MATERIAL PROPERTIES OF
ACETYLATED JUTE-MAT COMPOSITES

M.Phil Thesis

TAIMUR-AL-MOBARAK

B U E T

Department of Physics

Faculty of Engineering

Bangladesh **U**niversity of **E**ngineering and **T**echnology (BUET)

Dhaka-1000, Bangladesh

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A Dissertation submitted to the **Department of Physics, B**angladesh **U**niversity of **E**ngineering and **T**echnology (**BUET**), Dhaka, in Partial Fulfillment of the Requirement for the Degree of **MASTER OF PHILOSOPHY (M. Phil.) in Physics.**

By

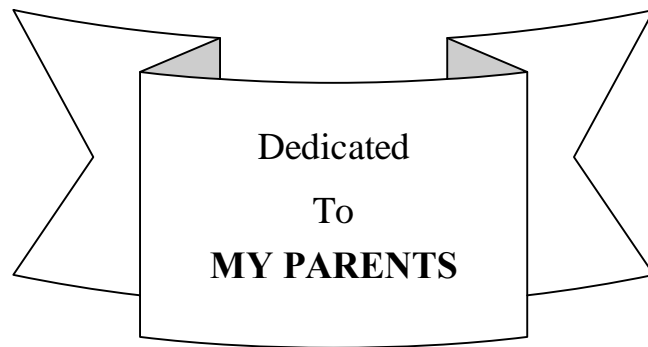## TAIMUR-AL-MOBARAK
Roll No.: 100714017F

Session: October-2007

B U E T

Department of Physics
Faculty of Engineering

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September 2010

Dedicated

To

MY PARENTS

BUET

CANDIDATE'S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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TAIMUR-AL-MOBARAK
Roll No.: 100714017F
Session: October 2007

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY (BUET)
DEPARTMENT OF PHYSICS

CERTIFICATION OF THE THESIS

The thesis entitled **MATERIAL PROPERTIES OF ACETYLATED JUTE-MAT COMPOSITES** submitted by **TAIMUR-AL-MOBARAK**, Roll No.: **100714017F**, Registration No.: 100714017, Session: **October/ 2007**, has been accepted as satisfactory in partially fulfillment of the requirement for the degree of **Masters of Philosophy (M.Phil.) in Physics** on **August, 2010.**

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ABSTRACT

Jute-mat (JM) reinforced polyvinylchloride (PVC) composites were prepared with acetylated and non-acetylated JM by heat-pressed method at 160ºC with various contents of JM and PVC. Owing to the incompatibility between hydrophilic JM and hydrophobic PVC, their composites become incompatible having poor adhesion between them. Due to this poor interfacial adhesion, the PVC-JM composites show inferior properties. That is why fiber surface of JM is modified by chemical treatment, and acetylation of JM is one of the treatments followed in this study using acetic acid (CH_3COOH). When the JM fiber surface is treated with acetic acid, the chemical reaction between JM and CH_3COOH results in acetylated JM having chemical structure of JM-O-C=O-CH_3. This acetylated fiber represents hydrophobic character and exhibits better adhesion with hydrophobic PVC when combined. Structural, mechanical and thermal properties of a neat PVC sample and a series of untreated and treated PVC-JM composites were characterized by a Fourier transform infrared (FTIR) spectrometer, a universal testing machine and a coupled differential thermal analyzer (DTA)/thermogravimetric analyzer (TGA). Water intake measurements of these samples were also performed. FTIR spectra show distinct absorption peaks for neat PVC and untreated and treated PVC-JM composites, suggesting the adhesion between JM and PVC. While the neat PVC does not show any water absorption, the untreated PVC-JM composites exhibit higher water intake than the treated composites. This is due to the fact that after acetylation the hydrophilic moiety of JM is filled up by the acetyl group. Mechanical properties such as Young's modulus (YM) and tangent modulus (TM) of the acetylated PVC-JM composites are observed to be higher than those of the non-acetylated PVC-JM composites and the neat PVC, suggesting better performance due to chemical treatment. Surface micrographs reveal a better adhesion between acetylated JM and PVC than between untreated JM and PVC. The decomposing temperature (T_d) of the treated composites is observed to be higher than that of the neat PVC and untreated composite. Thus, the acetylation of JM produces the high performance biodegradable composites.

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LIST OF SYMBOLS & ABBREVIATIONS

- **ASTM:** American Standard for Testing of Materials
- **DTA:** Differential Thermogravimetric Analysis
- **DTG:** Derivative Thermogravimetric Analysis
- **EB:** Elongation-at-Break
- **FS:** Flexural Strength
- **FTIR:** Fourier Transform Infrared Spectroscopy
- **GPa:** Giga Pascal
- **HDPE:** High Density Polyethylene
- **IUPAC:** International Union of Pure & Applied Chemistry
- **IR:** Infrared
- **JM:** Jute-mat
- **Kgf:** Kilogram force
- **LDPE:** Low Density Polyethylene
- **LLDPE:** Linear Low Density Polyethylene
- **MPa :** Mega Pascal
- **MMA:** Methyl Methacrylate
- **PMCs:** Polymer Matrix Composites
- **PP:** Poly-propylene
- **PPC:** Poly-propylene Carbonate
- **PVC:** Poly-vinyl Chloride
- **SEM:** Scanning Electron Microscopy
- **TGA:** Thermogravimetric Analysis
- **T_g:** Glass Transition Temperature
- **TM:** Tangent Modulus
- **TS:** Tensile Strength
- **UTM:** Universal Testing Machine
- **UTS:** Ultimate Tensile Strength
- **UV:** Ultraviolet
- **UHMWPE:** Ultra High Molecular Weight Polyethylene
- **VLDPE:** Very Low Density Polyethylene
- **WA:** Water Absorption
- **YM:** Young's Modulus

CHAPTER-ONE
INTRODUCTION

1.1 GENERAL DISCUSSION

Nature provides us with an abundance of valuable natural fibers whose wide uses are yet to be fully materialized, because much importance on research for the development and usage of these fibers has not been given earlier. Jute fiber is such a soft natural fiber extracted from the jute plants and is extensively grown in Bangladesh like the other jute-producing countries in the South Asia. It is cheap, easily available as renewable resources, easily processable and above all environment-friendly. This fiber is largely used in the production of twins, upholstery, padding and mat-making, fishing nets, fancy articles such as purses, wall hanging, table mats, bags, cloths and so on. Although it is used in manufacturing cheap house-hold commodities, its potential and delicate application is still under research. Recently, use of jute fiber as reinforcing material in fabrication of polymer-jute composites has raised great interest and expectations among materials scientists and engineers [1ó22].

