CHAPTER 1
GENERAL INTRODUCTION

1.1 REVIEW OF THE PREVIOUS WORK:

The natural plant fibres such as Jute, Ramie and Cotton are organic polymers. These fibres have potential importance in textile and in other industrial fields as well.

For Jute fibre, Jute stems have to be retted in water in order to free the bark and to loosen the fibres from the gummy and other adhering materials. After the retting is completed the fibre has to be stripped from the Jute stems. Then the fibre is to be washed in clean water and dried in the Sun. This bast fibre (Jute) contains substances as follows:

- Cellulose - 60.5%, Hemicellulose - 23.0%, Lignin - 13.3%, Ash - 1.6% and Protein - 1.6%.

The Ramie fibre is prepared from the stems by hand. This preparation involves stripping, retting, scraping and drying. The elementary compositions of this fibre are:

- Cellulose - 83.32%, Pectins and other intercellular materials - 7.51%, Moisture - 6.9%, Ash - 2.05% and Fats and waxes - 0.22%.

The Cotton fibre that surrounds the seeds of cotton plants is collected from the seeds by hand. This fibre has the following compositions:

- 94% -Cellulose, 1.3% - Proteins, 1.2% - Ash, 0.9% - Pectins, 0.9% - Unidentified substance, 0.8% - Organic acids, 0.6% - Wax like substance, 0.3% - Noncellulosic polysaccharines.
The cellulose part of the fibres pertains to the class of Carbohydrates. It contains Oxygen, Carbon and Hydrogen. The fibrous cellulose is a high molecular compound. The elementary unit of this macromolecule is anhydro-d-glucose, \((C_6H_{10}O_5)^n\), which is repeated a great number of times in the cellulose molecule. For native cellulose, the molecules are very asymmetrical. They are not rod-like in shape but more or less curved. In general, cellulose macromolecules inside the fibrils are arranged along the fibre axis. They may be represented as follows:

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\begin{array}{c}
\text{CH}_2\text{OH} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{H} \\
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\text{H} \\
\text{OH} \\
\text{C} \\
\text{H} \\
\text{C} \\
\text{CH}_2\text{OH} \\
\text{O} \\
\end{array}
\]

\(n\)

The end units of the cellulose macromolecule chain differ somewhat in composition from the middle glucose units, \(C_6H_{10}O_5\). One of the end units \(C_6H_{11}O_6\) has an aldehyde group. The other end unit \(C_6H_{11}O_6\) contains four hydroxyls. As the cellulose macromolecule is very long and contains many functional alcohol groups, the appearance of two new functional groups at the ends of the chain does not influence the chemical properties of cellulose.

Polyester is the synthetic fibre. Synthetic fibres are divided into two groups: hetero-chain and carbo-chain fibres. The macromolecules of hetero-chain fibres contain in their main chain carbon atom and other atoms such as oxygen and nitrogen. These polymers are usually obtained by polycondensation or
polymerization of cyclic compounds. Polyester is the hetero-chain fibre. This fibre is prepared from dimethyl terephthalate and ethylene glycol in two stages. First as a result of ester interchange, diglycol terephthalate is obtained and then follows the polycondensation reaction. Polyester fibre possesses a well-ordered internal structure; interaction between the greatly extended macromolecules which is attributed to 'Vander Waals' forces and according to the assumptions of certain authors, to hydrogen bonds between the oxygen atoms of the ester or carboxyl groups and the hydrogen in the benzene ring.

The natural silk fibres Eri, Muga and Pat are mainly protein fibres. The fibre is composed of two brins of fibroin stretched from two glands of the silk worm. The brins are stuck to and coated by the silk gum called sericin. Besides fibroin and sericin (protein), raw silk contains small quantities of matter which are extracted by ether and ethyl alcohol. Some ash remains after burning the silk. The content of these substances varies widely depending on the species of silk worm and on the place and conditions of rearing. The average compositions of raw silk are as follows:

<table>
<thead>
<tr>
<th></th>
<th>%</th>
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<tbody>
<tr>
<td>Fibroin</td>
<td>70-75</td>
</tr>
<tr>
<td>Sericin</td>
<td>25-30</td>
</tr>
<tr>
<td>Substance</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td>Mineral matter</td>
<td>1.0</td>
</tr>
<tr>
<td>Substance</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fibroin is a fibrous protein. These fibrous proteins are high molecular substances and contain carbon, hydrogen, oxygen...
and nitrogen. The fibre diagram of silk indicates the presence of both amorphous and crystalline regions. The crystalline parts of the fibre consist of sections of polypeptide chains containing glycyl, alamine and serine with the unit cell of dimension 6.95Å along the fibre axis and have the following structure:

The individual chains are cross-linked mainly by hydrogen bonds between the -NH-CO- groups of adjacent chains and also by Vander Waals forces.

