Chapter 3

EXPERIMENTAL STUDIES

3.1 Objective of the Study

Although previous membrane separation method of concentrating any form of natural lattices was confined only to epoxidised natural rubber (ENR), with a suitable preservation system the feasibility of concentrating natural rubber latex was investigated. This is further enhanced by the availability of membrane material: PVDF, that has a high chemical resistance and suitable to be used for a highly alkaline feed. Of all the membrane separation processes ultrafiltration was found to be more suitable for this process due to the fact that natural rubber latex has a wide range of molecular weight distribution and also has a high solid content.

This study therefore focuses solely on establishing the possibility of using ultrafiltration as an alternate method of concentrating natural rubber field latex. Thus the specific objectives of this investigation are:

i.   To identify a suitable composite preservation system between two available options

ii.   To study the effects of feed flow-rate and TMP on permeate flux.

iii. To identify the optimum TMP for the concentration process

iv.   To determine the degree of concentration achievable

3.2 Research methodology

A flow chart (Figure 3.1) illustrates the research methodology for this study. Two types of feed material were investigated. The first type consists of 10 different latex samples which are sold on a commercial basis to the latex product manufacturing factories. The laboratory scale experiment conducted on these samples includes determining particle size, zeta potential, pH and viscosity.

The second type of feed material consists of 12 samples of actual natural rubber field latex each weighing 20kg. One of the two types of latex preservatives to be evaluated was added to these samples and ultrafiltration runs were carried out. For each of the 10 samples used as the feed material, the following tests were carried out: dry rubber content, total solid contents, pH and volatile fatty acid number. The tests were carried out both before and after ultrafiltration runs.

The experimental rig consists of a tubular cross flow ultrafiltration system designed and assembled for the ultrafiltration of 20kg latex sample. During ultrafiltration run, the parameters investigated include the following: the system running procedure; membrane cleaning procedure; water-flux tests; cleaning in place technique; and cleaning protocol. From these investigations, the objectives of the study mentioned earlier were determined.
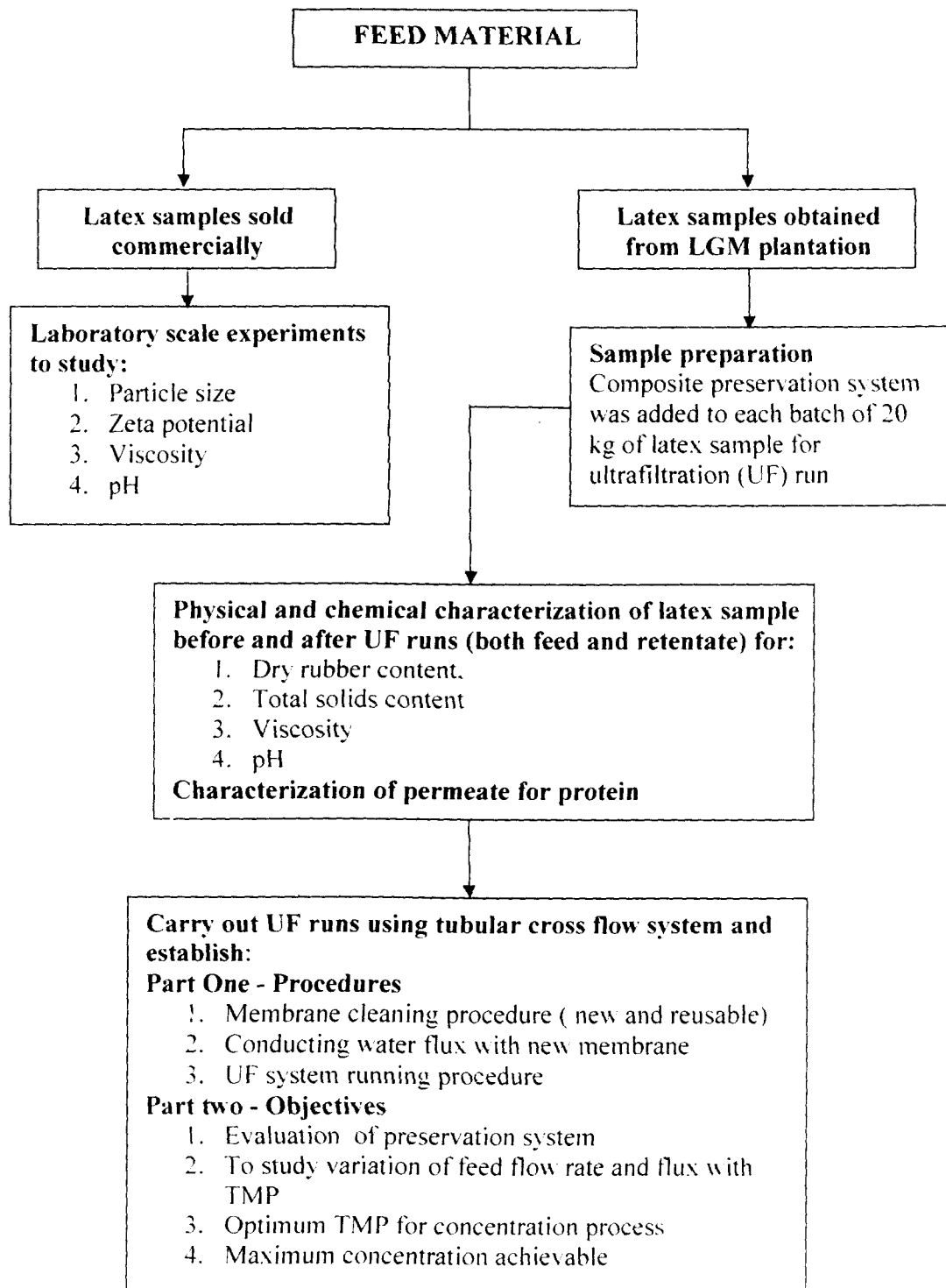
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┌─────────────────────────────────┐
│          FEED MATERIAL          │
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FEED MATERIAL