The primary advantages of using this fiber as additive in polymer are that it has low cost, low density, non-abrasive nature, high possibility of filling levels, low energy consumption, high specific properties, biodegradability, wide varieties, availability throughout the world and a generation of rural/agriculture based economy. Due to the low cost of this fiber, the natural fibre reinforced polymer composites can be very cost-effective materials and can find applications in [1ó2]: *(i)Building and construction industry:* as panels for partition and false ceiling, partition boards, wall, floor, window and door frames, roof tiles, mobile or pre-fabricated buildings which can be used in times of natural calamities such as floods, cyclones, earthquakes, etc., (ii) *Storage devices:* as post-boxes, grain storage silos, bio-gas containers, etc., (iii) *Furniture:* as chair, table, shower, bath units, etc., (iv) *Electric devices:* as electrical appliances, pipes, etc., (v) *Everyday applications:* as lampshades, suitcases, helmets, etc., (vi) *Transportation:* as automobile and railway coach interior, boat, etc. and (vii) *As toys*.

However, the main components of jute fiber are cellulose and lignin of which the amount of the former one is é 40 wt%. The elementary unit of cellulose macromolecules is anhydro-D-glucose, which contains three hydroxyl (-OH) groups per unit. These hydroxyls form hydrogen bonds with the intramolecular, intermolecular and hydroxyl groups from moist air. Lignin is an insoluble, resin like substance of phenolic character. It is built up to a large

extent of phenyl propane building stones, often having a hydroxyl group in the para position and methoxyl group/groups in meta position/positions to the side chain.

Despite of its great advantages and scopes, jute fiber has two major drawbacks that preclude its promising uses in composites fabrication. One of these disadvantages is that jute fiber is hydrophilic in nature, and its moisture content can reach up to 3ó13 wt%, which reduces its durability. The other one is its poor adhesion with synthetic polymers. Therefore, it is necessary to modify the fiber surface without genetic manipulation in order to alleviate hydrophilicity of the fiber so that its impact with the hydrophobic moiety can be improved.

Surface modifications and treatments of natural fiber have become usual procedures to improve its adhesive properties with other material that meet desired engineering requirements. Without surface modification by chemical treatment, a fair number of research works have been carried out [3ó7]. Jute-reinforced polymer composites with untreated jute fiber were studied by Roe *et. al.* [3]. Mechanical and thermo mechanical failure mechanism of fiber reinforced phenolic matrix composites without any modification of fiber were analyzed by Wang *et. al.* [4]. Mechanical properties of untreated woven jute-fabric/polyester composites were investigated by Gowda *et. al.* [5]. Mechanical properties of coir or oil pump fiber reinforced polyester composites were studied by Hill *et. al.* [6]. In all of these investigations, decreases of mechanical properties such as tensile strength, flexural strength, Youngøs modulus were observed. As a consequence of this decrease, the authors claimed that the poor adhesion between fiber and polymer matrix is responsible for the decrease of mechanical properties. Thus, different chemical treatments have been suggested to enhance natural fiber/polymer matrix interaction. Some of these are (i) alkali treatment, (ii) potassium permanganate treatment, (iii) thermal alkali treatment, (iv) scouring, (v) bleaching, (vi) dewaxing, (vii) grafting etc. [1].

Effect of chemical treatments develops roughness of fiber surface, thereby increasing surface area available for surface contact with polymer matrix. The effect of alkali treatment of jute fiber on mechanical properties of jute-reinforced polymer composites has been studied by many researchers [8ó14]. They have shown that the surface texture can be considerably modified by alkali treatments. When the modified fiber is added to polymer matrix, the treated fiber-reinforced polymer composites exhibit a significant increase of tensile strength and Youngøs modulus as compared to the untreated ones. In the above-

mentioned investigations, natural fiber has been used as an additive or filler whose property when combined with that of polymer gives a new property of the resultant composites.

On the other hand, apart from natural fibers introduced as filler in polymer matrix, other organic or inorganic fillers can be incorporated into the matrix in order to find an emerging property of the filler loaded polymer composites. A considerable number of research works on inorganic filler loaded polymer composites have been reported [15ó19]. In all these work, a unique property modification found to be common in all composites other than the change in electrical and thermal properties, is the decreases of tensile and flexural strengths. A possible explanation regarding this fact has been attributed to incompatibility among the multi-components, resulting in poor impact among them.

It is obvious from the above discussion that an improvement of the compatibility between the components of the composites is an essential requirement. The improvement of compatibility between fiber and polymer matrix depends on the appropriate choice of chemical treatments. As stated earlier that, chemical treatments make the fiber surface rough, which produces a good surface contact for polymer molecules. Other possibilities of making a good adhesion between the modified fiber and polymer molecules are invariably referred to the suitable processing techniques.

However, most of the early works for improving the fiber surface have been performed frequently with alkali treatment. Except alkali treatment, the addition of expensive compatibilizers or coupling agents like silane and maleic anhydride are reported in the literatures improves the adhesion between fiber and polymer [20ó22]. In the present study, instead of alkali treatment an alternative way of surface modification by using a less expensive chemical like acetic acid is proposed to fabricate jute-mat/polyvinylchloride composites. The resulting composite is thus called acetylated jute-mat composites.

