Chapter – 3 Materials and Experimental Method

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHOD

It has been established in recent years that polymer-based composites reinforced with a small percentage of strong fillers can significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix. Moreover, these improvements are achieved through conventional processing techniques without any detrimental effects on process ability, appearance, density and aging performance of the matrix. Now-a-day's hybrid polymers, which are the hybrid structure of inorganic-organic nano-composite materials are being used to impart the combination of scratch resistance with dirt-repellent effect, high transparency, special barrier properties or antimicrobial function to the material.

From the available literature and the best possible commercial applicability of polymer/SiO_2 nanocomposite product, the entire study is based on effect of SiO_2 nano particles on different polymers used in textiles. In the present study selection of material has been made on the bases of commercial viability and utility of particular polymer in specific form, like polyamide in film form, polypropylene in filament form and polyester in fabric form.

The experimental plan was based on application of silica nano particles to different textiles in various forms viz. film, filament and fabric. The prepared polymer silica nanocomposite textiles were analyzed by standard techniques for evaluating changes in structural and mechanical properties and compared with respective pure material.

For effective evaluation the experimental work was conducted in three parts;

Part – I: deals with preparation of polymer (polyamide) silica nanocomposite film and its evaluation in terms of structural and mechanical behavior. The selection of PA silica nanocomposite film was made on the bases of its commercial applicability as packaging material.

Part – II: In this part, filament containing different proportions of silica nanoparticles were prepared using melt spinning pilot plant. The evaluation of prepared polymer (polypropylene) silica nanocomposite filaments was evaluated in terms of improvement in their structural and mechanical properties and compared with pure filament. This was selected on the basis of wide applicability of polypropylene in technical textile.

Part – III: Polymer silica nanocomposite fabrics were prepared by incorporating different proportions of silica nano particles to polymeric (polyester) fabric by pad-dry-cure method. The prepared composite fabric was analyzed in terms of change in their structural and mechanical properties and compared with pure polymeric fabric.
The main purpose of selecting polyester fabric with nano silica particles was to investigate the structural and mechanical properties to consider it as high performance textiles.

3.1 MATERIALS

3.1.1 Film

Polymer Chips: Material used in the experiment was polyamide chips procured from reputed company of India having following specifications.

Table 3.1 Specifications Polyamide chips

Type	Viscosity (poise)	H_2O (ppm)	TiO_2 (%)	Chip Size (mm)
Semi Dull (SD)	2.47± 0.03	≤ 800	0.29 ± 0.05	2.5 D x 2.5 L

ppm: parts per million

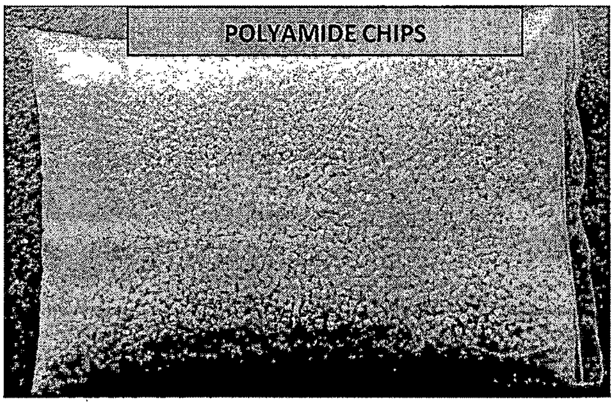

Figure 3.1 Polyamide chips

Chemicals:

Silica (SiO_2) nano particles with average size less than 100 nm were procured from a reputed international company, having specifications as mentioned below.

Table 3.2 SiO_2 Specifications

Particle size	< 100 nm
Molecular weight	60.08 Mw
Surface Area	175-225 m^2/g
pH	9
Melting point	>1600°C
Density	2.2 to 2.6 g/ml at 25°C
Bulk density	0.068 g/ml

Formic acid LR (Laboratory reagent grade) supplied by reputed local supplier. All the chemicals and chips were used in the experiment without any further purification.

3.1.2 Filament

Polymer Chips: The polymer used for the manufacturing of nanocomposite filaments was polypropylene homopolymer chips were supplied by one of the reputed company of India. The polymer is fibre grade polymer with 16 MFI (melt flow index).

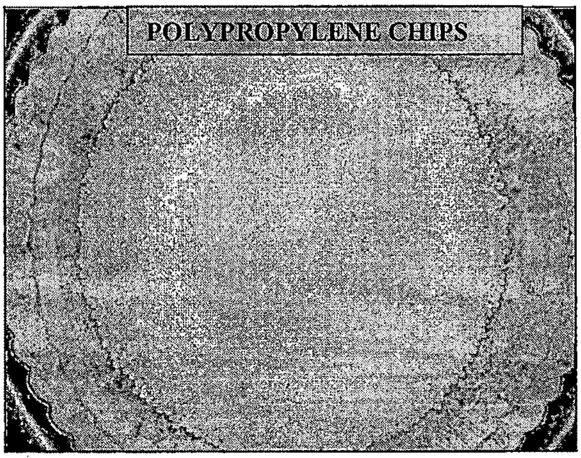

Figure 3.2 Polypropylene chips

3.1.3 Fabric

Polymeric fabric: Polyester fabric was mild scoured (5% soap Lisaapol L, 2% soda ash and boiled for 15 min.) before use. Table 3.3 shows the specifications of polyester fabric.

Table 3.3 Fabric specifications

Sample	**Material Specification**					
	Denier/fil.		**Fabric Setting**	**Weave**	**GSM**	**Thickness (mm)**
	Warp	**Weft**	**Ends/cm, Pick/cm**			
100% Polyester	128/36	146/36	36/28	Plain	109.7	0.21

Chemicals:

Polyacrylamide, Lissapol L were used for this experiment without further purification. The chemicals are of laboratory reagent grade supplied by reputed supplier.

