

CHAPTER 2

MATERIALS PREPARATION AND CHARACTERIZATION METHODS

In this chapter a detailed outline about the materials prepared for various experiments and the details of the characterization techniques throughout the work are dealt with.

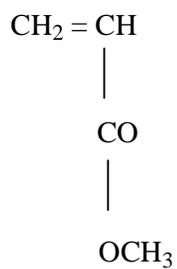
2.1 Purification of Chemicals

Peroxodisulphate

Potassium Peroxodisulphate (PDS), (E-Merck, Germany) was twice recrystallised in distilled water and its purity was found to be 99.8% by the iodometry assay. A stock solution was prepared daily and estimated by iodometry. [1] .

Monomers

Methyl acrylate(MA) monomer was a commercially available sample (E-Merck, India) from which the stabilizer (hydroquinone) was removed immediately prior to polymerization by successive washings with a dilute sodium hydroxide solution, water, and a saturated sodium chloride solution, drying with anhydrous sodium sulfate, and molecular sieves, following which it was Vacuum distilled and stored under oxygen-free nitrogen. Gas liquid chromatographic analysis showed the resulting purity to be in excess of 99.0 %. The structure of MA is shown below



Methyl methacrylate (MMA) monomer was a commercially available sample (E-Merck, India) from which the stabilizer (hydroquinone) was removed immediately prior to polymerization by successive washings with a dilute sodium hydroxide solution, water, and a saturated sodium chloride solution, drying with anhydrous sodium sulfate, and molecular sieves, following which it was Vacuum distilled and stored under oxygen-free nitrogen. Gas liquid chromatographic analysis showed the resulting purity to be in excess of 99.0 %.

Water

This was first deionised by using Ion Exchange India Limited deionizer plant and then this was distilled over alkaline permanganate in an all glass unit. This water was used for the preparation of all the reagents and solutions.

Other Reagents

Sulphuric acid, sodium hydroxide, sodium thiosulphate, starch, potassium iodide, potassium bromide and potassium bromate were from mostly Analar quality samples available in the market and used without further purification. (E.Merck, India). They were diluted in water to get the required strength. Winkler's solution (11.16 g of KBrO_3 and 80 g of KBr) was prepared and this solution had strength of 0.2M.

2.2 Low Power Ultrasonic Interferometer

The ultrasonic interferometer consists of two parts: (i) the high frequency generator and (ii) the reaction vessel.

The high frequency generator is designed to excite the quartz plate fixed at the bottom of a cylindrical reaction vessel at its resonant frequency (1Mhz) to generate ultrasonic waves of this known frequency (1Mhz) are applied at the bottom of the vessel.

The vessel is a specially designed double walled one for maintaining the temperature of the reaction solution taken in the cell as constant during the

experiment. The vessel has a total capacity of 12ml and it has a quartz plate fixed at its bottom. The manufacturer M/s. Mittal Enterprises, New Delhi, India, supplied this.

The temperature effect can be studied when water at various desired constant temperatures is made to circulate through the double walled jacket of the vessel. The nipples are provided at the long portion of the vessel for circulating water around the experimental solution.

The salient feature of the instrument is that experiments can be performed over a wide range of the temperatures from -30°C to $+80^{\circ}\text{C}$

On all liquids except those which react with the plating of the cell bottom and crystal. There is no danger of any change, such as depolymerization, due to the ultrasonic effect since a very small ultrasonic energy was used ($5.5\text{mW}/\text{cm}^2$). The intensity was measured and found as $5.5\text{mW}/\text{cm}^2$.

2.3 High Power Ultrasonic Water Bath

The ultrasonic water bath, is a rectangular metallic tub of capacity 5 liter is filled with water to three-fourth of its total capacity which gives out ultrasonic waves from the two transducers kept at the bottom of the vessel of fixed frequency 35 kHz which can be varied for various powers starting from $20\text{W}/\text{cm}^2$ to $140\text{W}/\text{cm}^2$ in steps of $20\text{W}/\text{cm}^2$. The ultrasound generated passes through the water bath and this can be used as a source of ultrasound. This is supplied by Elma, Germany, and the model is T490DH. A frequency of 35 kHz and a power of $100\text{W}/\text{cm}^2$ at a constant temperature of 50°C are employed throughout our experiment. This instrument was used to prepare PMA samples.

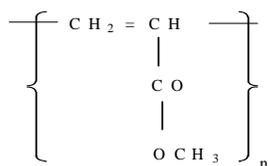
Thermostat

M/s. Toshniwal Brothers, Madras, India, supplied the thermostat used here and has a large rectangular tank (approximately 30-litre capacity of water) equipped with a heater, stirrer and mercury contact thermometer. The temperature of the thermostat was maintained making use of the contact thermometer with an accuracy of $\pm 0.01^{\circ}\text{C}$.