As synthetic fibers and polymers are imparting bad effect on the environment, natural fiber reinforced biodegradable polymer composites are eco-friendly materials, which can find their potentials as replacements of traditional engineering materials and can protect the environment from the threat.

1.2 OBJECTIVES OF THIS RESEARCH WORK

The aims of the present work are to fabricate and investigate jute-mat (JM) reinforced polyvinyl chloride (PVC) composites that would be biodegradable and environment-

friendly materials. The scientific and technical information obtained by examining the physical, mechanical and thermal properties of these materials can reveal their suitable applications in engineering requirements, i.e. the findings can exhibit potentials of PVC-JM composites as replacement of traditional engineering materials. Based on these views, the following work plans are designed:

i.   Surface modification of JM is done by acetylation using acetic acid.

ii.   Acetylated JMs are reinforced with PVC sheet by hot-pressed method to fabricate the composites.

iii. Various ratios of JM and PVC sheets are maintained in the composites.

iv.   Water absorption properties of the composites are examined.

v.   Adhesion between the molecules of JM and PVC is examined by Fourier Transform Infrared spectroscopy.

vi.   Mechanical properties such as tensile strength, flexural strength, elongation-at-break, Youngøs modulus and tangent modulus of the modified fiber reinforced PVC composites are determined by mechanical testing method.

vii. Scanning electron micrographs of the composites are taken on the fracture surfaces in order to study the adhesion between JM and PVC.

viii. Thermal degradation properties are monitored by a coupled differential thermal analyzer and thermogravimetric analyzer.

From the above discussion, the following outcomes are expected:

(i)   The observed mechanical properties of JM reinforces PVC composites can provide valuable information for their household and industrial applications.

(ii) Any changes in melting and degradation temperatures can reveal information of thermal stability of the fabricated composites, and this information can unveil their particular thermal uses.

1.3 OUTLINE OF THIS THESIS

This thesis consists of six chapters. *Chapter-One* contains a general **Introduction** with aims and objectives of this thesis. *Chapter-Two* provides the **Literature Survey** where a review of recent work is presented. *Chapter-Three* describes the **Theoretical Background**. *Chapter-Four* includes a detailed description of the **Materials and Methods** where the details of the sample preparation and measurement techniques are discussed. *Chapter-Five* contains **Results and Discussion** and the **Conclusion** belongs to *Chapter-Six*. References are added at the end of each chapter.

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CHAPTER-TWO

LITERATURE SURVEY

2.1 REVIEW OF RECENT RESEARCH WORK

2.1.1 Background

Synthetic fibers are expensive and not nature friendly. Increasing use of these fibers are increasingly polluting the environment and making risk to human life. As a result, the interest in using natural fiber obtained from different plant fibers as reinforcement in plastics increased dramatically during the last few years. With regard to the environmental aspects, it would be very interesting if natural fibers could be used instead of synthetic fibers as reinforcement in some structural applications.

Natural fibers have many advantages compared to synthetic fibers, for example, they have low density, and they are recyclable and biodegradable. Additionally they are renewable raw materials and have relatively high strength and stiffness. Their low-density values allow producing composites that combine good mechanical properties with a low specific mass. In tropical countries, fibrous plants are available in abundance and some of them like jute are agricultural crops. The strength, modulus, mode of failure and fracture toughness of a composite is not only dependent on the properties of the fiber and matrix, fiber volume fraction and fiber orientation but also on the interfacial parameters of the composite. A weak interface drastically reduces the off axis strength, the flexural strength and the compression strength. An increase in interfacial strength leads to a substantial increase in tensile strength and modulus of a short fiber composite.

Natural fibers such as jute, cotton, flax, coir, sisal, sawdust, etc. have attracted much attention as potential reinforcements of composites because of their easy availability as renewable resources, easy processability, low cost and above all environment-friendly characteristics. The development of high performance composites prepared using cheap natural fibers is particularly significant from their economic point of view [1].

Much research has been carried out with fiber-reinforced polymer composites [1618]. Almost all of these works have been done with jute fibers and different types of polymer matrix by several authors. But none of them has used PVC-foam sheet as matrix with natural fiber for composite fabrication.

2.1.2 Research works on natural fiber and polymer composites:

Sharma *et. al.* [1] investigated the PVC-sawdust composites. In the investigation, the effects of fiber addition on some physical and mechanical properties were evaluated. The density decreases with the increase of fiber addition. The tensile strength of fabricated product increases with the increase of fiber addition and flexural strength slightly increases with the increase of fiber addition. The Young's modulus increases but tangent modulus decreases with the increases of fiber addition. The fracture energy increases with the increases of fiber addition. The tensile strain decreases with the increase of sawdust addition, but the flexural strain increases with the increase of sawdust addition.

Sombatsompop, N. and Chaochanchaikul, K. [2] studied mechanical properties and thermal and structural properties of PVC-wood sawdust composites. The results were assessed with respect to the effect of moisture content, varying from 0.33 to 3.00 % by weight in the composite, for three different wood sawdust contents. The swell ratio and texture characteristics of the composite extrudates were also evaluated. Unique explanations were given to describe changes in the composite properties in terms molecular interactions between PVC, cellulosic sawdust and moisture, such as dipole-dipole interactions, interfacial defects and bonding, fibre swelling, and moisture evaporation. The results suggest that at low moisture content, the tensile modulus decreased and elongation-at-break of the composites increased with moisture content, the effect being reversed for high moisture content. Tensile strength decreased with increasing moisture content up to 1-2 %, and then unexpectedly increased at higher moisture contents. The effect of moisture content on flexural properties of the composite was similar to that on tensile properties. Impact strength of the composites was considerably improved with moisture content at low sawdust contents (16.7 wt %), and was independent of the moisture content at higher sawdust contents (28.6 and 37.5 wt %). A decrease in decomposition temperature with an increase in polyene content was evidenced with increasing moisture content, while the glass transition temperature did not change with varying moisture content. The extrudate swell ratio increased with the shear rate but remained unaffected by moisture content. The bubbling and peeling-off in the composite extrudate occurred as a result of the evaporation of water molecules and the application of a high shear rate.

