes by the application of heat and pressure. Alexander Parke was the first person to take advantage of this combination of properties and in 1862 he exhibited articles made from parkesine, a form of plasticized cellulose nitrate. In 1870, John and Isaiah Hyatt patented a similar but more easily processed material, named celluloid, which was prepared by using camphor as plasticizer. Unlike Parkesine, celluloid was a great commercial success. In 1892, Charles Cross, Edward Bevan and Clayton Beadle patented the 'viscose' processes for dissolving and then regenerating cellulose. The process was first used to produce viscose rayon textile fibers, and subsequently for production of cellophane film. The polymeric materials described so far are semisynthetic in nature since they were produced from natural polymers.

In 1907, the oldest recorded synthetic plastic was fabricated by Leo Bakeland. Bakelite's hardness and high heat resistivity made it an excellent choice as an electrical insulator. Leo Bakeland's Bakelite phenol-formaldehyde resins have the distinction of being the first fully-synthetic polymers to be commercialized, their production began in 1910. The first synthetic rubber to be manufactured, known as methyl rubber, was produced from 2, 3-dimethylbutadiene in Germany during World War I as a substitute, albeit a poor one, for natural

rubber. In 1913, X-ray crystallography was used as a method of analysing crystal structures of a polymer. Eight years later, this method was used by M. Polanyi to discover the chemical structure of cellulose. This established the fact that polymer unit cells contain sections of long chain molecules rather than small molecular species.

Although the polymer industry was formally established, its growth was restricted due to lack of understanding the molecular nature of polymers. For over a century, this remained inconclusive. However, in 1920 Hermann Staudinger proposed that polymers are composed of very large molecules containing long sequences of simple chemical units linked together by covalent bonds. Staudinger introduced the word 'macro-molecule' to describe polymers. He carried out the synthesis and studied structure and properties of polyoxymethylene and polystyrene, the results obtained from which left little doubt about the validity of macromolecular viewpoint. Staudinger's hypothesis was further substantiated by the crystallographic studies of natural polymers reported by Herman Mark and Kurt Meyer, and by the classic work of Wallace Carothers on the preparation of polyamides and polyesters.

In 1956, German Karl Ziegler for the first time discovered the titanium-based catalysts, which was used by Italian Giulio Natta to prepare stereo regular polymers from propylene. For that work they were jointly awarded the Nobel Prize in Chemistry in 1963. Ziegler-Natta catalysts have been used in the commercial manufacture of various polyolefin since its discovery. The theoretical and experimental work of Paul Flory was famous in this period, and for his long and substantial contribution to Polymer Science he was awarded the Nobel Prize in Chemistry in 1974. As the science of macromolecules emerged, a large number of synthetic polymers went into commercial production for the first time. These include polystyrene, poly (methyl methacrylate), nylon 6.6, polyethylene, poly (vinyl chloride), styrene-butadiene rubber, silicones, polytetrafluoroethylene as well as many others. Several important terms and concepts must be understood in order to discuss fully the synthesis, characterization, structure and properties of polymers.

2. ANALYTICAL TECHNIQUES

Analytical techniques are used for the identification of the materials either qualitatively or quantitatively. The former relates just to the identity of the material, while the latter requires the precise determination of amounts, quantities, and percent compositions by weight. Characterization, when used in materials science, refers to the use of external techniques to probe into the internal structure and properties of a material.

The different techniques that are used to characterized the smart materials with detail discussion. The techniques used for the characterization of the samples are UV/VIS, FTIR, Powder XRD, High Frequency Impedance Analyzer (HFIA) and SEM.

2.1 UV/VIS Spectroscopy

Spectroscopy is the technique of producing spectra, analyzing their constituent wavelengths, and using them for chemical analysis or the determination of the energy levels and molecular structure.

Ultraviolet-visible spectroscopy (UV-VIS) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region as shown in Fig. 2.1. This means it uses light in the visible and adjacent [near-UV and near-infrared (NIR)] ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum molecules undergo electronic transition. This technique is complementary to fluorescence spectroscopy, in which fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state[1].