2.4 PMA Sample Prepared using Low Power Ultrasound

A solution of methyl acrylate (MA) and initiator PDS was prepared and then was characterized by bromometry¹⁶ and iodometry after the initial cleaning and purification of the materials and the apparatus. Polymerization was performed in a thermostable, double-walled metallic cell of an ultrasonic interferometer, which could provide ultrasound at a frequency of 1 MHz (with a measured power of 0.7mW/cm²) continuously to the reaction solution. MA (0.1M) was mixed with PDS (0.01M) in a ratio of 8:2 (the total volume was 10 mL) in a thermostable cell, and water was circulated through the outer jacket of the cell with a thermostat maintained at 30°C (with an accuracy of $\pm 0.1^\circ\text{C}$). The total volume of the reaction contents in the cell was 10 mL. Ultrasound of a predetermined frequency and intensity was continuously passed through the solution for a period of 45 min. exactly at the end of 45 min; the reaction mixture was poured into pure methanol for precipitation. After a precipitation interval of 48 h, a semi crystalline, solid, semitransparent, nonconducting polymeric material (PMA) was obtained in the solution. The solid mass was filtered with a 0.45- μm filter and was washed with distilled water and dried under atmospheric air. Only one PMA sample was prepared under a sonication period of 300 minutes at a temperature of 30°C with ultrasound power of 5.5 W/cm² and frequency 1 MHz.

The structural formula for PMA is given below



where 'n' is the Degree of Polymerization.

2.5 PMA samples synthesized using high power Ultrasound

Small Scale Synthesis

Polymerization was carried out by keeping the experiment solution mixture in a 100-mL flat-bottom glass test tube immersed in a (transonic digital ultrasonic) water bath (Elma T 4goDH, Germany). The Ultrasonic water bath, a rectangular

metallic tub (10 h capacity) filled with water to three-fourth of its total capacity, gives out ultrasonic waves of fixed frequency 35 kHz, which can be varied for various powers starting from 20 to 140 W/cm². A frequency of 35 KHz and a power of 100 W/cm² at constant temperature of 50°C were employed throughout the experiment. By performing trial experiments with various powers and keeping the glass test tube at different parts inside the Sonicator bath it was found that at a particular part and at the power of 100 W/cm² the polymer was obtained without any turbulence and precipitation. Methyl acrylate solution of strength 0.33M was mixed with a solution of potassium Peroxodisulphate of strength 0.005M in a clean flat-bottom glass test tube to a total volume of 25mL. A solution of MA (20mL) and PDS (5mL) was used throughout this part of the work for synthesizing PMA. Ultrasound was passed for 30 minute continuously and stopped exactly at the end of the 30th minute. The reaction test tube was taken out from the ultrasonic bath and a fixed volume (75mL) of Sulphuric acid of strength 2N was slowly and gently added to the reaction mixture and was allowed to settle down. After an interval of 48 h, a thick solid layer of PMA was settled at the bottom of the test tube. The remaining liquid mixture was poured out and the thin layer of PMA was taken out gently from the test tube and placed over a filter paper, which absorbed all the liquid content and dried the thin layer of PMA. This layer was washed with distilled water 10 times and dried under atmospheric conditions in a clean environment. Thus PMA wafer, which was semitransparent and colorless, was obtained. Using the same procedure as given earlier, PMA was synthesized by varying the period of sonication for 30, 60, 90, 120,150,180,210,240,270,300 and 330 minutes. There were eleven PMA samples of thickness 0.35mm for eleven different sonication periods available for further studies. The samples were cut in highly symmetric directions to have uniform dimension of 4 X 4 X 0.35 mm³.

Large Scale Synthesis

In this type of synthesis the experimental vessel was a 600 mL glass beaker. MA (400mL) and PDS (100mL) were taken throughout the synthesis. The

strength of MA was 0.33M and the strength of PDS was 0.005M. The sonication period employed were 60,360,420 and 540 minute. For synthesizing 60minute sonicated PMA sample, at the end of the 60th minute the 600 ml glass beaker which contained PMA liquid of 500ml was transferred to a 1000 ml glass container and 500 ml of Sulphuric acid of strength 2N was slowly and gently added to the reaction mixture and was allowed to settle down. After an interval of 48h a thick solid layer of PMA was settled at the bottom of the glass beaker. The remaining liquid mixture was poured out and the thick layer of PMA was taken out gently from the glass beaker and placed over a filter paper, which absorbed all the liquid content and dried the thick layer of PMA. This thick PMA sample was washed with distilled water several times and dried under atmospheric conditions in a clean environment. The same procedure was adopted to synthesize PMA samples for sonication periods of 360, 420 and 540 minutes. Throughout this experiment a constant temperature of 50°C was employed. These four PMA samples were used for electrical conductivity studies.

In total there are 11 PMA samples prepared in small scale and 4 PMA samples prepared in large scale using high power ultrasound. Hence eleven PMA samples (thin)one for each period 30,60, 90,120,150,180,210,240,270,300, 330 minutes and 4 PMA samples (thick) one for each 60 minutes, 360minutes, 420minutes and 540minutes were prepared for investigation.