Sombatsompop, N. and Chaochanchaikul, K. [3] also performed research on average mixing torque, tensile and impact properties, and thermal stability of PVC-sawdust composites with different silane coupling agents. They observed that the changes in the

tensile and impact properties of the composites with low sawdust content were more sensitive to the addition of silane coupling agents than those with high sawdust content. The differences in the mechanical and thermal properties of the PVC-sawdust composites were dependent on the characteristics of the functional groups in the silane coupling agents used, such as hydrophilic level, number of functional groups, self-condensation reaction, and effectiveness of the hydrolysis reaction. Silane coupling agents above 1.0 wt % resulted in an increase in polyene sequences in the PVC structure.

Khan *et. al.* [4] studied the composites of jute fabrics (hessian cloth) and PC. The effect of coupling agent in the modification of fiber surface as well as in the performance of jute polymer composite was investigated by the methods of XPS, FTIR, ESEM, DSC, DMA and mechanical testing. XPS and FTIR assured that the silanes play important role to form interfacial bonding with the jute fibers and PC. ESEM helps to clarify the adhesion characteristics between the fibers. DSC indicates that the melting temperature increases in the case of silanized fibers. On the other hand, among all the untreated and treated jute-PC composites investigated by DMA treated composite shows the improved storage and loss moduli with remarkable less loss factor as compared to others. Enhanced mechanical properties observed by a mechanical test method and new bond formation observed by FTIR and XPS strongly suggest that the silanized jute-PC composite exhibits the best performance among all other agents used in this investigation.

Mohanty *et. al.* [5] reported the effects of temperature, yarn amount, chemical modification like dewaxing (defatting), alkali treatment, graft copolymerization and orientation of yarn winding on the performance of jute-bipole composites. The mechanical properties like tensile strength, bending strength, impact strength and bending-E-modulus increased substantially in comparison to pure Biopole as a result of reinforcement with jute yarns. The most remarkable observations of their investigation include more than 150 % enhancement in tensile strength, impact strength, bending-E-modulus and more than 50 % enhancement in bending strength of the resulting composites as compared to pure Biopole sheets. Amount of jute yarn, chemical modifications and measurement of mechanical properties on the direction of winding of yarns contribute significantly to the mechanical properties of resulting composites.

Misra *et. al.* [6] reported kinetic studies on redox-initiated grafted copolymerization on to modified jute fibre. Comparative account of graft copolymerization of methylmethacrylate

on different modified jute fibre using V^{5+} cyclohexanol redox initiator in aqueous solution was presented. The high lignin content of natural jute was responsible for the low grafting yield. The softening of jute fibres, however, after removal of certain impurities and lignin, enhanced grafting considerably.

Graft copolymerization of methyl methacrylate (MMA) onto jute fibre was reported by **Haque** *et. al.* [7] by using ferric ion initiator. Effects of temperature, time of reaction, lignin content of jute, monomer concentration and initiator concentration have been studied. After studied the maximum percentages of grafting and grafting efficiency have been found to be 132% and 71% respectively. A kinetic study and activation energies have also been realized.

Ray *et. al.* [8] worked out research on impact fatigue behavior of untreated and alkali treated jute fiber reinforced vinyl ester composites. Jute fiber was kept immersed in the alkali solution for 4 and 8 hours. They reported that longer alkali treatment removed the hemicelluloses and improved the crystallinity and gave better fiber dispersion. For 35% jute/vinyl ester composites containing both untreated and alkali treated fibers, the flexural strength of the composite made from treated fiber was superior. Four hr alkali treated jute fibers gave the optimum combination of improved interfacial bonding and fiber strength properties.

Ray *et. al.* [9] also reported that vinyl ester-resin-matrix composites reinforced with untreated and 5% NaOH treated jute fibers for 4 and 8 hours with different fiber loading were subjected to dynamic mechanical and thermal analysis to determine their dynamic properties as a function of temperature. For all the composites, the storage modulus E` decreases with the increase in temperature, with a significant fall in the temperature range $110\text{-}170^0C$. For the treated composites the rate of fall, dE`/dt, had an inverse relationship with the defect concentrations in the 4hr treated composites corresponded to the highest rate of fall. The glass transition temperature, TG, of the unreinforced resin corresponding to the loss modulus peak was 101.2^0C whereas that of the composites increased by nearly 28^0C on account of the restricted mobility of the resin molecules in the presence of the fibers. In the case of treated composites the TG value showed a decreasing trend from 128^0C to125^0C unlike the plain resin for which a tiny hump was observed in the loss modulus E, curves of all the composites around 166^0C, which became broader and more prominent with the increase in the jute fiber content. The very high tan value of the resin decreased in the

composites, indicating that the addition of the fiber lowered the damping capacity of the composites.

Islam *et. al.* [10] carried out research on development, structure and strength properties of PP/jute blends. The composites of biodegradable PP reinforced with short jute natural fiber was prepared by melt mixing followed by hot press molding. The mechanical properties, thermal properties, microstructural analysis, morphologies of the composites were studied via universal testing machine (UTM), thermo gravimetric analysis (TGA), infrared (IR) spectroscopy and SEM techniques respectively. The mechanical properties like tensile and flexural strengths were measured for both treated and untreated specimens and compared. The result shows that alkali treated jute reinforced have much better properties than the untreated properties one. Both tensile and flexural strengths and modulus have decreased with increasing of untreated fiber and increased with increasing treated fiber in PP-jute composites (PPJC). The changes in the mechanical properties were broadly related to the accompanying modification and interfacial bonding of PPJC. SEM observations indicated good interfacial contact between the short fiber and PP matrix. TG/DTG revealed that the introduction of short jute fiber led to a slightly improved thermo oxidative stability of PP-jute composites.