Latex samples sold commercially

Latex samples obtained from LGM plantation

Laboratory scale experiments to study:
1. Particle size
2. Zeta potential
3. Viscosity
4. pH

Sample preparation
Composite preservation system was added to each batch of 20 kg of latex sample for ultrafiltration (UF) run

Physical and chemical characterization of latex sample before and after UF runs (both feed and retentate) for:
1. Dry rubber content.
2. Total solids content
3. Viscosity
4. pH

Characterization of permeate for protein

Carry out UF runs using tubular cross flow system and establish:

Part One - Procedures
1. Membrane cleaning procedure (new and reusable)
2. Conducting water flux with new membrane
3. UF system running procedure

Part two - Objectives
1. Evaluation of preservation system
2. To study variation of feed flow rate and flux with TMP
3. Optimum TMP for concentration process
4. Maximum concentration achievable

Figure 3.1 - Flow chart illustrating research methodology

3.3 Feed material

3.3.1 Feed material for laboratory scale experiments

Feed material for laboratory scale experiments consists of commercially available latex samples which were obtained from various sources where it was used as an industrial raw material for the manufacturing of latex products. The list of latex samples used is as given below:

i.   Fresh field latex (3 hrs after tapping)

ii.   Low ammonia (0.4%) preserved field latex (30% DRC)

iii.   High ammonia (1.0%) preserved field latex (30% DRC)

iv.   High ammonia latex concentrate (60% DRC)

v.   Low ammonia, tetra methyl thiuram di sulphite (TMTD) and zinc oxide preserved latex concentrate (60% DRC) [LA TZ latex concentrate]

vi.   25% Epoxidised natural latex (ENR 25) latex concentrate (55% DRC)

vii.   ENR 50 latex before concentration by UF (26% DRC):

viii. ENR 50 (59%DRC) latex concentrate after concentration by UF

ix.   ENR60 (26%DRC)

x.   Nitrile rubber latex type 48/4D

One liter of each of these samples was used to carry out the following tests: particle size, zeta potentials, pH and viscosity.

3.3.2 Feed material for ultrafiltration runs

For subsequent experiment involving pilot-plant ultrafiltration experiments, natural rubber latex was obtained from Rubber Research Institute Experiment Station (RRIES) of multi-clone type. The RRIES rubber plantation is planted with rubber

trees with different clones. Each clone has its distinctive character. Latex collected from various sections of the plantation is bulked as it arrives at the factory so as to minimize the clonal characteristics differences. The latex. which arrives from the field in big containers. is poured. into a bulking tank. 20 kg of latex was withdrawn from the bulking tank. The dry rubber weight of the latex was determined for the formulation of preservation system. One of the two preservation systems to be evaluated was added and left overnight for maturation. Two samples were prepared for each preservation system adding up to a total of 4 samples (for Experiment UF1). Variation in latex properties such as viscosity and DRC for latex samples prepared using field latex from the same source for subsequent experiments on different days would not bring about appreciable inconsistencies [1-3].

3.4 Composite preservation system

3.4.1 Preservation system 1 (PS1)

This preservation system consists of a mixture of chemicals (% by weight) of primary preservative of 1.0 % of ammonia and secondary preservatives of 0.1% ammonium laurate (from 10 % solution) with 0.025%TMTD/ zinc oxide (from 50% dispersion with a ratio of 1:1).

Field latex treated with Preservation System 1 remained stable during the centrifugation process. rotating at a speed of about 7000 r.p.m.. with an average centrifugal force equivalent to about 8000G being exerted on the latex particles and causing the latex to separate into two fractions during latex concentrate production as described in section 2.3.1.

3.4.2 Preservation system 2 (PS2)

Preservation System 2 consists of a primary preservative of 0.5% of ammonia and a secondary preservative of 3 parts per hundreds of Teric 16A16 (commercial name) flake non-ionic surfactant (stabilizer and wetter for latex). This preservation system was administered during the concentration of ENR latex using plant frame type of ultrafiltration equipment as. described in section 2.19.1.
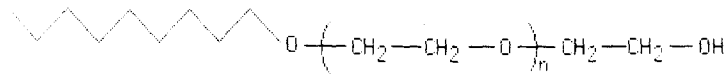
Basic molecule structure of Primary Alcohol Ethoxylates (PAE)

Figure 3.2 Molecular Structure of Teric 16A16 [K]

3.5 Physical and chemical characterization

3.5.1 Analytical methods

Latex samples prepared for ultrafiltration runs were characterized by testing its properties of dry rubber content (DRC). total solids content (TS). pH and viscosity. These analyses were performed in accordance with procedures described in Section 2.6. which follows that of MS 281/ASTM D 1076. The full descriptions of the procedures are given below.