The crystalline regions of the fibre scatter X-rays to give sharp reflections and the non crystalline regions form diffused background in the X-ray diffraction pattern. Using X-ray diffraction, the structural investigation of silk fibroin has been carried out by many workers.

The crystallinity of Jute fibre has already been measured by various workers based on arbitrary drawing of the background line. But Ray and Montague studied the crystallinity in Jute fibre as revealed by multipeak resolution. The crystalline orientation in cellulose fibres has drawn the attention of many workers since some of the physical properties of these fibres depend on it. The degree of crystallinity and crystallite dimension of chemically treated Jute fibres have been studied with X-ray diffraction technique by Moharana. Sen and Woods studied the orientation factor of Jute and Ramie. Ray studied
the crystallite orientation in Jute and Mesta fibres under different moisture conditions. Different workers\textsuperscript{26-28} have studied the various effects of removal of lignin and hemi-celluloses on the crystalline structure of Jute. Ray\textsuperscript{29} observed the effects of methods of drying on the fine structure, density and some mechanical properties of Jute and allied fibres.

Ramie fibre is characterized by high crystallinity. The X-ray and optical properties of the fibre has been the subject of study of many workers\textsuperscript{30-34}. Iyer et al\textsuperscript{35} also correlated crystallite orientation with the optical orientation of fibre. Hu, Hengliang\textsuperscript{36,37} et al studied the crystallinity of cotton fibre. The fibrillation of silk fibres has been revealed by electron microscopic analysis\textsuperscript{38}. Some workers on the measurement of the size of elementary fibrils of some cellulose fibres using transmission electron microscope have been reported\textsuperscript{39}. But very few studies have been reported on the fibrillar arrangements in plant fibres.

Infrared absorption spectroscopy has served as a powerful tool in the study of the basic structure and chemical properties of molecules. The analysis of IR absorption spectra is greatly facilitated by the fact that certain grouping in the molecules gives rise to characteristic group frequencies which in most cases are not strongly affected by neighbouring atoms. Nadiger et al\textsuperscript{40,41} studied the structural and chemical properties of natural Indian silks with the help of IR spectroscopy. Baruah et al\textsuperscript{42} studied these properties of Muga, Eri and Pat fibres. Rowen and Plyler\textsuperscript{43} described the effects of deuteration, oxidation and
hydrogen bonding of the IR spectrum of cellulose. Mann and Marrinan have carried out detailed studies of deuterium exchange with cellulose and shown that the exchange takes place first in the amorphous regions. The crystalline regions are affected only after considerable time. In all the forms of cellulose, there is no free O-H stretching frequency in the crystalline region and all the hydroxyl groups are hydrogen bonded. For detailed information on the structural properties of cellulosic materials, several workers have used the potassium bromide disc technique to record the IR spectra. The infrared absorption spectrum of cellulose shows many bands that are poorly resolved or of lower intensity. But second derivative infrared spectra may provide more detail on structural information. Pandey studied the derivative Infrared spectra of Cotton and Ramie cellulose.

But no such study on X-ray analysis and Infrared spectroscopy have been noticed under thermal treatments of plant fibre (Jute, Ramie and Cotton).