2.6 Ultrasound Power Measurements

The acoustic power entering the system was determined by calorimetry. The temperature (T) of the reaction mixture was recorded, using a thermocouple, against time (t), at 5 minutes intervals from the commencement of sonication. The acoustic powers were calculated using the following equation [238,239,240]

$$P_{us} = (dT/dt)C_pM \quad (E 2-1)$$

where (dT/dt) is the temperature rise, C_p is the specific heat capacity of water ($4186\text{Jkg}^{-1}\text{k}^{-1}$) and M is the mass of water used (kg). For the low power ultrasonic instrument the measured power was 5.5 W/cm^2 and for the high power ultrasonic instrument the measured power was 100 W/cm^2

2.7 Synthesis of PMMA- MMT Clay Nanocomposites

Polymerization of Methyl methacrylate (MMA) was carried out by keeping the experimental solution in a flat bottom glass beaker of capacity 500 ml immersed in a Transonic Digital Ultrasonic water bath (Model Elma T490DH, Germany). The ultrasonic water bath which is a rectangular metallic tub filled with water to three-fourth of its total capacity gives out ultrasonic waves of fixed frequency 35 kHz at a constant power 100 W/cm^2 . The MMA (E-Merck, India) solution of strength 0.1 M was mixed with a solution of Peroxodisulphate (E-Merck, India) of strength 0.02 M in a 500ml glass beaker. MMA of 400 ml volume was mixed with 100 ml of aqueous peroxodisulphate.

Ultrasound was passed for a period of 300 minutes continuously at a constant temperature of 30°C . The passage of ultrasound was stopped at the end of the 300th minute. The reaction vessel was taken out from the ultrasonic bath and 100 ml of Sulphuric acid (E-Merck, India) of strength 2 N was slowly and gently added to the reaction mixture along the inner walls of the glass vessel and contents were allowed to settle down. After an interval of 24 hours, a thick mass of PMMA was found to settle at the bottom of the glass beaker. The contents of the beaker were filtered and wet powder of PMMA was obtained. This was air dried under atmospheric conditions and then kept in a hot oven at 50°C for 60 minutes to eliminate water content. Thus fine powder of PMMA was obtained for further studies. MMT (K-10) was used as such without further purification supplied by Aldrich Chemical Company, India.

PMMA/MMT nanocomposites were synthesized by two different processes viz., magnetic stirring and ultrasonic mixing methods. The experimental details, results obtained for these nanocomposites are discussed in chapter 6.

2.8 Characterization and Measurement Techniques

Photoacoustic Technique

Among the different photothermal methods, the photoacoustic effect is credited with the first observed photothermal phenomena noticed in 1880 during Alexander Graham Bell's voyage for new inventions [2,3]. Though Bell has prophesied the scope of his novel observation, after the initial flurry of interest generated by his original work, experimentation with the photoacoustic effect is almost in a dormant state. After the advent of microphones, Viengerov is able to observe this effect in gaseous sample [4]. Still the growth of this new branch of spectroscopy is in a hopeless state due to many of the experimental limitations. The emergence of lasers in early sixties paved a new way in the photoacoustic spectroscopy of gaseous samples. But the applications of this technique have been efficiently extended to liquids and solids only after the successful formulation of a general theoretical model by Rosencwaig and Gersho in mid-seventies [5]. Subsequent developments in the theoretical aspects of photothermal phenomena are mere extensions or modifications of Rosencwaig-Gersho model. Though Bennett and Forman in 1976, and Aamodt *et.al.* in 1977 have modified the basic theoretical model by treating the acoustic wave transport in the gas using Navier-Stokes equations, the basic results of Rosencwaig-Gersho model remains the same [6,7]. Modification to the R-G theory by McDonald and Wetsel in 1978 by taking into account the contributions from thermally induced vibrations in the sample is somewhat intriguing [8]. By this time, a new form of photoacoustic configuration, namely the open photoacoustic cell has emerged [9]. Nowadays, the open cell photoacoustic technique is in widespread use for the thermal characterisation of solid and even liquid samples [10-20].

The principle of photoacoustic spectroscopy is that a fraction of the incident-chopped optical radiation, when absorbed by the sample, raises the molecules of the sample from the ground electronic state to the excited electronic state and these excited molecules relax to the ground state through non-radiative de-excitation, ie, periodic heat emission. This process is shown in figure 2.1. This periodic heat emission produced in the sample is diffused through an air medium in front of the sample. This temperature variation changes the pressure in the PA cell, which is detected as acoustic signal by microphone.

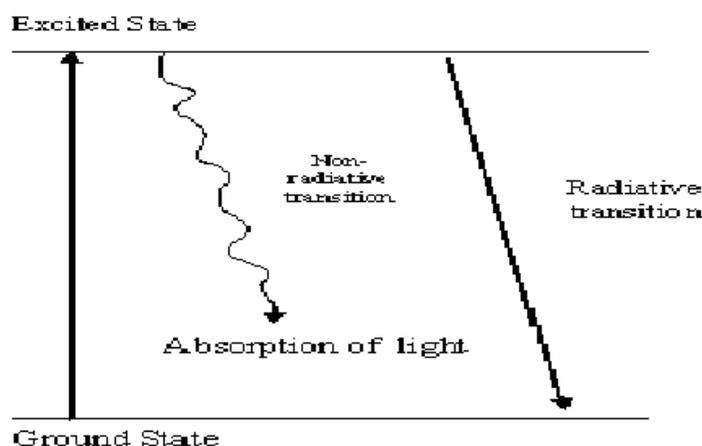


Figure 2.1: PA Principal

In this work the researcher had used the same experimental set up one without lock-in amplifier for the PMA sample prepared with low power ultrasound, with lock-in amplifier for the PMA samples prepared with high power ultrasound. The simple reason for this was that when the low power sample was investigated the lock-in amplifier setup with the lock-in amplifier is shown in figure 2.2.