3.5.1.1 Dry rubber content test (DRC)

Weighing by difference was done from a weighing bottle to a dish to the nearest 1 mg: $10g \pm 1g$ of latex sample. 5 cm^3 of 20g dm^3 acetic acid solution was

poured down the inside edge of the dish and the dish was rotated slowly while the acid was being added. The acid was added to coagulate the latex sample. The coagulated sheet of rubber was gently depressed below the surface of the acid. A watch glass was placed on the dish and heated on a steam bath for 15 min to 30 min. The coagulated rubber was removed from the dish and placed on a clean stainless surface. The rubber was pressed to a uniform sheet against the stainless surface using a roller to a thickness not exceeding 2 mm. The sheet was thoroughly rinsed in running water for 15 min. The rinsed sheet was let to drip for a few minutes before it was transferred to a drying oven. The sheet was dried in an oven at a temperature of 70°C ±2°C until it had no white patches. The dried sheet was cooled in a desiccator and weighed. The operation of the drying, cooling and weighing was repeated until the loss in mass was less than 1 mg after heating for 30 min.

3.5.1.2 Determination of total solid contents (TSC)

An empty dish was weighed to the nearest 1 mg together with its cover. 2.0 g ± 0.5 g latex sample was poured by replacing the cover and weighed to the nearest 1 mg. The contents of the dish were swirled gently to ensure that the latex covered the bottom. The dish was placed uncovered in the oven by placing it horizontally and heated at 105°C ±2°C for 2 hrs until it had lost its whiteness. It was then allowed to cool to ambient temperature in the dessicator. The cover was replaced and weighed. The dish was returned to the oven uncovered for 15 min. It was then allowed to cool to ambient temperature in the desiccators. The cover was replaced and reweighed. The drying procedure at intervals of 15 min. was repeated until the two successive weighing were less than 1 mg.

The total rubber solids content (TSC) expressed as a percentage by mass. using the formula:

$$TSC = M_1/M_0 . 100 \hspace{4cm} (3.1)$$

Where: M_0 = the mass of the test portion (gm)

M_1 = the mass of the dried material (gm)

The results of duplicate determinations shall not differ by more than 0.2% by mass.

3.5.1.3 Viscosity

The viscosity of the samples was determined using a Brookfield Viscometer Model LVF with spindle no. 2 at a rotation of 60 rpm. The results are expressed in centipoises (cP). Latex sample of weight 200 g was placed in a special stainless steel beaker. The beaker was covered with a watch glass and placed in a water-bath of 25 °C until an equilibrium temperature was reached. A guard and spindle No. 2 was attached to the viscometer. The viscometer was leveled and the spindle was lowered into the latex until the surface of the latex was level with the groove marked on the spindle. The spindle was placed at the centre of the beaker. The speed 6 rpm was selected. with the clutch depressed. the motor was switched on. The clutch was released and the dial was allowed to rotate until a steady reading was obtained. Reading was taken by depressing the clutch and switching off the motor. The clutch was released only after the reading was taken. This procedure was repeated for a second reading. The procedure was also repeated at 30 and 60 rpm (spindle No. 3 was used if the viscometer readings were too high. and spindle No. 1 if they were too low).

The Brookfield viscosity in centipoises was calculated by multiplying the dial readings by the factors for various spindles as shown in Table 3.1.

Table 3.1- Multiplying factors for spindle number and speed

Spindle No.	Speed (r.p.m)		
	6	30	60
1	10	2	1
2	50	10	5
3	200	40	20
4	1000	200	100

3.5.1.4 pH determination

The pH meter (Model Radiometer PHM 92) was calibrated according to the manufacturer's instruction manual. Calibration using aqueous solutions to read the known pH is the standard procedure. Buffer standard solutions of pH 4.01, 7.01 and 10.01 were used for calibration at room temperature. After the calibration procedure the electrode of the pH meter was washed with water and, wiped dry with soft absorbent paper.

Sufficient latex was weighed to give 50 g total solids into a 250 ml beaker. The weight of latex required is

$$W = \frac{50x100}{TS} \tag{3.2}$$

Where: TS = total solids content.

Clean electrode was lowered into the latex, where the electrode remained without touching the beaker. The knob of the pH meter was turned on from "zero" to "read" and the pH reading was taken. The procedure was repeated until a constant reading was obtained. The electrode was removed from the latex sample and washed with deionised water until the electrode was free of latex and wiped dry with soft absorbent paper before dipping into a buffer solution of pH 7.01.

3.5.2 Laboratory scale experiments

The details of laboratory scale experiments as mentioned in section 3.3.1 are as follows. Besides testing these samples for viscosity (see section 3.5.1.3) and pH (see section 3.5.1.4) other test parameters include the following:

3.5.2.1 Particle size

Ultrafiltration is a low-pressure (1 – 10 bar) membrane process, which relies on particle size as the primary factor affecting separation. The particle size values were important to select suitable membrane with a required pore size and also to investigate the effect and variation in particle size during preservation and concentration of the latex.