Mukhopadhay *et. al.* [11] carried out research on infrared spectra of jute fibres grafted with poly methylmethacrylate. IR spectra of methyl methacrylate grafted jute fibres showed that the major portion of grafting was associated with the lignin fraction of the fibres.

Kanakasabai and Abhijit [12] investigated the effect of the fabric treatment and filler addition on the mechanical performance and moisture absorption characteristic of polyester composites. Alkali and thermal treatment was carried out on commercially available fabrics. When used for reinforcement with isophthelic polyester resin, alkali and thermal treated fabrics lead to comparable mechanical performance of the composites. $CaCO_3$ up to 45% (based on resin weight) was used as filler in that work. The mechanical properties of filler polyester decreased with increasing filler content. However, mechanical properties of filler jute/polyester composites were affected less significantly by the filler content. Generally, the mechanical properties such as tensile modulus and impact strength decreased with increasing filler content. Alkali treated jute fabrics exhibited the best moisture resistance and filler addition reduced the moisture resistance for all the material system investigated.

Abu-Zied *et. al.* [13] reported a graft copolymerization of styrene, methylmethacrylate and acrylonitrile on to jute fibers. The effect of jute compounds i.e. water-soluble materials, waxes, pectins, lignin, hemicellulose and - cellulose on graft copolymerization with styrene, methylmethacrylate or acrylonitrile were determined using a Fe^{2+}/H_2O catalyst system at 80^0C. The water-soluble materials, pectins accelerated graft co-polymerization reaction during the initial stage and impeded termination during the later stages.

Abdullah *et. al.* [14] investigated the mechanical properties of jute/glass fiber-reinforced unsaturated polyester hybrid composites and observed that composite having 25% jute show higher mechanical properties. The composites were prepared by hand lay up technique. The composites with a jute to glass ratio of 1:3 shows improved mechanical properties as tensile strength (TS) 125%, tensile modulus (TM) 49%, bending strength (BS) 162 % and bending modulus (BM) 235% over untreated jute composites. To further improve the properties, the surface of jute and glass fiber was irradiated under UV radiation of different intensities. UV pre-treated jute and glass fibers (1:3) at optimum intensities showed the highest mechanical properties, such as TS 70%, TM 33%, BS 40% and BM 43% compared to untreated jute and glass-based hybrid composites. UV-modified jute/glass-reinforced hybrid composites also showed the best of impact strength ($40kJ/m^2$). The interfacial adhesion between jute/glass and USP is monitored by a scanning electronic microscope (SEM).

Mobarak *et. al.* [15] worked on the effect of additives/coupling agents on the mechanical and thermal properties of jute-vinyl ester (VE) composites. They found that bending strength (BS) and bending E-modulus of 2-hydroxythyl methacrylate (HEMA) treated jute fiber and VE composites were increased by 70% and 45% compared to the untreated jute/VE composites respectively. Thermodynamic properties such as storage modulus and loss modulus of the HEMA treated jute/VE composites were increased by 72% and 65% compared to the untreated jute/VE composites at 30^0C respectively. The tan values of composites were found to be minimal compared to VE and untreated jute óVE composites. The chemical nature of the interfacial bond between jute and VE was monitored by Fourier transform infrared spectroscopy (FTIR) which showed that HEMA might react with VE. The tensile fracture surfaces were investigated by environmental scanning electronic microscope (ESEM). The results of ESEM showed an improved interfacial adhesion treated jute with VE.

Tran *et. al.* [16] found that the use of graft copolymer of maleic anhydride polypropylene (MAPP) as a coupling agent in jute-polypropylene (PP) composites improved the mechanical properties of the composites. The scanning electron microscope (SEM) observation of fractured surfaces of unmodified and modified jute-PP composites confirmed that the increase in performance was due to an increase of fiber-matrix adhesion. Jute and glass fibers were hybridized and the hybrid composites had superior mechanical properties.

Shah and Lakkad [17] studied mechanical properties of jute reinforced plastics. They investigated about tensile strength, flexural strength, compressive strength and again tensile strength after accelerated weathering. Their results showed that the addition of jute as a reinforcement by about 25% weight increases the ultimate tensile strength (UTS) by 100%. The compressive strength did not increase, the flexural modulus increased considerably but the increased in flexural strength was marginal. The increase in the strength and modulus was naturally dominated by the content of glass fibers in the composites due to their higher modulus and strength. The results of the tests on the mechanical properties clearly showed that the jute fibers, when introduced in to the resin matrix as reinforcement, considerably improved the mechanical properties. But the improvement was much lower than that obtained by introduction of glass and other high performance fibers. Hence, the jute fibers can be used as reinforcement where modest strength and modulus are required.

Razera and Frollini [18] studied composites based on phenolic matrices and both untreated and alkali and ionized air treated jute fibers. Different fiber lengths and fiber content were used to reinforce the phenolic matrices. The jute fibers were characterized with respect to lignin, holocellulose, ash and humidity contents and also to the crystallinity index. The mechanical properties were investigated by means of tensile analysis and morphology by SEM. The treated and untreated jute fiber-jute fiber reinforced composites were characterized as to water absorption (WA). Among the jute-fiber treatments considered in that work, the treatment with a solution of 5% NaOH presented the best result: (i) the fiber presented a higher tensile strength and a large percentage of elongation-at-break, (ii) the composites reinforced with this fiber percentage the highest impact strength results when this was unique treatment (20 wt% of fiber) as well as when it was combined with ionized air (30 wt% of fiber) and (iii) the composites that presented the lowest water uptake was that reinforced with this fiber.