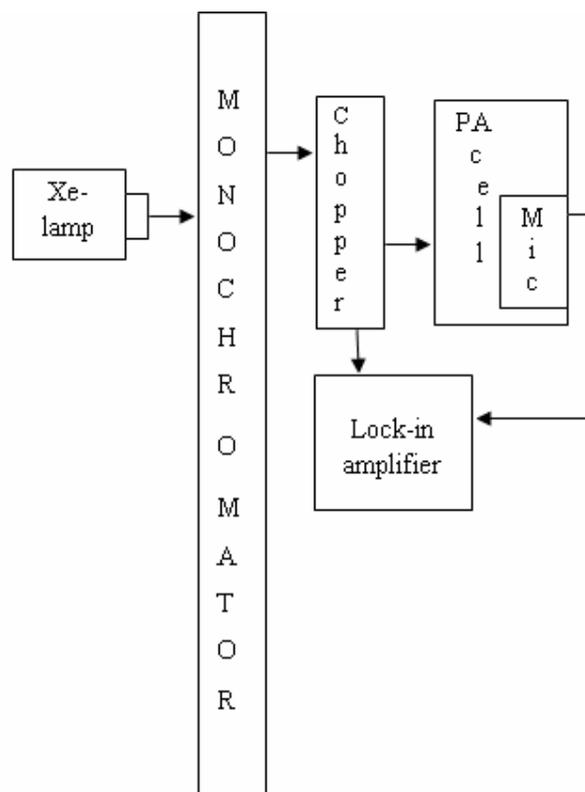


Figure 2.2: Photoacoustic Setup

The advantage of using lock-in amplifier is to confirm that unwanted signals are absent and an additional phase of 180° is added to the output signal. This PA spectrometer, for measurement of thermal diffusivity is set up with a xenon lamp (450w, SPEX); monochromator (100-1000nm,SPEX); electromechanical chopper (EG and G, model 601-1); an innovatively designed photoacoustic (PA) cell which is kept inside a vibration-free metallic cylindrical vessel of length 45 cm and diameter 21 cm weighing nearly 40 kg, with slits and adjustable screws; a sensitive electret microphone; a lock-in amplifier (EG and G, model 7225) in which provisions are made to measure amplitude and phase difference between incident modulating light signal and emitted acoustic signal for different chopping frequencies. Before carrying out the experiment with PMA sample, the PA setup was calibrated with air and also quartz glass for which

thermal diffusivity agrees well with the literature values. As the PMA sample is kept inside the PA cell, the light absorbed by the sample would generate thermal waves and subsequently the sensitive electret microphone detects the acoustic waves. This signal is fed into the lock-in-amplifier in which there are provisions to note down values of the PA signal.

The PA spectra recorded in the following ways

Depth Profile Analysis

Here the wavelength was fixed and the chopping frequency was varied. For every chopping frequency the amplitude and the phase of the PA signal were recorded in the same lock-in-amplifier setup.

Wavelength Scanning

Here the chopping frequency was fixed and the wavelength of the incident chopped radiation was varied. For every wavelength the amplitude and phase of the PA signal were recorded in the same lock-in- amplifier setup.

In this work for PMA sample synthesized by low power ultrasound the PA setup without lock-in- amplifier was used. Depth profile analysis and wavelength scanning were done. The output PA signal was measured using Digital storage oscilloscope (DSO; 20 MHz; Gould, Brookhaven, Inc.). and hence amplitude was only measured. Phase difference measurements were not possible. Moreover this was done for only one PMA sample. The experimental was conducted at a temperature of 303°k

For PMA synthesized by high power ultrasound the PA setup with lock-in-amplifier was used. Depth profile analysis alone was done. Wavelength scanning was not done because of fluctuating amplitude and phase. The amplitude and phase of the PA signal was measured using the same lock-in amplifier (EG and G Model 7225). This was done for all the eleven samples. The experiment was conducted at the temperature 303°k.

2.9 Density Measurements

The densities of the PMA samples were found out by floatation method using p-Xylene (density = 856 kg/m^3) and Carbon tetrachloride (density= 1590 kg/m^3) mixture. Since p-Xylene and Carbon tetrachloride are highly miscible and having large differences in densities, they are used for density measurements. Here, in a beaker of 50ml capacity 10 ml of carbon tetrachloride is taken and one of the PMA samples is put in this liquid. The sample floats on the surface of the liquid. Then, slowly p-Xylene is added to this liquid little by little and stirred gently. Every time the PMA sample is observed whether it completely sinks or floats on the surface. If the density of the solution is equal to the sample, it will float in the middle (level in the beaker) of the solution i.e., it neither sinks nor floats. Then this liquid is taken in a 10 ml specific gravity bottle for density measurements. Following the same procedure density of all the eleven PMA samples is found out. The density ranges from 1051 kg/m^3 for the thirty minutes ultrasonicated samples to 1325 kgm^3 for 330 minutes ultrasonicated PMA sample. Every density value is taken as the average of five density measurement trials with an experimental error ranging from 0.5 % to 1% for the entire measurements.