The particle size determination of the commercial latex samples (list mentioned in section 3.3.1) was determined using a particle size analyzer (SHIMADZU SALD-2001-WEA2:V1.00).

The operation started with the rinsing of the flow cell and stirrer bath. The stirrer bath was filled with pure water which is a dispersing medium. File name, sample ID and sample number were entered. The blank was measured. The latex sample was introduced into the stirrer bath. Pure water was added for dilution and dispersion so as to create a most suitable measuring condition. Ultrasonic was radiated if the sample got agglomerated. The particle size measuring analysis commenced when illuminating laser beam into the particles contained in the suspension generates the light-intensity-distribution data. These data were stored in the computer memory. The particle-size-distribution data were calculated from the light intensity distribution data which was displayed on the console screen. The particle-size-

distribution data was saved in the computer as a copy and the results were printed out.

3.5.2.2 Zeta potential

Zeta potential is the overall charge a particle acquires in a particular medium. It depends on both the nature of the surface and dispersant. Small changes in the pH or concentration of ions can lead to drastic changes to zeta potentials. If all particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability. If particles have low zeta potential then there is no force to prevent the particle coming together and there is dispersion instability.

In general, the higher the value of zeta potential the more stable the particle dispersion is likely to be. The dividing line between an aqueous particle dispersion being stable and not being stable is considered to be +30mV or –30mV. So if the entire particle has a zeta potential which is more negative than –30mV or more positive than +30mV the dispersion should remain stable. Studying the effect of pH, conductivity or concentration of an additive on the zeta potential of dispersion can lead to greater understanding of the mechanism of dispersion stability.

A zeta potentiometer, Zetamaster (Malvern Model ZEM 5002 Australia) is used to measure the zeta potential of samples dispersed or suspended in a polar dispersant. The Zetamaster operates by detecting light scattered from a suspension of particles (usually in the size range 5 nm – 5000 nm) and interprets the spectrum to extract a measurement of the velocity of the particles in the direction of applied electric field. This velocity arises from the presence of a charge on the individual particle. This velocity measurement is used to determine the sign of the charges on the particles

and also the electrophoretic property. The mobility is related to the surface charge and zeta potential.

Samples on the Zetamaster are dispersions of a particulate phase in a suspending liquid which need to be polar like water. Once suitable sample dispersion was achieved the sample was injected into the cell from the sample entry port. Care was taken not to introduce air bubble into the cell. In the analysis, about 5 ml. of the sample is injected into a cleared electrophoresis cell. For each sample an average of 6 readings was taken. The best check for a correct functioning system is to use the AZ55 electrophoresis standard. This comprises carboxylated polystyrene latex dispersed in a 0.20M phosphate buffer at pH7.

3.5.2.3 Scanning electron microscope (SEM) analysis of latex particle distribution

JSM-5300 JEOL Scanning Electron Microscope was used to study the particle distribution of preserved latex. For this study, latex preserved using preservation system PS1 was used. This preservation system is very commonly used to stabilize latex for concentration using centrifugation to prepare latex raw material for glove factories.

One part of latex was diluted 20 times with distilled water and shaken thoroughly. A few drops of the latex suspension was placed in a specimen tube and fixed with 2% of osmium tetroxide solution for 2 hours. It was then centrifuged for 10 minutes at 5000g and the supernatant was removed. A drop of supernatant suspension was placed onto the specimen stub which has an ultra thin layer of gold which provides a conducting layer that permits SEM examination.

3.6 Design of the experimental set-up

3.6.1 Experimental apparatus

The schematic diagram of the semi-pilot scale unit of the set-up is shown as in Figure 3.3 and a photograph of it as in Figure 3.4. This unit was fabricated and supplied by Solution Engineering Sdn. Bhd. The following is a list of major components of the system.

3.6.1.1 Piping

The flow line piping is of stainless steel with an OD of ½" tubes have been incorporated into many joints to enable the system to be opened in order to clean whenever blockages occur.

3.6.1.2 Feed pump

This unit is supplied with a diaphragm feed pump (Sand Piper Model (EB ½ - A Type). It works on air supply pressure not exceeding 100 psi (6.89 bar) and connected to compressed air supply of 6 bar[39].

3.6.1.3 Tanks

The unit was supplied with two aluminium tanks. A feed tank and a back wash tank both of 50 litres capacity. The back wash tank was for storing deionised water for cleaning purposes. A two-way ball valve V6 connects both the tanks. At the end of each UF run, the backwash tank valve V5 and valve V6 were both opened to let in deionised water into the system for cleaning operation.

3.6.1.4 Membrane module

A tubular membrane interchangeable module (Model MICRO 240) encased in a stainless steel housing was obtained from PCI Membrane Systems Ltd. (United Kingdom). The system consists of 2 tubes connected in series by special cap ends. with each measuring 0.4 m in length and 12 mm inside diameter. The membrane material is polyvinylidene fluoride with a 100.000 MWCO and an effective membrane area of 0.024 m^2.