- Violet : 400-420 nm
- Indigo : 420-440 nm
- Blue : 440-490 nm
- Green : 490-570 nm
- Yellow : 570-585 nm
- Orange : 585-620 nm
- Red : 620-780 nm

Ultraviolet and visible spectra of the virgin and all the irradiated samples were recorded by JASCO V-530 UV/VIS spectrophotometer, in the wavelength range 190 nm to 900 nm. The photograph of UV/VIS spectrophotometer is shown in Fig. 2.2. Films of pristine and irradiated samples were mounted on a black sheet, having a window of area 0.5 X 0.5 cm². All the UV/VIS measurements were carried out by taking air as the reference.

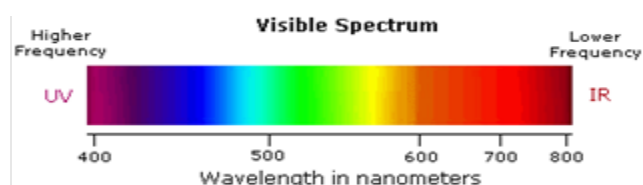


Fig. 2.1: UV/VIS spectrums



Fig. 2.2: UV/VIS spectrophotometer

The UV/VIS absorption spectroscopy is the measurement of the attenuation of a beam of light with wavelength after it passes through a sample or after reflection from a sample surface. The short-wavelength limit for simple UV/VIS spectrometers is 190 nm due to absorption of ultraviolet light of wavelength below 190 nm by the atmospheric gases. The absorbance A, is related to the input and output intensities according to the Beer-Lambert Law [2] given by the equation

$$\frac{I}{I_0} = e^{-A} \dots\dots\dots (2.1)$$

The absorbance A is divided by the path length l, to yield the absorption coefficient [3] α which qualifies the absorbance per meter. Thus taking the film thickness into account one can write

$$\alpha(\lambda) = 2.303 \frac{A}{l} \dots\dots\dots (2.2)$$

The absorption of UV or visible radiation corresponds to the excitation of outer electrons.

When an atom or molecule absorbs energy, electrons move from the ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on the top of each electronic energy level as shown in Fig. 2.3. Absorbance of ultraviolet and visible radiations in molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy. The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band. The various possible electronic transitions in organic molecules are shown in Fig. 2.3.

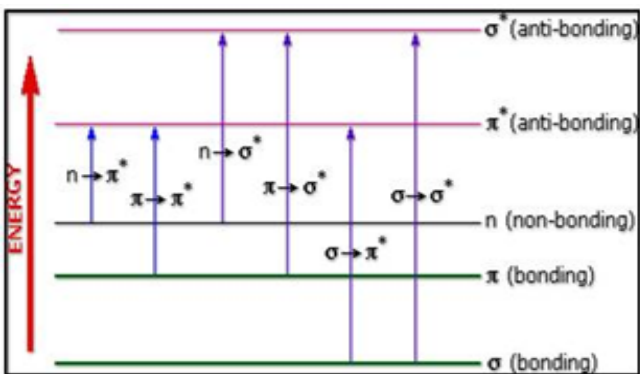


Fig. 2.3: Energy level diagram for different electronic transitions.

The n – σ* transition requires lesser energy and hence transitions of this type appear at longer wavelength.

These transitions are of interest in the study of gamma induced optical modification in polymers. Irradiation of polymer

samples results in the shifting of absorption edge from UV towards the visible region.

This shift can be correlated with the optical band gap (E_g) using Tauc's expression [3].

$$\omega^2 \epsilon_2(\lambda) = (\hbar \omega - E_g)^2 \dots\dots\dots (2.3)$$

where ε₂(λ) is the imaginary part of complex refractive index, i.e. the optical absorbance and λ is the wavelength.

$\sqrt{\epsilon_2}/\lambda$ The intersection of the extrapolated spectrum with the abscissa of the plot versus 1/λ yields the gap with wavelength λ_g from which the energy gap is obtained.

$$E_g = hc/\lambda_g \dots\dots\dots (2.4)$$

2.2 Powder X-Ray Diffraction

For X-ray Diffraction, only short wavelength X-rays in the range of a few angstrom to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of the X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials [5-7]. An X-ray tube generates X-rays by focusing an electron beam that has been accelerated across a high voltage field and bombarded to the stationary/rotating metal target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which is termed as Bremsstrahlung radiation. The high energy electrons also eject inner shell electrons in atoms through the ionization process. When an electron from the outer shell fills the vacancy in the inner shell, an X-ray photon with energy characteristic to the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV with corresponding wavelength of 1.54 Å and 0.8 Å, respectively. A Panalytical (PW 1830) X-ray powder diffractometer containing Cu target is shown in the Fig. 2.2.1. This provides us the X-rays of wavelength 1.54 Å.