The natural silk fibres (Eri, Muga and Pat) are hygroscopic and semicrystalline in nature. Due to their essential characteristics of external forms and of physico-chemical behaviours, they have great utilities in various textile industries. It is evident that reaction kinetics, enthalpy etc. of a material are based on its physico-chemical properties. Therefore the study of the thermo-physical behaviours of these natural silk and plant fibres certainly have great importance in textile and some other technologies.
The study of thermal behaviours of cellulose materials has been made by many investigators. The Differential Thermal Analysis (DTA), Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC) techniques are becoming important tools for investigation of thermophysical properties of various materials. Tang and Bacon have studied the pyrolysis of cellulose up to 773K using Infrared spectroscopy, Static Thermogravimetric analysis, gas evolution and physical property data. The determination of kinetic data from Thermogravimetry (TG) curves has been widely reviewed by many workers. Murphy investigated the effect of physically absorbed water on cellulose degradation. Kilzer and Broido have offered a reasonable explanation of the Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) profiles from pure cellulose. The thermal decomposition of cellulose powder in inert and oxidizing atmospheres was studied using TG and Scanning Electron Microscopy of gaseous products by Fairbridge et al. The pyrolysis of cellulose resulted in the formation of carbonyl and carboxyl containing compounds was investigated by Clifford and Fargher. Breger and Whitehead using the vacuum DTA apparatus studied the thermal properties of cellulose. Schwenker and Beck studied by DTA technique, the thermal degradation of polymeric materials in air and nitrogen atmosphere. They observed that the thermal degradation mechanisms are different for the air and nitrogen atmospheres. Soulen has developed an electronic digital computer programme for the calculation of reaction kinetics by the Freeman and Carroll method. The programme involves computation of temperature,
weight and rate of reaction from the values of dc millivolt signals originating from the thermobalance. The thermal decomposition of organic fibres using TG curves has been studied and activation energies at different temperature range are calculated by Venger et al.\(^7^1\).

Investigation on the reaction kinetics of organic complexes with the technique Differential Scanning Calorimetry (DSC) has been made by many workers\(^7^2-7^8\). Evaluation of kinetic data from these techniques has also been made by Lengyel et al.\(^7^9-8^1\). Ishikawa\(^8^2\) has studied the reaction kinetics of silk fibroin with the DSC thermograms.

But no such studies on silk fibres (Muga, Eri and Pat) and plant fibres (Jute, Ramie and Cotton) under different chemical conditions have been noticed till now.

Natural and synthetic fibres are electrical insulating materials. The electrical properties of these polymeric fibrous insulators make them important in electric and electronic industries. Therefore, in recent years much attention has been made to study the electrical behaviours of natural and synthetic fibres.

The dielectric properties of various kinds of polymers have been studied by some investigators\(^8^3-8^7\). Dergunov\(^8^8\) has studied the dielectric constant of cellulose as a function of moisture content at a frequency of 10,000 MHz. The dielectric properties of Cotton cellulose and viscose rayon were measured at frequencies of 0.1--1000 KC/S over the temperature range of 273-333K by Abdel Moteleb et al.\(^8^9\). Further the electrical
conduction in polymers has also been measured earlier by various workers. Blazas studied the electrical conductivity of textile fibres. Investigations on electro-chemical behaviours of textile fibres have also been reported by Kitamura. Mc Cubbin has studied the conduction processes of Jute and allied fibres. Baruah et al has studied recently the dielectric properties of natural silk fibres. However the study about the role of absorbed water and gum on electrical behaviour of plant and synthetic Polyester fibres has not been reported.

1.2 THE PRESENT WORK:
In the present investigation, attempts have been made to study the crystallographical, physical and electrical properties under different thermal and chemical conditions of plant (Ramie, Jute and Cotton) and synthetic Polyester fibres readily available in the North Eastern region of India.

The crystalline nature of these fibres has been investigated by x-ray techniques: X-ray diffractograms and front reflection photographs. The effects of moisture and temperature on their fine structures have been studied by X-ray method.

The functional groups present in these fibres and the effect of chemicals and temperature on the behaviour of these groups have been investigated with the help of Infrared Spectroscopic method.

Attempts have been made to study the various thermo-dynamical properties of the silk fibres (Muga, Eri and Pat) abundantly found in the North Eastern Region (specially Assam) by Differential Scanning Calorimetry (DSC). The other thermo-
physical properties of these silk, plant and synthetic Polyester fibres have also been investigated by Thermogravimetry (TG), Derivative Thermo-gravimetry (DTG) and Differential Thermal Analysis (DTA) methods from room temperature to about 673K. From weight loss (%), time and temperature, the activation energies of these fibres have been computed.

The study of the dielectric properties of plant and synthetic Polyester fibres in audio frequency range 200 Hz to 20 KHz in the extended range of temperature from 292K to 573K has been calculated. The DC conductivity of these fibres have been studied in the temperature range from 293K to 513K. From the conductivity variations with temperature, their activation energies have also been computed.

Efforts have been made to investigate the feasibility of these fibres to be used in various industries on the basis of these experimental observations.

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