3.6.1.5 Valves

The system consists of 6 units of $\frac{1}{2}$" stainless steel housing ball valves. Valve V1 was a by-pass valve so that excess volume and pressure capacity would be diverted and recycled back to the feed tank. Valve V2 was installed so that permeates could be collected. The weight of the sample permeates collected. down stream of valve V2 was registered using a digital scale connected to a computer. Permeate is collected directly onto a digital balance and the reading shown in the PC was recorded. The retentate is recycled back into the feed tank. The feed flow rate is measured manually as it enters the feed tank. Ball valve V3 was used to generate back pressure in order to obtain the required TMP. Valve V4 was used to collect retentate samples for chemical analyses and to drain off the final concentrated latex into containers. Valves V5 and V6 were to let in deionised water from the washing tank into the system for cleaning purposes at the end of a UF run.

3.6.1.6 Pre-filter

The plant is equipped with a "Y" strainer in the line from the feed tank to feed pump. The strainer fitted was of size 250 μm. It is necessary to remove or pre filter particles of coagulants that were usually found in latex (feed solution) before it enters the membrane module.

3.6.1.7 Pressure gauges

There were two oil-filled types of pressure gauges in the system. They are both graduated from 0 – 10 bar with a 0.2 bar divisions.
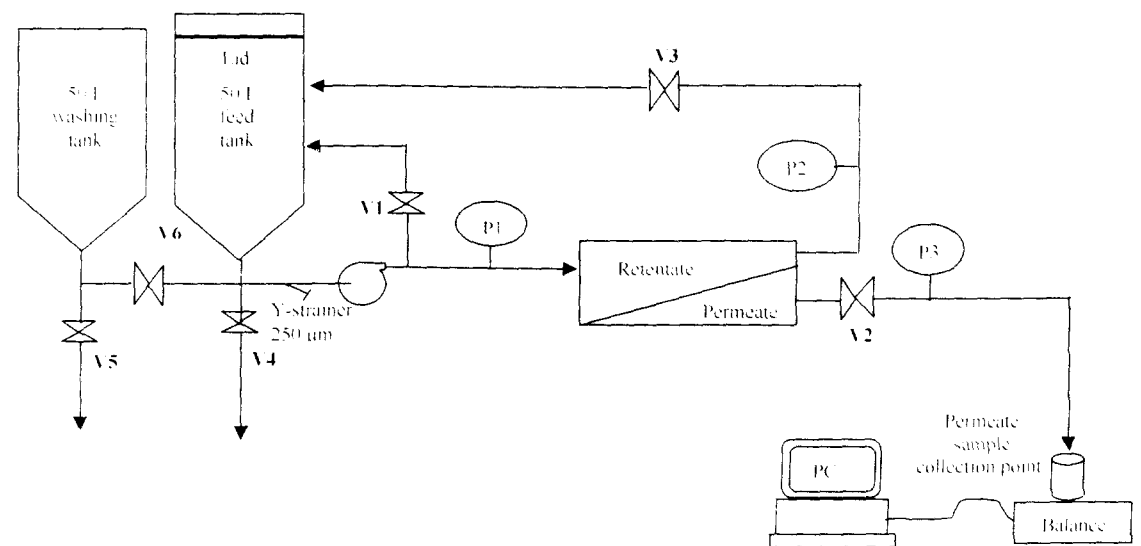

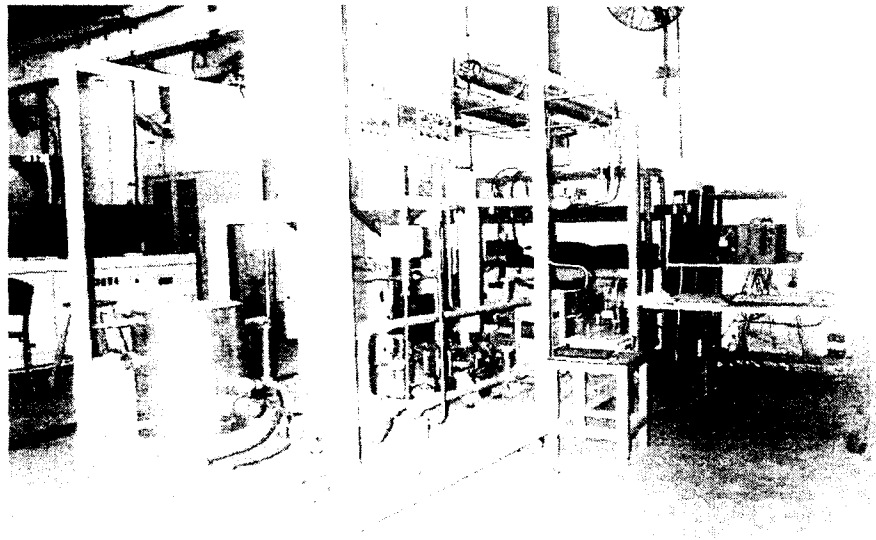Figure 3.3 Schematic diagram of tubular ultrafiltration system

Figure 3.4 Experimental setup

3.6.2 Choice feed pump

Of the many types of pumps available. those having regions in which the fluid is subjected to a high rate of shear strain. and those having regions of sliding contact. are generally unsuitable for use with lattices. because colloidal destabilization of the latex may occur in these regions. Not only may the latex thereby become contaminated with lumps of coagulum: it is also possible that blockage and seizure of the pump may occur. A further subsidiary requirement is that the pump should not introduce significant quantities of air into the latex. These considerations tend to restrict the designer of latex-processing plant to pumps of the centrifugal. single-screw. and diaphragm types.