2.3 Fourier Transform-Infra Red (FTIR) Spectroscopy

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a irradiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a different types of spectroscopy including optical spectroscopy, infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and magnetic resonance spectroscopic imaging (MRSI) and electron spin resonance (ESR) spectroscopy[9]. There are methods for measuring the temporal coherence of light including the continuous wave. For example Fourier transform spectrometer and the pulsed Fourier transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques, but is only applicable in a laboratory environment).

The term Fourier transform spectroscopy reflects the fact that in all these techniques, a Fourier transform is required to turn the raw data into the actual spectrum. In many cases, the optics involving interferometers are based on the Wiener-Khinchin theorem.

FTIR spectra of the pristine and all the irradiated samples were recorded using Perkin Elmer FTIR spectrophotometer in the range 400 cm^{-1} to 4000 cm^{-1} . The scanning rate was $2\text{ cm}^{-1}\text{ s}^{-1}$ with an average of 21 scans per sample. The infrared double beam spectrophotometer instrument plots intensities (as percent transmission) versus wave number (wavelength). The spectrum of air is also taken as reference spectrum for all spectra of polymer samples. The irradiated samples were cut as per holder size. The photograph of FTIR spectrophotometer is shown in Fig. 2 3.1.



Fig. 2.3.1: Photograph of FTIR Spectrophotometer

Infra-red spectroscopy is particularly applicable to the study of orientation in polymers.

Infra-red absorbance is due to the interaction between the electric field vector and the molecule dipole transition moments due to molecular vibrations. The absorbance is at a maximum when the electric field vector and the transition moments are parallel to each other, and zero when they are perpendicular. The orientation of molecular components can be characterized by using the dichroic ratio which is defined as A_b/A_p , where A_b is the absorbance parallel to the chain axis and A_p is the absorbance along perpendicular direction [10, 11]. Different alignment of the molecules results in the change of intensity of a number of infra-red modes and therefore acts as an indicator of crystallinity. The inter atomic bonds may vibrate in several different modes (stretching or bending), where individual bond may absorb more than one IR frequency. Stretching absorptions usually produce stronger peaks than bending, however the weaker bending absorptions can be useful in differentiating similar type of bonds (e.g. aromatic substitution). It is also important to note that symmetrical vibrations do not cause absorption of IR radiation. In general, the important factors where a chemical

bond will absorb the radiation or not are determined by the bond order and by the type of atoms joined by the bonds. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore, the same or similar functional group in different molecules will typically absorb within the same and specific frequency range. Hooke's law states that the IR frequency at which a chemical bond absorbs is inversely proportional to the square root of the reduced mass of the bonded atoms.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad (2.7)$$

where,

ν = frequency in cm^{-1}

μ = reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$, m_1 and m_2 are the atomic masses.

K = force constant (bond-order) e.g. single, double or triple.

A more useful quantity for the quantitative work is the absorbance (A) or optical density, given by

$$\text{Absorbance} = -\log(\text{percent transmittance}/100) \quad (2.8)$$

Where, $I_{\text{out}} / I_{\text{in}} = T$ (Transmittance)

Further, in the % form we can write

$$A = \log_{10} \frac{100}{\%T}$$

$$A = \log_{10} 100 - \log_{10} \%T$$

$$A = 2 - \log_{10} \%T \dots \quad (2.9)$$

The transmission data is converted to absorbance data using equation (2.7)

2.4 High Performance Impedance Analyzer (Electrical Response)

An Impedance Analyzer Interface provides all of the functions offered by an LCR active head but with a wider frequency and impedance measurement range plus higher nominal accuracy. This is achieved by a more sophisticated design that includes an additional internal shunt range, a current amplifier to increase low impedance signal levels and calibration together with the PSM1735 with which it will be used.

PSM1735 NumetriQ is the latest addition to the N4L range of phase sensitive millimeters, providing engineers with an exceptionally versatile measuring instrument. Utilizing an innovative design that incorporates both direct digital analysis and heterodyning techniques, the PSM1735 provides a broad range of measurement functions over a wider frequency range than any other instrument available today.