2.10 Differential Scanning Calorimetry (DSC)

This technique measures the amount of energy or (heat) absorbed or released associated with transitions in the sample as it is heated, cooled or held at constant, temperature (isothermal). Such measurements provide quantitative and qualitative information about physical and chemical changes that involved endothermic or exothermic processes or changes in heat capacity. The equipment used was Differential scanning Calorimeter Model ZG10 supplied by TA Instruments, USA. The DSC cell is based on a 'heat flux' design which uses a constant disc as the primary means of transferring heat to the sample and reference

positions. As heat is transferred through the disc, the differential heat flow to the sample and reference is measured by thermocouples. This device was used for finding specific heat capacity (C_p) of PMA samples, and glass fragility of PMA samples. These are explained in chapters 4 and 8 Glass transition temperature of synthesized PMA agrees well with the available literature values of glass transition temperature of PMA. The photograph of the DSC instrument at UGCDAECSR, Indoor, India is shown in figure 2.2a



Figure 2.2a: DSC Setup used by the Researcher

2.11 Thermal Expansion

The thermal expansion coefficient for this PMA sample was also determined with Fizeau's method in the direction of higher symmetry. This method is an accurate ($\pm 0.05\%$ error) optical method for determining the linear thermal expansion coefficient for metals and alloys by forming interference fringes. This method was used here for the first time to measure the thermal

expansion coefficient for a polymer. We used our PMA sample for the measurements. This measurements is explained in chapter 3.

2.12 Thermogravimetric Analysis (TGA)

His technique allows the mass of a substance to be measured as a function of temperature whilst the substance is being subjected to a controlled temperature programme in a flowing gas atmosphere (Dynamic Thermo Gravimetry). In isothermal thermogravimetry, sample weight is to be measured as a function of time at a constant temperature. TGA can be used to investigate any chemical or physical process that involves a change in the weight of a material. The apparatus used was the METTLER TA 3000 SYSTEM which consisted of a TA PROCESSOR (TC 10A), a THERMOBALANCE (TG 50) and a matrix printer. The TA 10 processor controls all the test variables [ref no. Instruction Manual, Mettler TA 3000 system and TG 50, 207.] Viz. The initial temperature heating rate, final temperature, the size of TG plot required, pure gas admission time temperature, purge gas change over and evaluation required. The TGA figures of normalized mass and derivative thermogravimetry (DTA) data of the derivative of mass as a function of temperature for PMA samples at a heating rule of 5°C/min in nitrogen environment is explained in chapter 4 In this investigation degradation kinetics could not be established because the heating rate was kept uniform for all the PMA samples. However semi-quantitative thermal degradation process of PMA is explained in chapter 4.

2.13 Sinclair's 'Apparatus-method of Mixtures

Description

The Sinclair's model of the apparatus consists of a steam boiler (A), along the axis of which runs a cylindrical cavity. From the lower end of this cavity leads out an outlet (O). Into the cavity fits a brass tube. B, whose lower edge is beveled such that the protruding portion could act as a cover for the outlet, When the head

of the tube is turned, the slant opening of the tube will move against the outlet and any solid kept inside will quickly drop out into a calorimeter. The boiler is heated by a burner and the heat of the burner is prevented from directly affecting the calorimeter by means of a wooden shutter.