3.2 EQUIPMENTS FOR EXPERIMENTAL WORK

Various equipments used at different stages of the work are mentioned below;

3.2.1 Equipments used for preparation of nanocomposite materials

3.2.1.1 Magnetic stirrer with heater (for preparation of film)

Specifications: High speed magnetic stirrer with temperature range of 40 to 120°C.

3.2.1.2 Melt spinning pilot plant (for preparation of filament)

Specifications: Melt spinning pilot plant was manufactured by reputed manufacturer of Vadodara, Gujarat with following specifications:

Table 3.4 Melt spinning pilot plant specifications

Make	AEC/25-4/MUL
Denier range	50 to 2000
Product	POY, FOY and FDY
Extruder	Four zone extruder with 25mm diameter of screw
	L/D ratio of screw: 30
	Screw rpm: 0 to 50
	Barrel with 75mm outer diameter and 25mm inner diameter
	Four heating zone with individual temperature control
	Maximum output capacity: 10 kg/hr.
	Ceramic perforated heater
Melt pressure regulator	350 bar maximum
Metering pump assembly	3 C.C. metering pump of rectangular type design with single inlet and outlet.
	3 Kw one temperature control zone with cartridge type heater
Spinning Head	Stainless steel
	02 pack body
	02 distribution plates

	3 Kw Cartridge heater
Quenching Chamber	MOC stainless steel
	Honey comb type S.S. chamber
	Water chilling unit of 1 ton capacity with temperature range from 5°C to 20°C.
	Blower with 400 CFM
Spin finish pump	Capacity: 0.08 cc/rev
Godets	Two godets with hard crome mirror finish
	Godet with cold and hot facility: 0 to 200°C
	Godet dia: 125 mm, 150mm length, 3500 mpm speed
Winder	speed: upto 3500 mpm
Spinneret cleaning oven	Ultrasonic cleaning oven for cleaning the spinneret: 500°C

3.2.1.3 Equipment used for preparation of polymeric nanocomposite fabric

3.2.1.3.1 Padding mangle with curing chamber

The specifications of the machine are given below:

- Padding mangel: Two bowl padding mangle with digital hydraulic pressure gauge
- Curing Chamber
- Pin type rail with to and fro facility
- Digital control of temperature 60 to 300°C and speed 30 sec to 180 sec. for 2 meter length of fabric.

3.2.2 Equipments for testing and analysis

To achieve the aim i.e. structural and mechanical changes in polymer silica nanocomposite, for testing these properties, equipments were classified into two groups:

1) Structural properties
2) Mechanical properties

1) Structural properties

- **Scanning Electron Microscope (SEM)** Model JSM-5610 LV Japan, used for analyzing surface morphology, size and shape; with Oxford Inca software for elemental analysis (EDX).
- **Fourier Transform Infrared Spectroscopy (FTIR)** FTIR Spectroscopy Nicolet iS10 FT-IR Spectrometer (Thermo Scientific, Japan) was used for analysis of chemical composition.
- **X-Ray diffraction (XRD)** Model X'Pert Pro PANalytical, Singapore for evaluation of crystalline/amourphous structure of prepared nanocomposite material.
- **Differential scanning calorimeter (DSC)** Model DSC 6000, Perkin Elmer, USA; for thermal analysis.
- **Melt flow Indexer (MFI)** Model from Hem-Tech Corporation, India; for determining melt flow index.

2) Mechanical Properties

- **Tensile strength Tester** (Lloyd LRX Model, U.K), for tensile tests of the samples.
- **Tearing Tester** Elmendorf tearing tester used for the study of tearing property of fabric.
- **Crease recovery tester** Shirley Crease Recovery tester used for the study of crease recovery angle of fabric.

3.3 EXPERIMENTAL METHODS

3.3.1 Part-I: Preparation of Polymer/SiO$_2$ nanocomposite film

Accurately weighed silica nano particles were suspended in formic acid under continuous stirring as shown in figure 3.3. The polyamide (PA) chips were added and mixture was heated to 60°C for 1 hr. The nanocomposite mixture was poured on a cleaned smooth petridish glass surface, compressed manually with another glass surface and solvent was allowed to evaporate up to dryness for 12 hrs at room temperature. Schematic presentation of polyamide/nano silica composite film preparation is shown in figure 3.4.