The features of this system have high performance dielectric, conductivity, electrochemical, impedance and gain phase measurements in the frequency domain. It is the latest, most powerful and a flexible system. The system is modular and based on an Alpha-A mainframe unit which usually combined with one or more test interfaces optimized for special functionality. All test interfaces for impedance measurement offer high general purpose performance like highest accuracy and ultra wide impedance and frequency range. This makes the Alpha-A system a unique and easy to use instrument with an exceptional overall performance suitable in many special requirements like 4 electrode high impedance, high voltage, high current measurements and potentiostat, galvanostat functions for electrochemical impedance spectroscopy EIS. The Alpha-A family covers 18 orders of magnitude impedance range (16 orders for each impedance test interface), 12.5 orders of magnitude frequency range and 2m° basic phase accuracy. This combination makes the Alpha-A High Performance Frequency system, a powerful tool which sets the pace for electric frequency domain analysis instrumentation. As a result, permittivity, conductivity and impedance of nearly all materials or components including special functions can be measured throughout the broadband and over a wide temperature range without changing sample geometry or sample cells.



Fig. 2.4.1: The Photograph of High Frequency Impedance Analyzer (HFIA)

2.5 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with

the atoms of the sample, producing signals which contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The first SEM image was obtained by Max Knoll in 1935 of silicon steel showing electron channeling contrast [12]. Further pioneering work on the physical principles of the SEM and beam specimen interactions was performed by Manfred von Ardenne in 1937[13, 14] who produced a British patent [15] but never made a practical instrument. The SEM was further developed by Professor Sir Charles Oatley and his postgraduate student Gary Stewart and first marketed in 1965 by the Cambridge Scientific Instrument Company as the "Stereoscan". The first instrument was delivered to DuPont.

The Scanning Electron Microscope (SEM) is one of the most versatile and widely used tool of modern science as it allows the study of both morphology and composition of a large range of materials.

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Different signals are used by the corresponding detectors for image formation:

Secondary electrons: image of the surface and topography.

Backscattered electrons: contrast arising from the average atomic number.

X-rays with energies characteristic of the atoms in the specimen: qualitative and quantitative information about the elemental composition. Thus detailed maps of elemental

distribution can be produced from multi-phase materials or complex materials.

In scanning electron microscopy (SEM) an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. The three signals which provide the maximum information in SEM are the secondary electrons, backscattered electrons, and X-rays. Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology. A high resolution image can be obtained because of the small diameter of the primary electron beam. Backscattered electrons are primary beam electrons which are reflected from atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are emitted from a depth in the sample, the resolution in the image is not as good as obtained from secondary electrons. Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The emitted X-ray has an energy characteristic to the parent element.

images. The beam of electrons is produced by heating the filament at the top of the microscope assembly shown in Fig.2.5.2