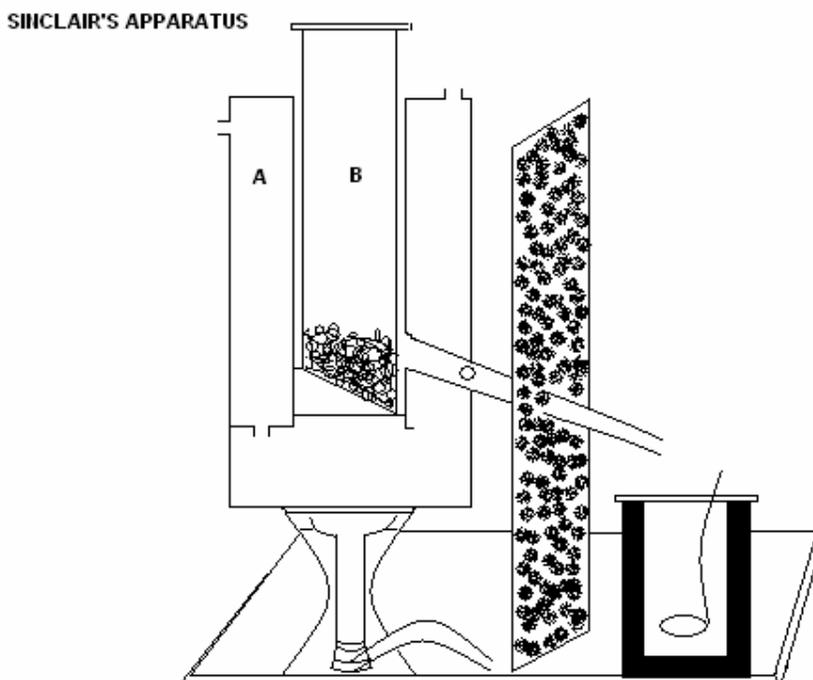


Figure 2.3 Sinclair's apparatus to measured specific heat capacity

Procedure

A calorimeter is weighed empty with stirrer correct of a centigram (w_1). Water is taken in it to about two-third the height and the calorimeter weighed again (w_2). The initial temperature ($\theta_1^\circ\text{C}$) is noted. The given solid whose specific heat (x) is required is heated in the Sinclair's steam heater. When its temperature has become steady as $\theta_1^\circ\text{C}$ and remained so for at least fifteen minutes, the head of the central tube is turned and the solid is dropped into the calorimeter. A Stop-clock is started simultaneously. The water in the calorimeter is stirred and the final

temperature is found. With a solid like granules of zinc, it may hardly be possible to apply a graphical correction and the half-time correction alone can be applied. But if the solid were a poor conductor like bits of rubber or broken glass beads, it may be possible to apply Barton's correction. Let the corrected final temperature be $\theta_3^\circ\text{C}$. The calorimeter and contents are weighed when cool (w_3).

Let the specific heat of the material of the calorimeter be s . Then,

$$\text{Heat gained by the calorimeter and contents} = (w_1s + w_2 - w_1)(\theta_2 - \theta_1) \text{ cal.}$$

$$\text{Heat lost by the solid} = (w_3 - w_2) \times (\theta_2 - \theta_3) \text{ cal.}$$

If there were no other losses or gain of heat.

$$(w_1s + w_2 - w_1)(\theta_2 - \theta_1) = (w_3 - w_2) \times (\theta_2 - \theta_3)$$

From which x can be found.

2.14 X-Ray Diffraction

Thick films of PMA were pasted on a glass slide. The sample was dried before it was placed in a diffractometer; X-Ray diffraction profiles were determined using a PHILIPS ROREXO X-RAY Diffraction Unit as per detailed procedure. X-ray radiation source is Cu $K\alpha$ Monochromatic. The sample was scanned over a wide angular range [5-50°(2 θ) for Cu $K\alpha$] to ensure that all the major diffraction peaks of the PMA samples are recorded. This is explained in chapter 8. The picture of the XRD instrument at UGCDAECSR, Indoor, India is shown in figure 2.3a



Figure 2.3a: Photograph of XRD used by the Researcher

2.15 Atomic Force Microscope (AFM)

During the past decade, the atomic force microscopy has been developed from an exotic instrument into a relatively widespread surface- imaging and probing instrument. Atomic force microscopy (AFM) and its related techniques have proliferated successfully into many fields. Today this method is used to obtain the high-resolution static and dynamics images in investigation of the physical and mechanical properties of the thin film molecules and biological molecules. The atomic force micrographs of all the PMA samples were taken with the Digital Instruments Nanoscope III, Version 2.2 at UGCDAECSR, Indoor, India. It works in the contact mode only. The tip is 'V' shaped and is made up of silicon nitride. The force constant $k = 0.38$ Newton/meter, the length of the

cantilever is 100 μm and the tip radius is ~ 20 nm. The photograph of AFM is shown in figure 2.4. The details of the AFM measurements are explained in chapter 5.

The Digital Instruments also provided processing software with the help of which we can quantify the surface properties of the sample. With the help of the software it is possible to calculate mean square roughness. This is defined in the following way [21]. In a given area of the surface we measure the height at N equally spaced points. The average values Z_{avg} of the height Z is given by

$$Z_{avg} = \sum Z_i / N \quad (E 2-2)$$

The root mean square roughness is given by

$$RMS_{roughness} = \left[\sum (Z_i - Z_{avg})^2 / N \right]^{1/2} \quad (E 2-3)$$

The program also gives mean roughness, which is the average of all the Z values within the enclosed area [22].

Atomic Force Micrographs give surface morphology of the sample which is an indicator of the internal crystal perfection. From the AFM scan of area of the order of $(\mu\text{m})^2$, one can get information of the nature of the polymerization process, the average size of the grains, knowledge about the connectivity of the grains and the surface roughness of the sample. We can also get information on how the microstructure is altered due to sonication



Figure 2.4 Photograph of AFM

2.16 Scanning Electron Microscopy and Energy Dispersive X-Ray

SEM is used to study surface and interface morphology as well as to do channeling patterns. Many units are equipped with EDAX, which can be used to verify compositions. The purified PMA Samples were analyzed by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray methods. The instrument used for microscopical studies was computer controlled scanning electron microscope F Model: JEOL JSM 5600

The basic function of the instrument is to produce, on a CRT display an image of three dimensional appearances, derived from the action of electron probe scanning the surface of the specimen. It has magnification range between X18 and X300, 000 (in 136 steps). which represents the scanned area of the specimen from 6 mm X 5 mm to 1.2 μm X 1 μm at 10 mm working distance. Additional variable magnification of up to X3 can be obtained using a zoom facility.