External-gear pump is not suitable as the spaces between the teeth become filled on the suction side of the pump. and emptied at the discharge side by a squeezing action. The grinding action between opposing gear teeth can be sufficient to cause

serious colloidal destabilization of lattices. The friction between the gear teeth and casing also has similar, though less drastic, effect. Other pumps which are unsuitable to pump lattices include: internal-gear pump, sliding-vane pump and reciprocating-piston pump. The pumps which are suitable for pumping lattices includes: (i) radial-flow single-volute centrifugal pump, (ii) single-screw rotary pump and (iii) diaphragm pump [2].

3.6.3 Choice of membrane module and material

The membrane used was made of polyvinylidene fluoride type FP100 PVDF. It has an apparent retention character of 100,000 MWCO with an effective membrane area of 0.024 m². The module consists of 2 tubes connected in series by special cap ends with each tube measuring 0.4 meter in length and 12mm inside diameter. From the manufacturer's literature, the membrane can be ideally used in an environment of pH ranging between1.5 – 12. This aspect enables the use of cleaning solutions comprising 0.3% nitric acid with a pH of 2 or 0.2% (0.05M) of sodium hydroxide (NaOH) with pH of 12. It functions well with the transmembrane pressure not exceeding 10 bars and temperature below 80°C. The hydrophilicity is rather low, which is a disadvantage factor when used for ultrafiltration applications with latex.

3.6.3.1 Membrane storage

The manufacturer has recommended for the first time use of membrane, it should be cleaned by running the system with 0.3% of nitric acid (approximately pH 2) so as to wash off preservative solution covering the membrane. The cleaning process involved running the system with this cleaning solution at a TMP of 3 bars

for about an hour followed by 0.2% (0.05M) of NaOH for 20 minutes. Membranes in the preservative solution could be stored for up to 1 year in temperatures ranging from -4°C to 30°C. The used membranes were cleaned and preserved in solutions of 0.25% meta-bisulphate [37]. This solution would be able to preserve the membrane for one month. The membrane must never be left dry as a drying membrane experiences structural stress that could cause the internal membrane pore structures to collapse. If the membrane was required to be stored in the module, it should be ensured that the membrane remains wet and there is liquid in the module. When left in the system for the following day's run, it must be packed with DI water in the membrane module by closing the appropriate valves. For membrane storage over the weekend, the membranes were taken out and submerged in DI water.

3.6.3.2 Analysis of membrane by SEM

JSM-5300 JEOL Scanning Electron Microscope was used to view the unused surface morphology as well as the cross section of the membrane FP100. In using SEM to view the surface morphology, the membrane sample has undergone several sample preparation steps. The cut piece of membrane was attached to the stubs with double sided-tape. Specimen was prepared for SEM examination by evaporative coating with ultra-thin layer of gold under high vacuum. This provides a conducting layer that permits SEM examination. The viewing angle under study was 10^c at 17mm of working distance.

3.7 Experimental Procedure

3.7.1 Sample preparation

Samples for ultrafiltration runs were prepared as mentioned in section 3.3.2. One of the two preservation systems. i.e. either Preservation System 1 or 2 as described in section 3.4 was added and left overnight for maturation. Only one sample was prepared each time.

3.7.2 Water flux test

The water flux test was carried out each time before the commencement of any experiment. The membrane was first cleaned. using 0.2% NaOH solution followed by rinsing the system with DI water and draining it off. Thirty litres of fresh DI was then fed into the feed tank. The process pump was turned on with valve V3 fully open and valves V2 and V4 fully closed. Valve V1 had been preset and required no adjustment. The system was left to stabilize for 20 minutes with the TMP being zero.

This step was then followed by the determination of water flux at various transmembrane pressures. The water flux was initiated by opening fully valve V2 and adjusting (throttling) Valve V3 until the required TMP was obtained. The water flux test consisted of a series of tests with different TMPs in sequence of 1.0 barg. 2.0 barg. 3.0 barg. 4.0 barg and 5.0 barg. At various TMP. the permeate was collected directly into a container on a digital balance and the readings recorded by the PC. Before each test data was collected. the membrane was allowed to adjust to the new TMP for about 10 minutes. For subsequent TMPs the valve V3 was throttled in order to generate the required TMP.

Water flux test result conducted on an unused membrane was used as a control and should be compared with water flux test conducted after using the membrane. Graphs of flux versus TMP were plotted for selected water flux tests. The slope of water flux graph of the unused membrane gives the L_p value (see section 2.15.2.1). defined as the pure water permeability of the fresh membrane. The values of L_p was used as a control and compared with the slope of water flux test graph conducted after using the membrane. Variations in water flux of more than 20% indicate that the membrane was fouled. Further cleaning was necessary. In this case the membrane should be further cleaned or replaced [25].