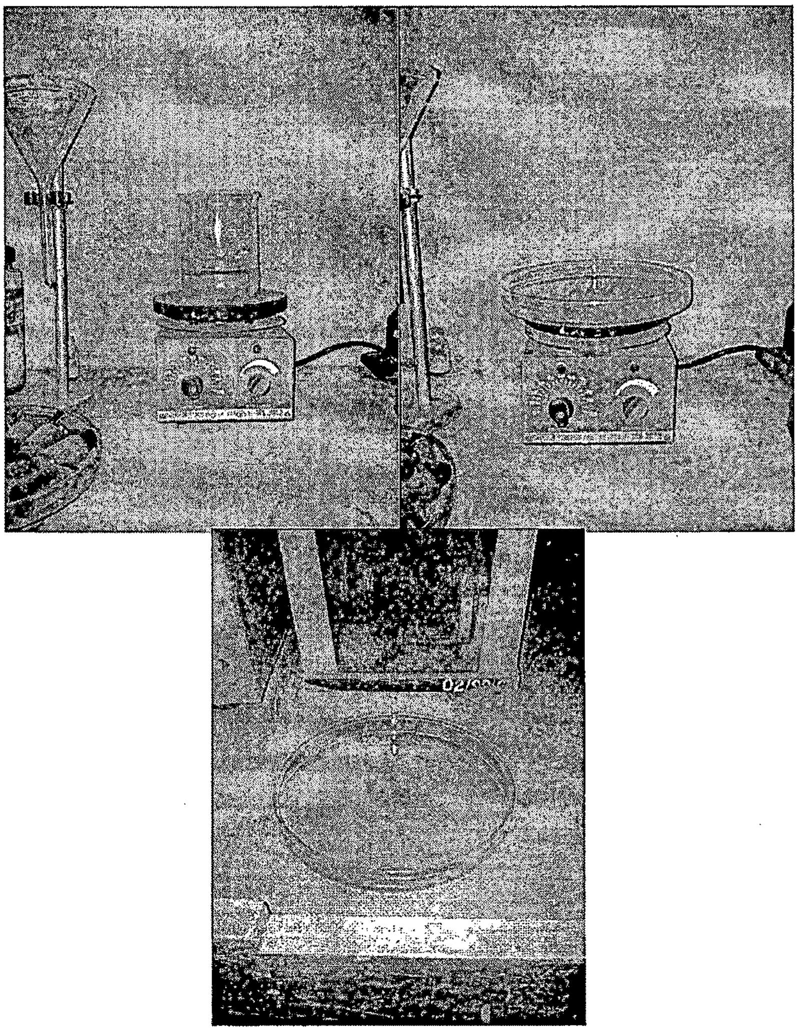

Figure 3.3 Magnetic stirrer with heater

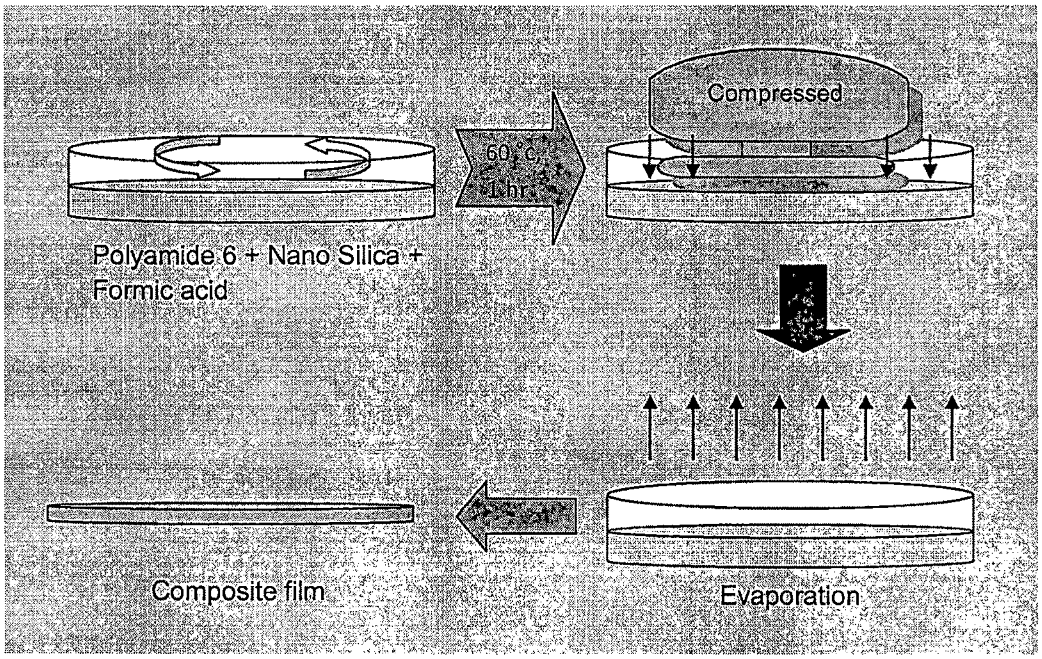

Figure 3.4 Schematic diagram of polyamide silica nanocomposite film preparation

Different formulations used to prepare polyamide silica nanocomposite film are given in table 3.5.

Table 3.5 Compositions of nanocomposites preparation by formic acid mixing

Sample	Silica (gm)	Silica (wt %)	Polyamide (gm)	Formic Acid (ml)
PA	0.00	0.0	10	100
NPA1	0.01	0.1	10	100
NPA2	0.03	0.3	10	100
NPA3	0.05	0.5	10	100
NPA4	0.07	0.7	10	100
NPA5	0.10	1.0	10	100

PA: polyamide, NPA: Nano silica loaded polyamide

3.3.2 Part-II: Preparation of Polymer/SiO_2 nanocomposite filament

Manufacturing of the Polypropylene / SiO_2 nanocomposite filaments were done in two stages: a) mixing of polypropylene (PP) granules with SiO_2 nanoparticles through twin screw extruder; b) extrusion of the nanocomposite filaments by melt spinning on pilot plant.

The SiO_2 nanoparticles were mixed with polypropylene chips in various concentrations of 0.10%, 0.30%, 0.50%, 0.70%, 1.00%, 1.25% and 1.50% on the basis of weight of PP chips. These values were selected to study the influence of increase in SiO_2 nanoparticles in PP structure on its performance. The mixing of the two components was done in twin screw extruder to get homogeneous mixture. The mixture of polypropylene with SiO_2 nanoparticle chips was then fed into the hopper of the melt spinning pilot plant as shown in figure 3.5. Monofilament yarn with above mentioned percentages of SiO_2 concentrations were spun at optimized spinning conditions on melt spinning pilot machine. The extruded filaments were passed through a water bath containing chilled water having temperature 4°C. Finally the filaments were wound on to package. A control sample of pure PP was also manufactured at the same spinning parameters for comparative study with the PP / SiO_2 nanocomposite filaments. The prepared samples are shown in figure 4.14. The pilot plant parameters were optimized experimentally by taking pilot trials. The optimized parameters were used throughout the study to retain consistent and desired quality of yarn. The parameters optimized and used for the study are appended in table 3.6.