The electron gun produces a beam of electron with an effective source of about 30 μm diameter. The condenser lenses produce successive stages of demagnification and the final lenses focuses the demagnified image on the source on to the specimen. The electron beam (or probe) is scanned across the specimen surface. Low energy secondary electrons (generated in the specimen by the probe) and high energy primary electrons (reflected from the specimen surface) travel towards a collector system. When electrons impinge on the scintillator, photons are emitted in the photomultiplier passes through a amplifier to the display unit. The resultant image has a marked three dimensional appearance because the contrast is produced by the variation in the number of electrons emitted or reflected from different parts of the specimen which is the function of the inclination to the surface to the incident electron beam. The apparatus setup is shown in the figure 2.4a and 2.4b



Figure 2.4a Scanning Electron Microscope

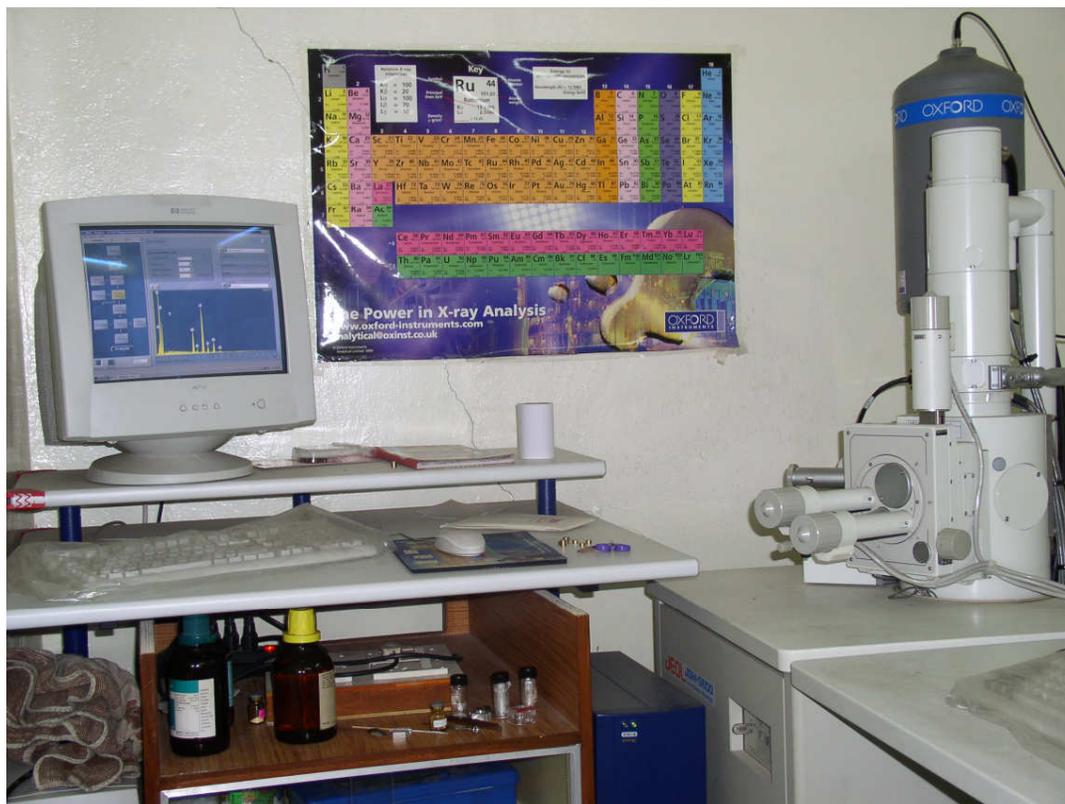


Figure 2.4b Energy Dispersive X-Ray

2.17 X-ray Photoelectron Spectroscopy (XPS)

In X-Ray Photoelectron Spectroscopy (XPS), the sample is illuminated with X-rays from a Alkyd' source photoelectrons are emitted from the surface as a result of X-rays excitation whose kinetic energy is characteristic of the elements present. Surface elemental analysis is determined from the position of the peaks in the XPS SPECTRUM. Since the chemical state of the atom in the surface alters the electron binding energy, chemical shifts of up to 10ev can occur in the kinetic energy of the photoelectrons. This enables chemical bonding information to be derived from the precise positions and shapes of the XPS peaks. In addition XPS is amenable to the widest range of surfaces since X-rays do not normally cause charging problems or beam damage. Hence the technique may be used for all

materials and is particularly useful for delicate surfaces such as polymers, catalysts, natural and synthetic fibers. In UGC-DAE consortium for scientific Research, Indore, India this facility is available with beam line synchrotron radiation. The figure 2.5 depicts the photograph of the XPS arrangement in the centre. This XPS spectra was used to find the chemical state of the molecules in PMA while studying for electrical resistivity characteristics.



Figure 2.5 X-Ray Photoelectron Spectrometer

The complete spectrometer consists of 1) 180° hemispherical electron energy analyzer, 2) experimental chamber, 3) sample preparation chamber and 4) load lock chamber.