3.7.3 Cleaning of membrane system

After the end of each run. the retentate from the feed tank was drained off by opening valve V4 allowing the recycled (retentate) latex to flow through the pipe and rubber hose into a container to be stored. As valves V2 and V3 remained fully opened the latex remaining in the pipes of the system was thus drained out. It was also necessary to disconnect certain parts of piping to enable removal of any latex trapped in the most inaccessible part of the system. Using this procedure the system was left free of any remnant latex.

The cleaning up phase of the experiment was immediately initiated by releasing the DI water stored in the backwash tank into the system with the feed pump turned on. With all valves opened the DI water was circulated for 30 minutes to flush out the system of any remnant latex. After 30 minutes of circulation the feed pump was stopped and the 'contaminated' DI water was drained out. This process was repeated twice with fresh supply of DI water until the recycled water was free of latex and

milky appearance. As a final cleaning step, 30 litres of 0.2% sodium hydroxide solution was circulated into the system for 30 minutes. At the end of that period the cleaning solution was drained off and 30 liters of fresh DI water was introduced into system to rinse the system of the 'membrane cleaning solution'(0.2% NaOH) with the feed pump turned on for 15 minutes. At the end of the 15 minutes, the retentate valve V3 and permeate valve V2 were closed so as to keep the DI water trapped in the membrane system. This is to keep the membrane system wet and protected so as to continue further experiments the following day.

3.8 Ultrafiltration experiments

3.8.1 Experiment to identify a suitable composite preservation system between two available options (UF1)

Once the cleaning of the UF system and water flux tests were performed on the membrane, preserved latex was fed into the feed tank after being sieved manually using 200-micron sieve to remove any small pieces of coagulum. The sieve was weighed before and after sieving so as to determine the mass of coagulum found in the preserved latex sample. The feed pump was then turned on to circulate the latex. At this stage valves V2 and V4 were fully closed. Circulation was maintained for 20 minutes before settling the system to a pre-selected TMP. This is achieved by valve V2 fully opened and valve V3 was throttled until the required TMP was read from the pressure gauges. The system has to be stabilized for about 20 minutes at the required TMP so that the membrane was fully soaked with the latex. Permeate collection was carried out after a 20 minutes wait. For each TMP, the permeate was collected for a predetermined time and was directly collected into a container, which

was placed on a digital balance and attached to a PC where the mass was recorded. The digital balance continuously monitored the mass of the permeate collected. The process was repeated at TMPs of 2.5, 3, 4, 5 and 5.5 bar and the corresponding permeate mass recorded accordingly. This set of experiments consisted of 4 UF runs using 4 different samples of feed and preservative (DV/UF/04, DV/UF/05, DV/UF/06 and DV/UF/07). Each sample feed weighed 20 kg preserved latex using 2 different preservation systems which are to be evaluated. The summary of Experiment UF1 is as shown in Table 3.2 and the details are recorded in the experimental raw data 1, 2, 3 and 4 in Appendix A.

At the beginning and the end of each UF run one litre of the sample was removed from the prepared samples after manual sieving before placing in the feed tank as well as from the retentate in the feed tank after each run respectively for the determination of DRC, TSC and pH.

Table 3.2 Summary of Experiment UF1

Latex sample reference	Type of preservation	Date of UF run
DV/UF/04	Preservation system 1	27.2.2001
DV/UF/05	Preservation system 2	28.2.2001
DV/UF/06	Preservation system 1	02.3.2001
DV/UF/07	Preservation system 2	15.3.2001

3.8.2 Experiment to study effects of feed flow rate and TMP on permeate flux characteristics (UF2)

For this series of experiments, the TMP was fixed by throttling valve V3. Once it was adjusted to the required TMP it was maintained at this value, a series of different feed flow rates were obtained by adjusting by-pass valve V1.

Corresponding variations in permeate flux was recorded. For each fixed TMP four pairs of feed flow rate and permeate flux were obtained. Starting with a TMP of 2 barg the experiment was repeated for 3, 4 and 5 barg. Feed for this experiment with sample reference: DV/UF/09 was preserved with Preservation System 1. The details were recorded in experimental raw data 6 of Appendix A

Table 3.3 Summary of Experiment UF2

Latex sample reference	Type of preservation	Fixed TMP values (bar)
DV/UF/09	Preservation system 1	2.3.4 and 5. Each TMP value to have four sets of permeate flux and feed flow rate readings

3.8.3 Experiment to identify optimum TMP for concentration process (UF3)

For this experiment, cleaning and the initialization of the UF system is the same as for experiment UF1. The feed is a sample of 20 kg latex preserved with a preservation system PS1.

The system was stabilized for about 20 minutes at a TMP value of 1 bar so as to make the membrane fully soak with the latex. Permeate collection was carried out after a 20 minutes wait. For each TMP, the permeate was collected for 30 minutes directly collected into a container, which was placed on a digital balance and attached to a PC where the mass was recorded. However, before proceeding to the next TMP the process pump was stopped, the latex was drained, cleaning procedure for the system and membrane was followed. Once these sequences were completed the TMP was adjusted to the next higher value. Starting with a TMP of 1 barg, the

whole procedure was repeated for 2. 3. 4 and 5 barg and the corresponding permeate fluxes were obtained.