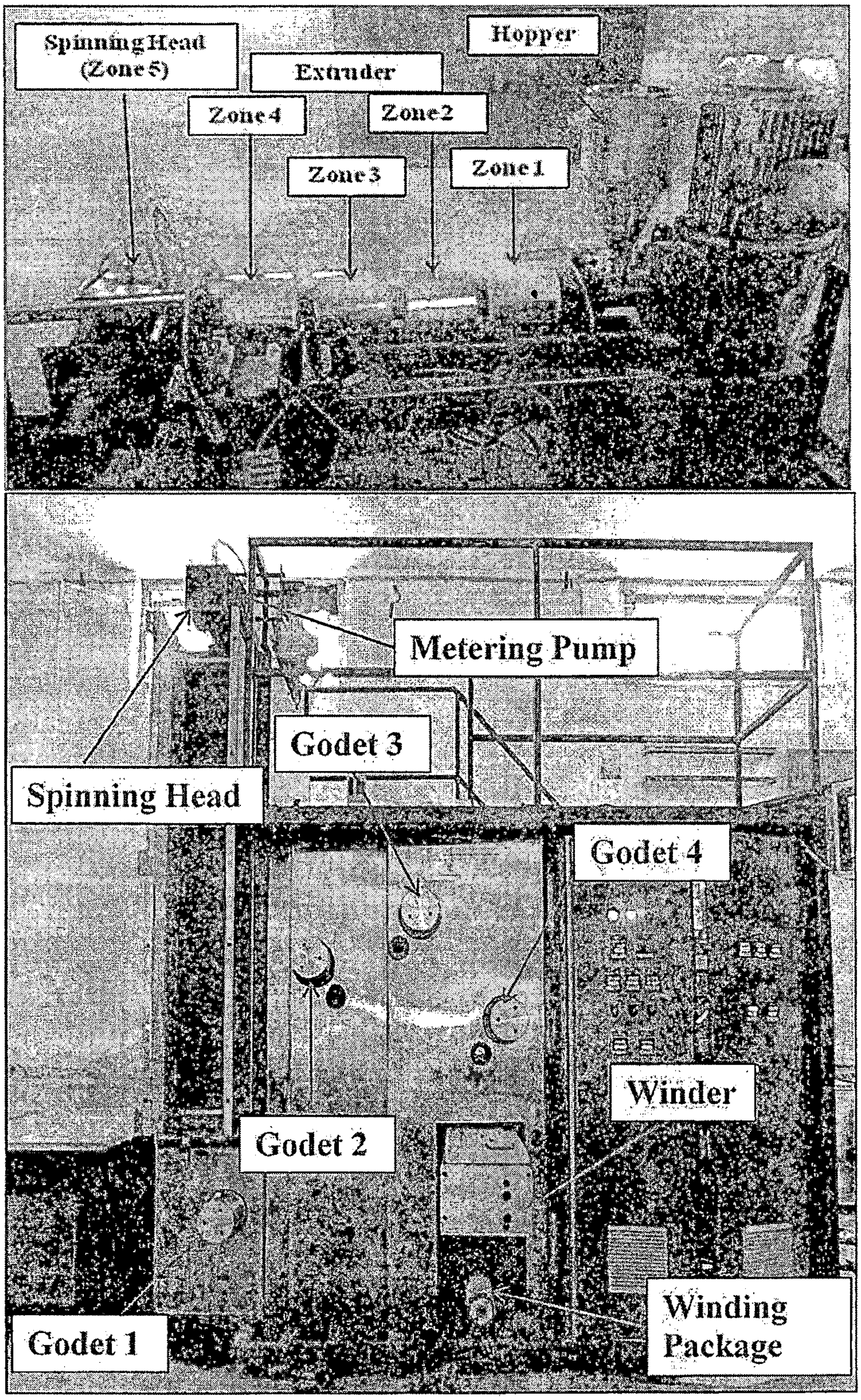

Figure 3.5 Melt spinning pilot plant

Table 3.6 Spinning Parameters

ZONES		PARAMETERS
Extruder Temperature	Zone 1	165 °C
	Zone 2	200 °C
	Zone 3	210°C
	Zone 4	215°C
Spinning Head	Zone 5	235°C
Metering Pump	Zone 6	230°C
Godet Temperature	Godet 1	R.T*
	Godet 2	R.T*
	Godet 3	R.T*
	Godet 4	R.T*
Extruder Pressure		40 bar
Metering Pump Speed		5 rpm
Godet Speed	Godet 1	0 mpm
	Godet 2	0 mpm
	Godet 3	300 mpm
	Godet 4	400 mpm
Winder	Friction Roller	400 mpm
	Grooved Roller	250 mpm

*R.T = Room Temperature

Different formulations used to prepare polypropylene silica nanocomposite filaments are given in table 3.7.

Table 3.7 Compositions of polypropylene SiO_2 nanocomposite filament

Sr. No.	Sample	Silica (wt %)
1	**PP**	0.0
2	**NPP1**	0.1
3	**NPP2**	0.3
4	**NPP3**	0.5
5	**NPP4**	0.7
6	**NPP5**	1.0
7	**NPP6**	1.25
8	**NPP7**	1.50

PP: polypropylene, NPP: Nano silica loaded polypropylene

3.3.3 Part-III: Preparation of Polymer/SiO_2 nanocomposite fabric

3.3.3.1 Preparation of silica nano padding liquor

Nano silica particles were applied to polyester fabric samples using pad-dry-cure method. The coating solutions were prepared using 1gpl, 2.5gpl, and 5gpl concentration. For 1 gpl solution, 0.1 gm nano particles were added in 100 ml water with 5 gm Lissapol L surfactant and 10gm polyacrylamide binder. The mixture was then stirred using magnetic stirrer at 250 rpm for 30 minutes at 60°C temperature. Likewise all concentration solutions were prepared.

3.3.3.2 Application to fabric

Polyester fabric sample (size : 40cm x 50cm) immersed in padding liquor at room temperature for 10 minutes and then passed through a two bowl laboratory padding mangle, which was running at a speed of 15 rpm with a pressure of 1.75 Kg/cm^2 using

2-dip 2-nip padding sequence at 70% expression for polyester fabric. The padded substrates were dried at 80°C for 5-6 minutes. Finally cured at 140°C temperature for 3 minutes, in a preheated curing chamber.