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CHAPTER-THREE

THEORETICAL BACKGROUND

3.1 Concepts of Composite Materials

Composites are produced when two materials are joined to give a combination of properties that cannot be attained in the original materials.

```
┌──────────────────┐
│      Matrix       │───────┐
└──────────────────┘        ▼
                      ┌────────────────┐
                      │  Composites     │
                      └────────────────┘
┌──────────────────┐        ▲
│   Reinforcement   │───────┘
└──────────────────┘
```
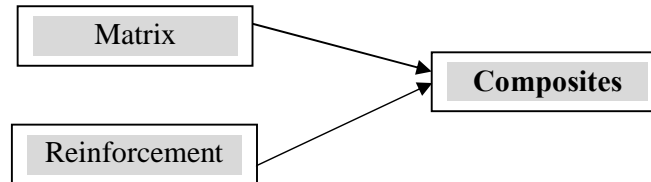
The above diagram depicts how composites are prepared. It must have a matrix and reinforcement [1]. Matrix may be- metal, ceramic, polymer, and reinforcement may be organic and inorganic materials such as natural fibers, glass fibers, carbon nano-tube etc.

To understand the insight of composite materials, it is necessary to describe their classification and to discuss their fabrication processes in details.

Composite materials have been classified in many ways depending on the ideas and concepts that need to be identified. A useful and all embracing classification in set out with some examples. Most naturally occurring materials derive their superb properties from a combination of two or more components, which can be distinguished readily. When examined in optical or electron microscopes. Thus, for example, many tissues in the body, which have high strength combined with enormous, flexibility, are made up of stiff fibers such as collagen embedded in a lower stiffness matrix. The fibers are aligned in such a way as to provide maximum stiffness in the direction of high loads and are also able to slide past each other, so that the tissue is very flexible. Similarly, a microscopic examination of wood and bamboo reveals a pronounced fibril structure, which is very apparent in bamboo when it is fractured. It is not surprising that bamboo has been called natural fiberglass.

Practically, everything is a composite material in this world. Thus a common piece of metal is a composite (polycrystalline) of many grains (or single crystals). Such a definition would make thing quite unwieldy. Therefore, it must be agreed on an operational definition of composite materials for our purposes in this text. We shall call a material as composite that satisfies the following conditions.

i) It is manufactured (naturally occurring composite, such as bamboo).

ii) It consists of two or more physically and/or chemically distinct, suitably arranged or distributed phases with an interface separating them.

iii) It has characteristics that are not depicted by any of the components in isolation.

There is no really adequate definition of a composite material but the preceding discussion give some indication of the scope of the subject. In term of the approach to be adopted here, there are main points to be included in definition of an acceptable composite material for use in structural application:

i) It consists of two or more physically distained and mechanically separable materials.

ii) It can be made by mixing the separate materials in such away that the dispersion of one material in the other can be done in a controlled way to achieve optimum properties.

iii) The properties are superior, and possibly unique in some specific respects, to the properties of the individual components.

The last point provides the main impetus for the development of composite materials. In fiber reinforced plastics, fibers and plastics with some excellent physical and mechanical properties are combined to give a material with a new and superior property. Fibers have very high strength and modulus but this is only developed in very fine fibers, with diameters in the range 7-15 μm, and they are usually very brittle. Plastic may be ductile or brittle but they usually have considerable resistance to chemical environments. By combining fiber and resin a bulk materials is produced with a strength and stiffness close to that of the fibers and with the chemical resistance of the plastic. In addition, it is possible to achieve some resistance to crack propagation and an ability to absorb energy during deformation.

3.1.1 Classification of composite

Composites are classified in various ways [2]. Generally, there are two kinds of composite materials:

   i) Natural composite materials
   ii) Synthetic composite materials.

Broad classification of composite materials may be as under:

   i) **Natural composite materials:** Wood, Bone, Bamboo, Muscle and other tissue.
   ii) **Micro composite materials:** Metallic alloys, e.g. steels, toughened thermoplastics, e.g., impact polystyrene, ABS, sheet-molding compounds, reinforced thermoplastics.

iii) **Macro composite materials:** Galvanized steel, reinforced concrete beams and helicopter blade skis.

3.1.2 Classification of micro composite materials

Micro composites include the following properties:

1) Continuous fibers in matrix: aligned, random

2) Short fibers in matrix: aligned, random

3) Particulates (Spheres, plates, ellipsoids, irregular, hollow or solid) in matrix

4) Dispersion strengthened, as for 3 above, with particle size $<10^{-8}$ m

5) Lamellar structures

6) Skeletal or inter penetrating networks

7) Multicomponent, fibers, particles etc. [3].

Composite materials can be classified based on reinforcement by the following ways:

i)   Fibrous

ii) Laminar

iii) Particulate.

3.1.3 Matrix based composite materials

Depending on the type of matrix, composites are classified as:

i)   Metal matrix composite (MMC)

ii) Ceramic matrix composite (CMC)

iii) Polymer matrix composite (PMC)

i) **Metal matrix composite:** As the name implies, for metal matrix composite (MMC). The matrix is a dilute metal. Their materials may be utilized at higher service temperatures than their base metal counterparts. Furthermore, the reinforcement may improve specific stillness, specific strength, abrasion resistance, creep resistance, thermal conductivity and dimensional stability. Metal matrix composites are much more expensive than PMC and therefore, their (MMC) use is somewhat restricted. The super alloys as well as alloys of aluminum, magnesium, titanium and copper are employed as matrix materials. Continuous fiber materials include carbon, silicon carbide, boron, alumina and the refractory metals.

ii) **Ceramic matrix composite:** Ceramic materials are inherently resident to oxidation. Deterioration at elevated temperatures, are met for their disposition to brittle fracture and some of these materials would be ideal candidates for use in high temperature specifically for components in automobile and aircraft gas turbine engine. Fracture toughness values for ceramic materials are low and typically lie between 1 and 5 MPa. Ceramic matrix composites may be fabricated using hot pressing, hot isolate pressing, and liquid phase sintering techniques. Relative applications sic, whisker-reinforced aluminas are being utilized as culling two inserts for machinery hard metal alloys, and tool lives for these materials are greater than for cemented carbides [4].

iii) **Polymer matrix composite:** Certain physical and chemical properties of the matrix are particularly significant with respect to the properties at a composite. The main advantages conferred by polymer matrices are low cost, easy possibility, good corrosion resistance, good dielectric properties, and low density. Low strength, low stiffness and low service temperatures, on the other hand, limit their application. The primary functions of a matrix are to bind the reinforcing element together, distribute the loading among them, and protect the reinforcing system. This in turn presupposes good adhesion between matrix and reinforcement.