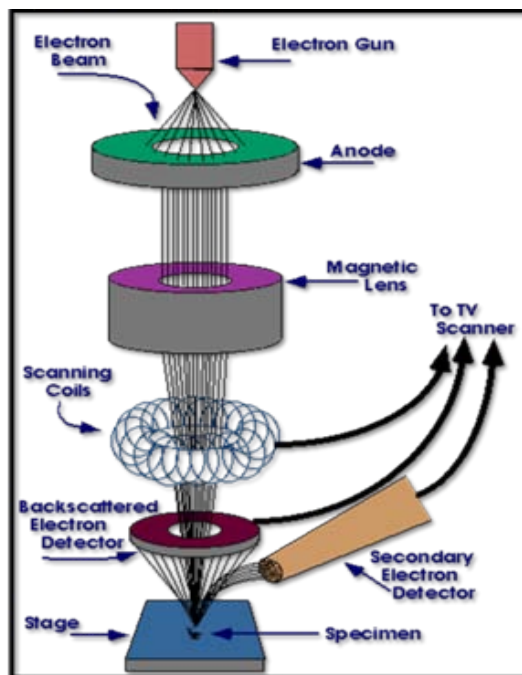


Fig. 2.5.1: Schematic diagram of the main frame of SEM

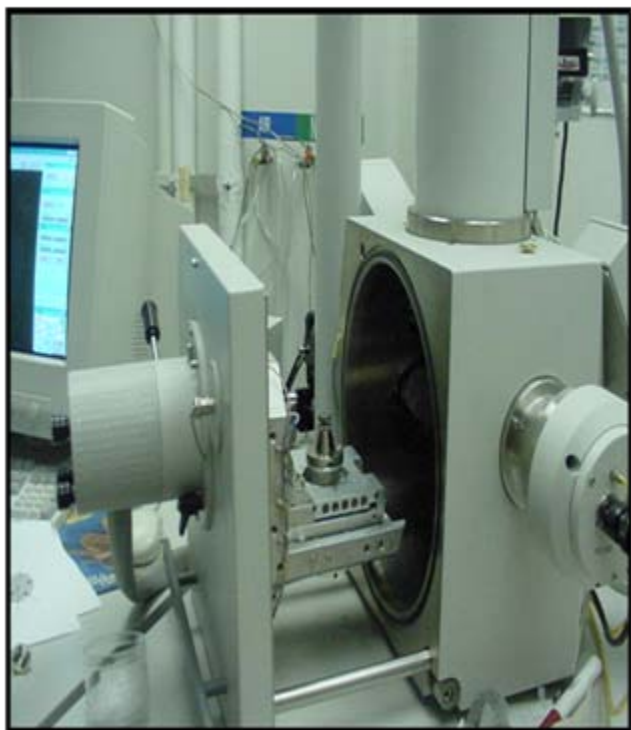


Fig. 2.5.2: SEM opened sample chamber

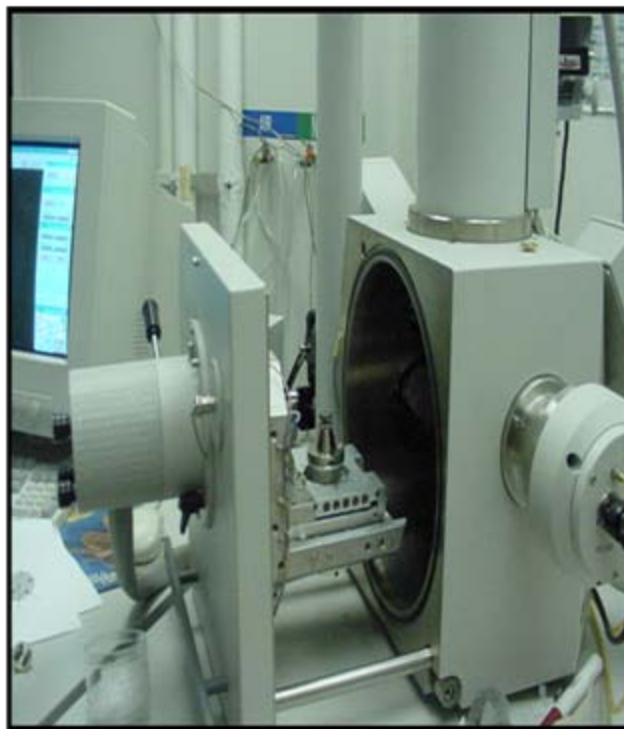


Fig. 2.5.2: SEM opened sample chamber

In the present work, the morphology and the structure of the sample have been characterized with the help of JEOL (Model No. 3300) SEM. An electron beam is used to produce SEM

The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. By using electromagnets one can have more control over the magnification. Once the electron beam hits the sample, other electrons (like backscattered or secondary electrons) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them into a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.

3. CONCLUSIONS

Smart materials have been analysed by using the different analytical techniques to characterize the materials with detail discussion. The techniques used for the characterization of the samples are UV/VIS, FTIR, Powder XRD, High Frequency Impedance Analyzer (HFIA) and SEM. The following conclusions have been drawn:

- UV-VIS spectroscopy gives Surface Plasmon of the materials before and after enhancement in the properties of the materials.
- X-Ray diffraction is used to display the structure of the materials.
- IR transmittance and Raman spectral analysis confirm the formation of conjugated structure between the functional groups.
- An Impedance Analyzer Interface provides all of the functions offered by an LCR active head but with a wider frequency and impedance measurement range plus higher nominal accuracy. The features of this system have high performance dielectric, conductivity, electrochemical, impedance and gain phase measurements in the frequency domain
- The SEM images reveal drastic influence of AgNO_3 content on the structural morphology of PVP films. A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms of the sample, producing signals

which contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

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