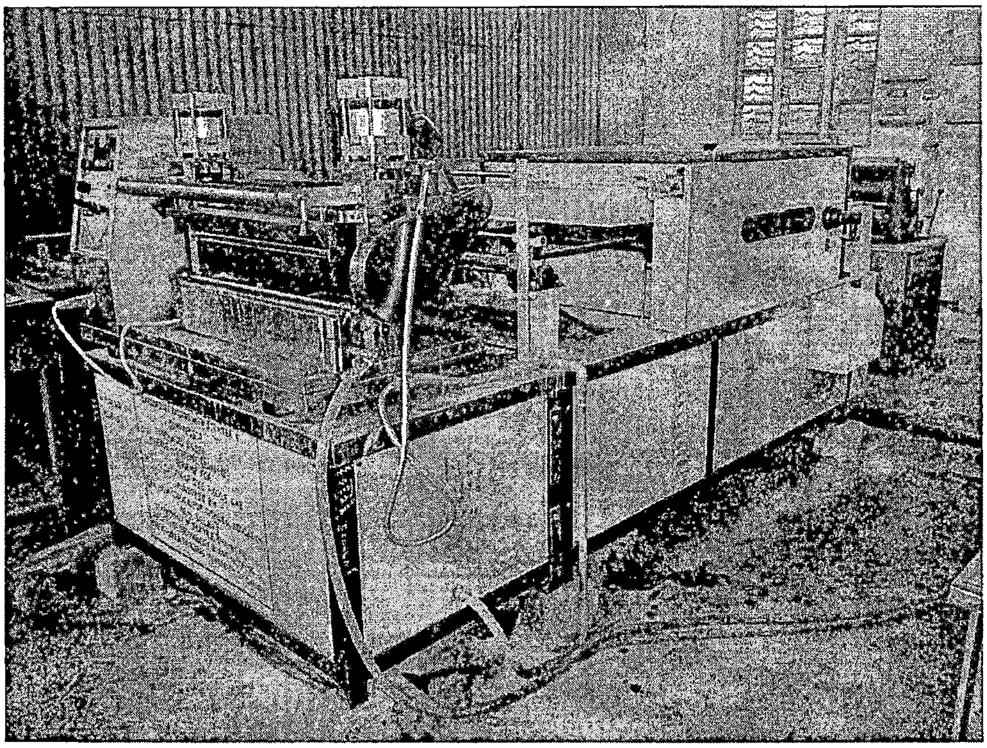

Figure 3.6 Two bowl padding mangle with stenter

Different formulations used to prepare polyester silica nanocomposite fabrics are given in table 3.8.

Table 3.8 Compositions of polyester SiO_2 nanocomposite fabric

Sr. No.	SAMPLE	COMPOSITIONS
1	PT	Polyester fabric without SiO_2
2	NPT1	Polyester fabric with 1 gpl SiO_2
3	NPT2	Polyester fabric with 2.5 gpl SiO_2
4	NPT3	Polyester fabric with 5 gpl SiO_2

PT: polyester, NPT: Nano silica loaded polyester

3.3.4 Testing and Analysis

3.3.4.1 Structural Properties

3.3.4.1.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy Model JSM 5610LV, Version 1.0, Jeol, Japan as shown in figure 3.8, was used to characterize the nano particles shape and size. The elemental analysis (EDX) of prepared pure and silica nanocomposite film, filament and fabric were performed on scanning electron microscope (SEM) using Oxford Inca Software for elemental analysis. The instrument reports the presence of elements in pure and oxide state qualitatively. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1,00,000 X with resolution up to 100A°. Stabilized solution of copper nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

The pure and silica nanocomposite film, filament and fabric were placed on carbon coated aluminum sheet and illuminated under scanning electron microscope. Scanned images with different magnification and resolution recorded on computer. The scanning electron microscopy has the great advantage of its much larger depth of focus.

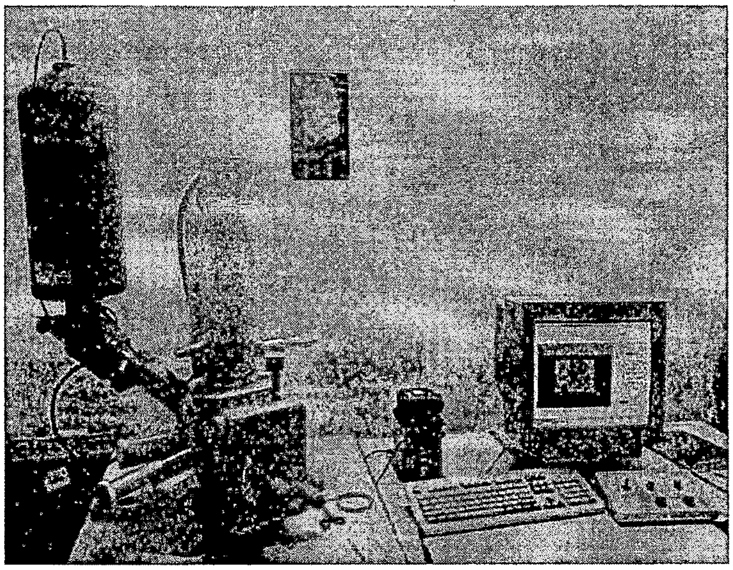

Figure 3.7 Scanning electron microscope

3.3.4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical composition of the control sample and nanocomposite filaments was evaluated using FTIR Spectroscopy, Nicolet IS10 FT-IR Spectrometer (Thermo Scientific). FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. A FTIR spectrometer simultaneously collects spectral data in a wide spectral range (400 to 4000 cm^{-1}). This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The photograph of FTIR instrument and its working principle is shown in figure 3.8.