Traditionally, thermoplastics are reinforced primarily with discontinuous fibers, but recently development of high-temperature resins such as polyether ketone, poly sulfur and polyamide has been made to produce thermoplastics competitive with thermosets in the area of high-performance continuous fiber composites as well. The most important matrices generally are alkyds, allyl esters, epoxies, furans, melamines, phenolics, poly butadienes, polyesters, polyamides, polyurethanes, silicones, and urea and vinyl esters. For thermosets, the dominant resins are unsaturated polyesters, followed by acrylic resins, phenolic resins, epoxies, vinyl esters, and unsaturated polyester-urethane hybrids. The complete list of applicable thermoplastic matrices, however, is more extensive and includes acrylonitrile-butadiene-styrenes, acetals, acrylies fluoro-polymers, polyamides, polyamide-imide, poly-arylsulfone, polycarbonates, thernoplastic polyesters, polyetherether ketone, polyethersulfones, polyethylenes, polyimides, poly (phenylene sulfides), polypropylenes, polystyrenes, polysulfones, poly (Vinyl chloride), and styrene-acrylonitriles.

According to the **Composites Committee of German Society for Metallurgy,** the following groups comprise the composite materials:

(a) Fiber composite: Refractory whisker or polycrystalline fibers are imbedded into a matrix for improvement of mechanical properties.

(b) Laminated composites: Metallic foils and foil-like structures respectively, as well as thin ribbons are imbedded into a matrix, or the composite is built up from layers of various materials or by layers made of laminates (i.e. foil, ribbons, sheet etc) and the matrix.

(c) Material with surface layers: In contrast to the ideal materials these layers are very thin. They are applied by different methods and include points. The layer thickness ranges from a few μm to 100m. They serve for corrosion and oxidation protections and improvement of wear, and impart other physical properties to the material surface.

(d) Particle composites: This group encompasses a wide range of materials. It includes for instance the embedding of nonmetallic inorganic particles for improvement of mechanical properties of matters (Dispersion hardened metals) and also materials, which consists of non-metallic inorganic particles bound by a small metallic binder phase (hard metals).

Since the present study is focused on fiber-polymer composites, detailed descriptions of polymer and fiber will be given in the following section:

3.2 Polymer

3.2.1 Definition

A molecule has a group of atoms, which have strong bonds among themselves but relatively weak bonds to adjacent molecules. Examples of small molecules are water (H_2O), methanol (CH_3OH), carbon dioxide (CO_2) and so on. Polymers contain thousands to million of atoms in a molecule which is large; they are also called macromolecules; polymers are prepared by joining a large number of small molecules called monomers. Polymers can be thought of as big buildings and monomers as the bricks that go into them. Monomers are generally simple organic molecules containing a double bond or a minimum of two active functional groups.

3.2.2 Classification of polymer

Polymers are classified in many points of view. According to-
   i)   Source
   ii) Nature of the backbone chain of polymers

iii) Characteristic towards heat.

iv) Ultimate nature

v) Chemical structure

vi) Method of synthesis

vii) Composition and

viii) Polarity.

3.2.3 Types of polymer based on thermal response

Based on thermal response, polymers are classified into the following two types:

i) Thermoplastic polymer

ii) Thermosetting polymer

i) **Thermoplastic polymer:** These polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times such polymers, that soften on heating and stiffen on cooling are termed thermoplastics polymers (e.g. polyethylene, PVC, nylon etc.).

ii) **Thermosetting polymer:** These polymers undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of the egg, which on heating sets into a mass, and once set, cannot be reshaped such polymer, that became and infusible and is soluble mass on heating are called thermosetting polymers. (e.g. - phenolics, polyurethane, polyester, epoxied resin).

Again, in terms of molecular structure different configurations of polymers are as follows-

i) **Linear polymer:** This type of polymer consists of a long chain of atom with attached side groups. Example- polyethylene, polyvinyl chloride and polymethyl methacrylate.

ii) **Branched polymer:** Polymer branching can occur with linear, cross-linked or another type at polymer.

iii) **Cross-linked polymer:** In this case molecules of on chain are burned with those of another, cross-linking of molecular chain results in a three-dimensional network. Cross-linking make sliding of molecules past one another difficult. Thus making the polymers strong and rigid.

iv) **Ladder polymer:** If we have two-liner polymers linked in a regular manner, we get a ladder polymer not unexpectedly. Ladder polymer are more rigid that linear polymerøs.

3.2.4 Types of polymer based on origin

Depending on their origin, polymers can be grouped:

    i)   Natural polymer

    ii) Synthetic polymer

Depending on their origin, polymers can be grouped as natural or synthetic. Those isolated from natural materials are called natural polymers. Typical examples are: cotton, silk, wool and rubber, cellophane, cellulose rayon and so on are in fact chemical modification of natural polymer. Polymers synthesized from low molecular weight compound are called synthetic polymer.

Typical example: polyethylene, PVC, nylon and Terylene.

3.2.5 Organic and inorganic polymers

Polymers are also classified as organic and inorganic polymers:

i)   Organic polymers: A polymer whose backbone chain is essentially made of carbon atom is termed an organic polymer. The atoms attached to the side valences of the backbone carbon atom are however, usually those of hydrogen, oxygen, nitrogen etc. The majority of synthetic polymers are organic and they are very extensively studied.

ii) Inorganic polymers: In fact, the number and variety of organic polymers are so large that when we refer to "polymers", we normally mean organic polymers. The molecules of inorganic polymers on the other hand, generally contain no carbon atom in their chain backbone. Glass and Silicone rubber are example of inorganic polymers.