For each TMP. care was taken so as to make sure the system was stabilized for a predetermined time before reading was taken The membrane cleaning process for every subsequent change in TMP was to ensure the membrane was free from gel layer and concentration polarization as a result of previous TMP influence.

Experiment UF3 was carried out using sample reference DV/UF/10 and repeated with sample reference DV/UF/11 with preservation system PS1. The summary of Experiment UF3 is as shown in Table 3.4. The details of the experiment were reported in experimental raw data 7 and 8 in Appendix A

The optimum TMP was calculated from results of this experiment and used in the following Experiment (UF4).

Table 3.4 Summary of Experiment UF3

Latex sample reference	Type of preservation	TMP values (bar)
DV/UF/10 DV/UF/11	Preservation system PS 1	1.2.3.4 and 5. Stopping and cleaning up the system for each TMP value

3.8.4 Experiment to determine degree of concentration achievable (UF4)

After performing the membrane cleaning procedure and water flux test done. 20 kg of preserved latex (PS1) with sample reference DV/UF/12 was fed into feed tank. The feed pump was turned on to circulate the feed for about 10 minutes. The optimum TMP value obtained from experiment UF3 was set by throttling valve V3.

The system was left to stabilize for 20 minutes before commencing the experiment. From then on, the reading of permeate was taken every hour with the TMP at optimum value. The last reading was taken after 7½ hours when the Polymer Processing Laboratory was closed for the day (9am to 4.30pm). After the last reading was taken the pump was stopped and the retentate was drained off into a container. Only rinsing of the system with DI water procedure was followed with the membrane system left soaking in DI water for the night.

The following day the rinsing DI water was drained off and the retentate from the previous day was fed into the feed tank. The whole procedure was followed for the 2nd and subsequently for the 3rd day. The concentration process was carried out for a total of 20 hours covering a period of 2½ days. Throughout the duration of Experiment UF4, the TMP was maintained at the optimum value. The summary of Experiment UF4 is as shown in Table 3.5. The details of the experiment were reported in experimental raw data 9 in Appendix A.

Table 3.5 Summary of Experiment UF4

Latex sample reference	Type of preservation	Permeate flux
DV/UF/12	Preservation system 1	Permeate flux calculated for every hour of concentration, for 21 hours covering a period 2½ days (working hours)

3.9 Chemical analysis for retentate and permeate

For all ultrafiltration experiments, samples of latex collected from the feed and retentate were analysed for DRC, TSC and pH as mentioned in section 3.5.1 while

the permeate was analysed for protein. Brief description of the procedure of protein analysis as given below:

3.9.1 Determination of total protein content of the permeate

The total protein content of permeates were carried out using the ASTM D5712 -99 or OVBM method.

Assuming the protein concentration of the natural rubber latex serum to be 10,000μg/ml. dilution of the serum was carried out with 25 milli mole of phosphate buffer solution (PBS). 1 ml of the serum was diluted 10 times by making up the volume to 10 ml with PBS so as to get a concentration of 1000 μg/ml. Subsequently further dilutions were carried out to get concentrations of 100 μg/ml. 50 μg/ml. 25 μg/ml. 12.5 μg/ml and 6.25 μg/ml respectively.

Acid precipitation

Acid precipitation was carried out to remove substances that may interfere with the assay. 1 ml of diluted serum was transferred to 1.5ml polypropylene micro-centrifuge tubes and precipitation was carried out by adding 100 μl of 0.15% Sodium Deoxycholate to all the above samples i.e. diluted serum samples. blanks and Ovalbumin Standards. Mixing was done using vortex mixer and allowed to stand for 10 minutes. Freshly prepared 200 ml of solution. 50:50 ratio trichloroacetic acid and phosphoric acid (both 72%) were mixed using vortex mixer and allowed to stand for 30 minutes. The acid precipitates were centrifuged for 15 minutes at 6000G. Then

the supernatant were decanted. The protein pellets were redissolved using 250 µl of 0.2M sodium hydroxide to obtain a clear solution.

Colour development

Redissolved samples of 400 µl were transferred into micro-centrifuge tubes. 830 µl of alkaline copper tartrate was added and mixed well and left at room temperature for 15 minutes followed by the addition of 100 µl of diluted foline phenol solution. There above components were mixed thoroughly and left at room temperature for 30 minutes as well. The absorbance was measured using a UV – VIS Spectrophotometer Model Shimadzu UV – 1601 (PC) S 220V.

Calculation

The spectro-photometric absorbance measurement of the re dissolved ovalbumin standards at various concentrations were plotted on the ordinate against their concentrations in µg/ml on the abscissa. The calibration curve is linear over the protein concentrations ranging from 0 µg/ml to 200 µg/ml. The calibration data should be curve-fit to a second degree polynomial function and forced through the origin of the plot.

The concentration of the protein in the sample was read from calibration curve in µg/ml. The absorbance of the samples were taken only from the linear range of 10 µg/ml to 100 µg/ml. Using the dilution factor the actual concentration of the serum samples were obtained.