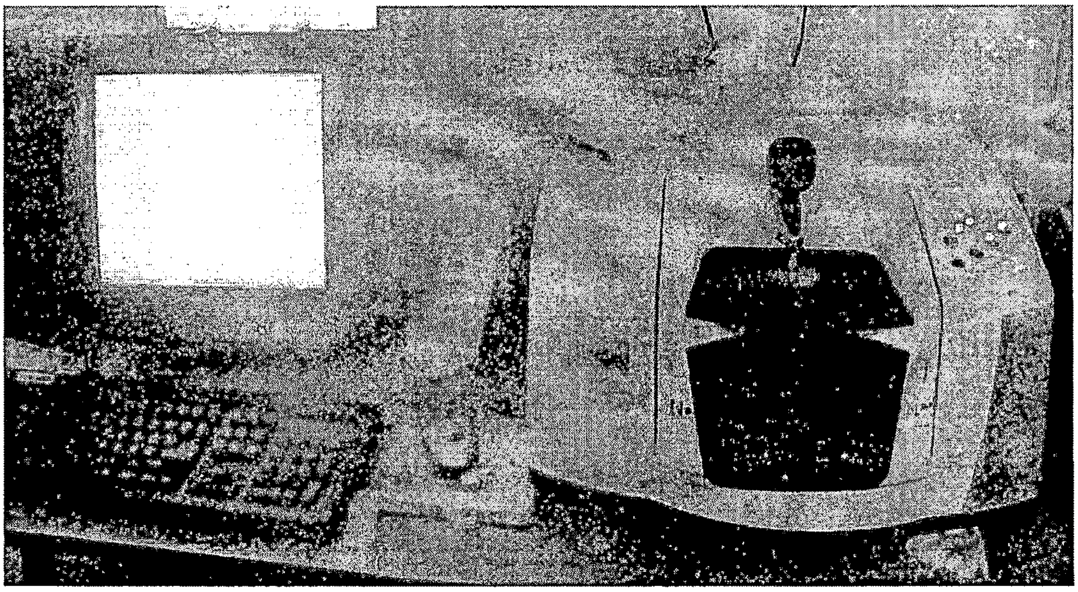

Figure 3.8 FTIR Spectrometer instrument

3.3.4.1.3 X-Ray diffraction (XRD)

The characterization of treated and untreated samples was done using PANalytical XRD as shown in figure 3.9. The XRD of all the samples was done within the 2θ range of 5° to 80° at the scan speed of 3° per minute, using Cu-K_α radiation of wavelength 1.5406Å. The diffraction profiles were obtained for individual samples. The X-Ray Diffractometer X'pert Pro PANalytical, Singapore make was used. Here in all XRD graphs the X axis represents 2θ values and Y axis represents intensity of the material.

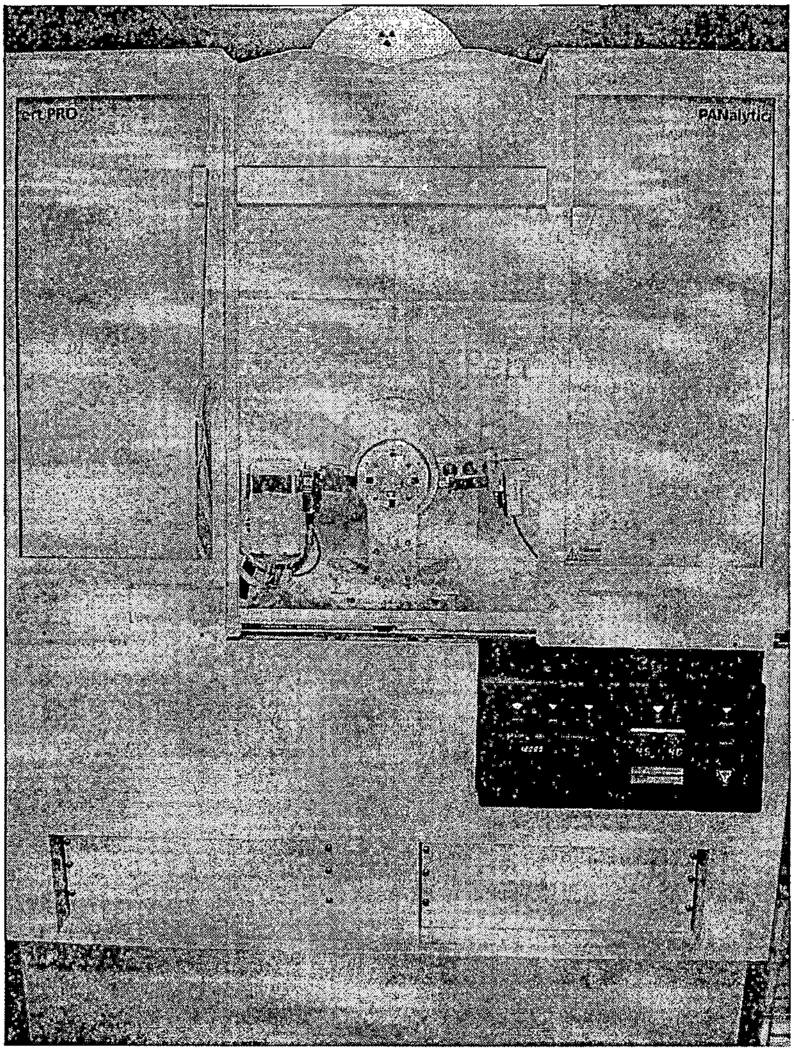

Figure 3.9 X-Ray diffractometer

3.3.4.1.4 Differential scanning calorimeter (DSC)

The thermal analysis of the prepared samples was performed using differential scanning calorimeter model 6000, Perkin Elmer, USA shown in figure 3.10.

The sample preparation was done by cutting the sample into small piece and weighing them accurately. The weighed sample was placed in aluminium pan and sealed. In DSC the given sample and the reference material (which does not undergo any transition in the temperature range of interest, here empty pan were taken as reference material) were kept in separate crucibles in the same furnace which is heated at programmed heating rate. There was an extra heater provided just below the crucible carrying the sample, which operates on the instructions received from the device measuring the temperature difference (ΔT) between the sample and the reference, to maintain the ΔT as zero. Thus the DSC records the extra heat (ΔH) supplied per unit time to the sample crucible as a function of the overall temperature of the furnace.