All experiments are performed under UHV conditions (Base pressure: better than $\sim 2 \times 10^{-10}$ Torr). The Sample preparation chamber contains A Diamond

file scraper for cleaning bulk samples and An ion-sputtering gun for cleaning thin film samples. The Whole chamber and analyzer are made from Mu-Metal to shield earth's magnetic field. The experimental station is equipped with angle integrated photoelectron spectrometer having 180° hemispherical electron energy analyzer (Omicron EA-125) to measure the kinetic energy of the photo-ejected electrons. This experimental chamber contains a twin anode (Mg $K\alpha$ and Al $K\alpha$) X-ray source (Omicron NG DAR 400). The heating up to 600°C and cooling up to LN_2 temperature is possible with present arrangement. An in-situ thin film deposition facility using micro-evaporator is also available. For the measurements, samples are loaded in the load lock chamber and after getting the desired vacuum; we transfer the sample to main chamber, where the spectrum recording is done. Energy calibration of the spectrometer is done using known core levels of standard samples such as Au, Ag and Pt. C-1s peak serves as internal reference.

2.18 DC Electrical Resisitivity Measurements

The DC electrical resisitivity for four PMA samples prepared with sonication period of 60,360,420 and 540 minutes were carried out using a high precision instrument from liquid nitrogen temperature to room temperature. The procedure is explained below.

We used an automated precise electrical system. Computer software and circuitry have been made such that resistivity measurements of samples with linear four-probe configuration was done. D.C four-probe technique (which is shown below in the figure 2.6c , but we used two-probe technique in our work because the PMA samples are of very high resistance in the order of $\text{M}\Omega$) was used to mesure resistance of PMA from low temperature ($\sim 80\text{K}$) to 300 K using an Advantest source meter, an SI7071 solartron hanovoltmeter and a Lakeshore temperature controller (DRC – 93CA) hooked to a personal computer. Silver paste was used in making contact on the sample. $160\ \mu\text{m}$ insulated copper wire was cleaned properly for the portions to make contacts silver paste was nicely painted

for each wire on the PMA sample so that all wires are well embedded in it. Once the silver plate was dried in ten to fifteen minutes, contacts were checked. Resistances were measured in the forward and reverse directions for different currents passed. Typical current was 1 – 10mA. If they are differed significantly for all the currents passed, the contacts having problems were sorted out and remade the contact(s) and confirmed the forward and reverse resistance are almost the same for a particular current. Once this check was done, the sample chamber was evacuated to about 10^{-3} torr. The evacuated sample chamber assembly was then allowed to cool down the maximum temperature in an indigenously fabricated crystal by gradually adding LH₂ in the cryostat. After reaching the minimum temperature (about 80K), measurements were done in the warming cycle. Temperature stabilization time was about 3.6 minutes for each temperature and the accuracy of temperature was better than 20mK. At stabilized temperature maintained by temperature controller, the appropriate constant current (50nA) was supplied from the current source through the inner terminals made on the sample and the voltage developed at the outer terminals was measured through the solartron nanovoltmeter, the same current was passed in the reverse direction at the same condition the voltage was measured. The average of the two voltages (forward and reverse) was used for calculating the resistance using the current passed. This avoid the thermo emf errors, if any thereby the obtained data are highly reliable and reproducible. Then measurements for the next temperature was done. These were done for the ranges 80 – 300K. once the resistance was recorded through the relation $\rho = R(A/L)$, where A is the cross sectional area and L is the distance between the two terminals. The resistivity measurements were made for 4 PMA samples of Ultrasonication periods of 60, 360, 420 and 540 minutes respectively under identical conditions. In the discussion to follow in chapter 4 the

samples will be denoted as PMA-A for 60min, PMA-B for 360min PMA-C for 420min and PMA-D for 540 min for conveniences



Figure 2.6a Low Temperature DC Electrical Resistivity Setup



Figure 2.6b Low Temperature DC Electrical Resistivity Setup

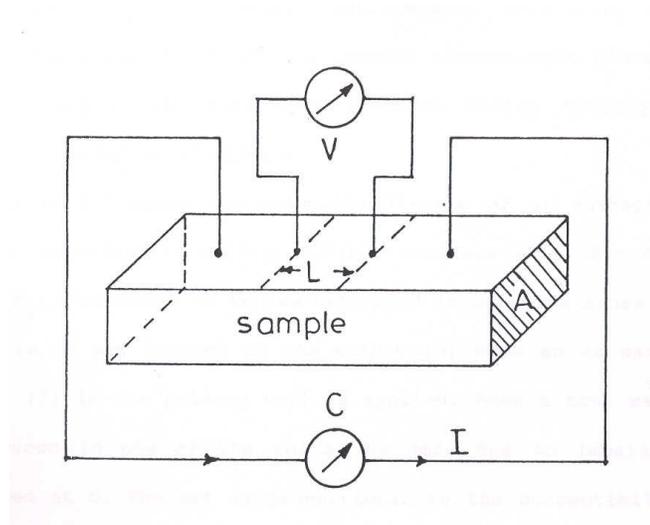


Figure 2.6c: Schematic of the terminals made on a parallelepiped shape sample (C is the current source; V is the nanovoltmeter).

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