The DSC of the samples was carried out under the heat – cool – heat mode as given below:

- 1st Heating – Heating from 30°C to 180°C (for Polypropylene), 30°C to 300°C (for Polyamide and Polyester); Rate of heating - 10°C/ min
- Cooling - From 180 °C to 30°C (for Polypropylene), 300°C to 30°C (for Polyamide and Polyester); Rate of cooling - 10°C/ min
- 2nd Heating – Heating from 30°C to 180°C (for Polypropylene), 30°C to 300°C (for Polyamide and Polyester); Rate of heating - 10°C/ min

Nitrogen gas was used as the purge gas for the above experiment. Pressure of about 3 bars was maintained for the gas flow of 20 ml/ min in the instrument.

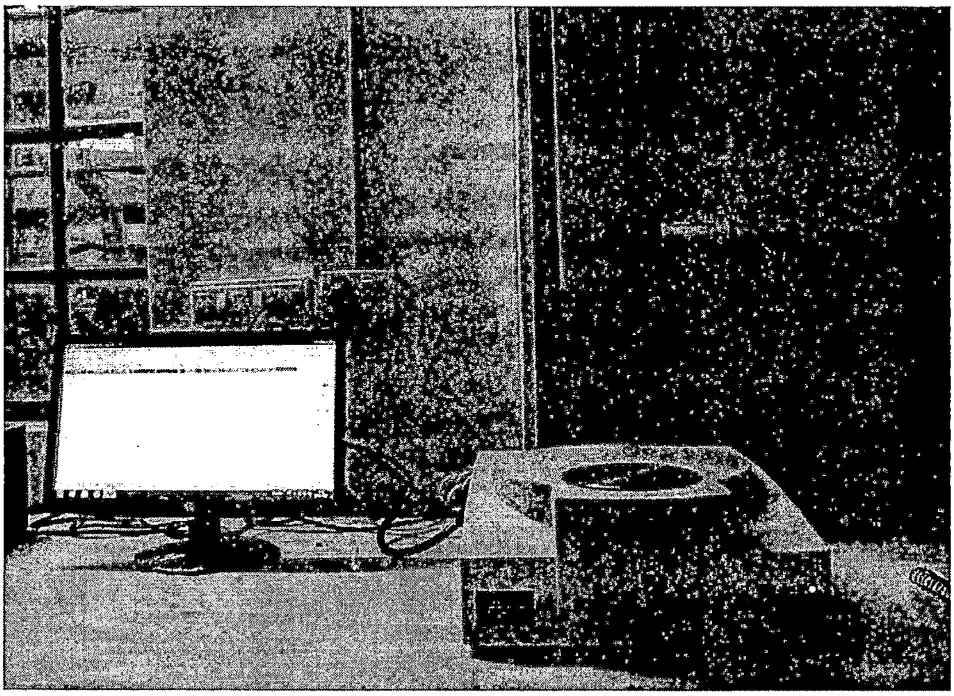

Figure 3.10 Differential Scanning Calorimeter

The thermograph obtained after the test was analyzed and the results were interpreted. The crystallinity percent (*X*) of studied samples was also calculated using the following equation.

$$X = \left(\frac{\Delta H}{(1-w_f)\Delta H^*}\right) \times 100 \quad \text{......................................Equation 3.1}$$

Where,

X = Crystallinity %

w_f = weight fraction of nanocomposite filler,

ΔH = measured melting enthalpy,

ΔH^* = extrapolated value of enthalpy corresponding to 100% crystalline polyamide and polypropylene are 230.1 and 209 J/g respectively [138, 139].

3.3.4.1.5 Rheological measurement (Melt flow index-MFI)

The Melt Flow Index (MFI) of the polymer chips was measured as per ASTM D1238 standard. The MFI was measured using an Extrusion Plastometer manufactured by HEM-TECH CORPORATION shown in figure 3.11. It is a dead-weight piston plastometer consisting of a thermostatically controlled heated steel cylinder with a die at the lower end and a weighted piston operating within the cylinder.

The apparatus was set at 230°C, on attaining the set temperature polymer chips were fed from the top portion of cylinder. The polymer chips were kept for around 5 minutes for melting. After the specified time, the piston rod was inserted in the cylinder and a weight of 2.16 kg was placed above the piston for loading. On attaining a uniform polymer extrusion from the die, the timer was started and the polymer was collected. The timer was stopped when there was discontinuity in polymer extrusion. The collected polymer was weighed and the MFI was calculated as per following equation.

Weight of polymer in "*x*" seconds = *w* gram

So, weight of polymer in 600 seconds = $\frac{w\times600}{x}$ gram ....Equation 3.2

So, MFI = weight of polymer (in gram) extruded in 10 minutes.

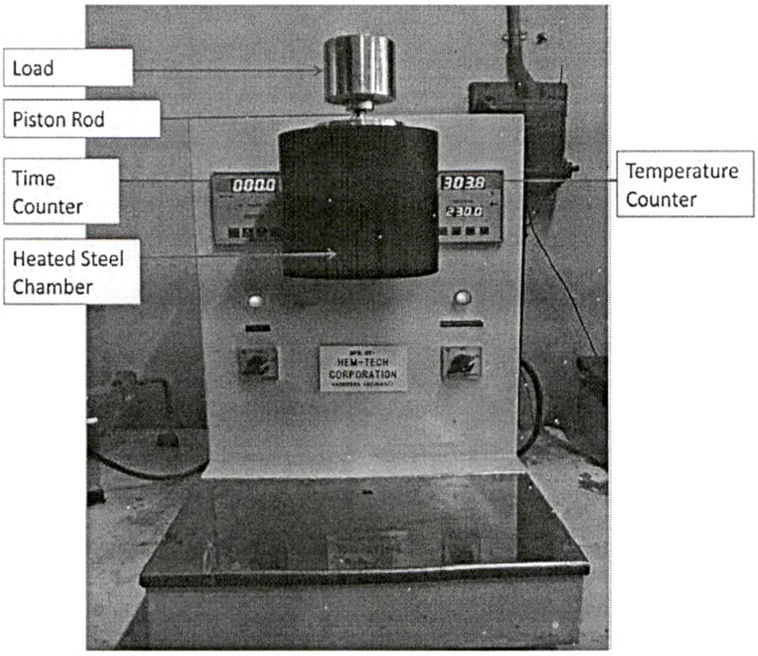

Figure 3.11 Melt Flow Indexer

3.3.4.2 Mechanical Properties

3.3.4.2.1 Tensile strength Tester

Tensile strength in terms of stress and strain of polymer/silica nano composite film, filament and fabric were tested for comparing the effect of incorporation of silica nano particles. Measurements of this physical property was performed on tensile tester (Model: LRX, Lloyd, UK.) in accordance with ASTM D882-02, which works on constant rate of elongation (CRE) principle as shown in figure 3.12. The capacity of the instrument is 0.5 – 2500N while the rate of extension can be varied from 0.1 - 1000 mm/min.

The test was conducted with following specifications:

Film:

- Gauge Length: 20 mm, Width: 25.4 mm, Rate of Extension: 50 mm/min

Filament:

- Gauge Length: 50 mm, Rate of Extension: 100 mm/min,

Fabric:

- Gauge Length: 80 mm, Width: 20 mm, Rate of Extension: 100 mm/min

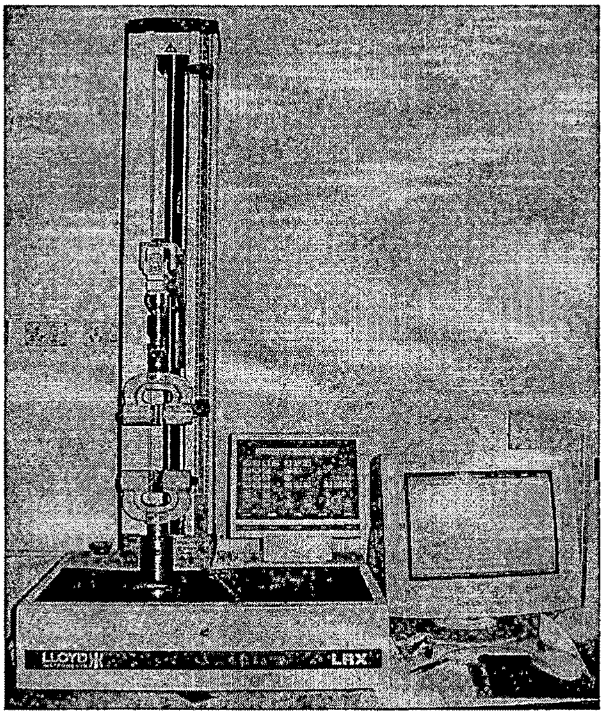

Figure 3.12 Lloyd LRX tensile strength tester

3.3.4.2.2 Tearing Tester

The tearing strength of treated and untreated fabric samples were measured on falling pendulum type tearing strength (Elmendorf) apparatus as per ASTM-D-1424-1996, shown in figure 3.13. The fabric specimen having a size 6 inches x 3 inches (cut slit of 2 cm) was fixed between the two clamps. When the pendulum was in the raised position, then it was released. The fabric gets teared off across its width. The force required for tearing the fabric, was indicated by the pointer on scale. The testing was carried out in standard atmospheric condition, the tearing strength of fabric measured separately for warp and weft direction. The tearing strength was calculated using following equation.

$$F = R.S. \times \frac{C.S.}{100} \qquad \text{.................................Equation 3.3}$$

Where,

F = Tearing force in gf

R.S. = Scale reading

C.S. = Full scale capacity in gf

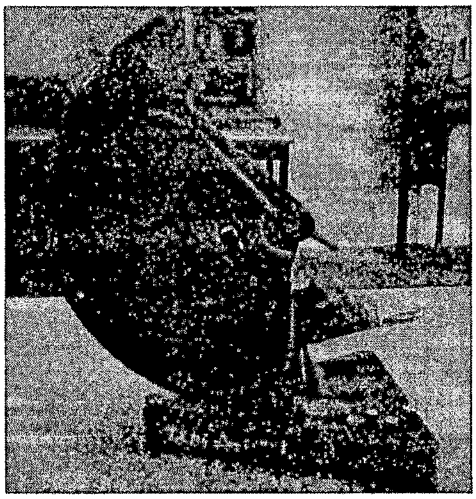

Figure 3.13 Elmendorf tearing tester

3.3.4.2.3 Crease recovery tester

Shirley Crease Recovery tester principle was used for the measurement of crease recovery angle after creasing under standard load as shown in figure 3.14. Standard weight of 2 kilogram was applied for one minute for crease formation to the strips conditioned at standard atmosphere.

Three Specimens each in warp and three weft way were taken, each of size 2 inch x 1 inch were tested. Average of three was considered. The test was performed as per AATCC test method 66-2003, AATCC Technical Manual /2006, page: 95.

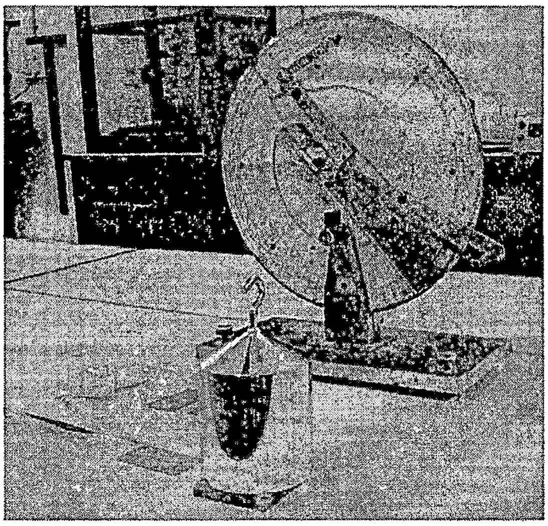

Figure 3.14 Crease recovery tester