3.2.6 Types of polymer based on modes of synthesis

Polymers are in to the following groups when they are polymerized from monomers:

    i)   Condensation polymer

    ii) Addition polymer

i) Condensation polymer: Condensation polymers are those in which the molecule formula of the repeat unit of the polymer chains locks certain atoms present in the monomer from which it formed.

So, condensation polymer in this process there occurs a stepwise reaction of molecule and each step a molecule of a simple compound generally water, form as a by product.

ii) **Addition polymer:** Addition polymers are those in which this loss of a small molecule does not take place. The most important group of addition polymers includes those derived form unsaturated vinyl monomer.

So, the addition polymer in the process monomers joins to form a polymer without producing any by-product. Addition polymerization is generally carried out in the presence of catalysts. The liner addition of ethylene molecules (óCH$_2$ó) results in polyethylene.

3.3 Polymerization

The process of forming large molecules form small oneøs is called polymerization; that is polymerization is the process of joining many monomers as the basic building blocks, together to form polymers.

Polymerization can be classified in the following way:

      i) Step Reaction Polymerization (Condensation)

      ii) Radical chain polymerization (Addition)

      iii) Ionic and coordination chain polymerization (Addition)

      iv) Copolymerization

Polymerization can also be classified in the following way:

      a) Bulk polymerization

      b) Solution polymerization

      c) Emulsion polymerization

      d) Suspension polymerization

      e) Granulation polymerization

a) **Bulk polymerization:** Polymerization in bulk, perhaps the most obvious method of synthesis of polymers, is widely practiced in the manufacture of condensation polymers, where the reactions are only mildly exothermic and most of the reaction occurs when the viscosity of the mixture is still low enough to allow ready mixing, heat transfer and bubble elimination. Control of such polymerization is relatively easy.

Except in the preparation of casting, for example, of poly (methyl-methacrylate), bulk polymerization is seldom used commercially for the manufacture of vinyl polymers.

b) **Solution polymerization:** Polymerization of vinyl monomers in solution is advantageous from the Stan point of heat removal and control, but has two potential

disadvantages. First, the solvent must be selected with care to avoid chain transfer and; Second the polymer should preferably be utilized in solution, as in the case of poly (vinyl acetate) to be converted to poly (vinyl alcohol) and some acrylic ester finishes. Since the complete removal of solvent from a polymer is often difficult to the point of impracticality.

c) **Emulsion polymerization:** The emulsifier and a water-soluble catalyst are first added to the water, followed by the monomer, which is dispersed by agitation, polymerization is then carried out by heating. Typical wateró soluble catalysts suitable for this reaction include hydrogen peroxide, ammonium per sulphate and potassium persulphate. Emulsifiers may be axionic surface-active agents but the nonionic are favoured because of their greater stability. Acrylic emulsions so formed are used for leather coatings and in the manufacture of water based paints.

d) **Suspension polymerization**: This method is very similar to emulsion and utilizes similar equipment. The monomer is added to water and broken into small droplets by agitation. A protective colloid is also added in order to prevent the possible coalescence of these droplets when polymerization is partially completed. Typical protective colloids include polyvinyl alcohol and sodium polyacrylate. In suspension polymerization, the reaction takes place in the monomer phase so that monomer-soluble catalysts must be used; the most common is being benzyl peroxide. The water acts as a heat transfer medium and the temperature of the bath remains constant. The product is obtained in the form of small beads, which are screened, washed and dried.

e) **Granulation polymerization:** This process is on often used for the production of molding powders and is a variant of the suspension technique. Only a small amount of water is used, together with some lubricant and either a water or monomer soluble catalyst. Polymerization is carried out in a heavy-duty mixer with a single blade agitator. Continual kneading of the material during polymerization results in the formation of fluffy, granular particles. No emulsifiers or protective colloids are added and the product is thus extremely pure.

3.4 Brief description of some polymers

There are two main branches of polymers; first type is olefin polymer and the second is olefin co-polymers. The olefin polymers are stated here [5]:

(i)   Polyethylene

      Monomer   : Ethylene ($H_2C = CH_2$)

      Polymerization   :

                            a) Low Density Polyethylene (LDPE) - Free radical initiated Chain polymerization

                            b) High Density Polyethylene (HDPE) - Ziegler-Natta or metal oxide Catalyzed chain polymerization

    Major uses- a) LDPE: Film and sheet (95%) house wares and toys (16%), Wire and cable coating (5%)

           b) HDPE: Bottles (40%), house wares containers, toys (35%) pipe and fittings 10%, film and sheet (5%)

(ii)   Polypropylene

      Monomer   : Propylene ($H_2C = \overset{\overset{\textstyle CH_3}{|}}{CH}$)

      Polymerization   : Ziegler-Natta catalyzed chain polymerization

      Uses   : Fiber products (30%), house wares and toy (15%), Automotive parts (15%); appliance parts (5%)

(iii)   Poly (vinyl chloride)

      Monomer   : Vinyl chloride ($HC_2 = \overset{\overset{\textstyle Cl}{|}}{C} - H$)

      Polymerization   : Free radicalô initiated chain polymerization

      Uses   : Pipe and fittings (35%), film and sheet (15%), flooring materials (10%), wire & cable insulation (5%), automotive parts (5%) adhesive and coating (5%)

(iv)   Poly (vinylidene chloride)

      Monomer   : Vinylidene chloride ($CH_2 = CCl_2$)

      Polymerization: Free radical-initiated chain polymerization

      Uses   : Film and sheeting for food packing

(v)   Poly butadiene (butadiene rubber)

      Monomer   : Butadiene ($H_2C=CH-CH=CH_2$)

      Polymerization: Ziegler- Natta catalyzed chain polymerization

      Uses   : Tires and tire products (90%)

(vi)   Polyisoprene

Monomer   : Isoprene ($\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array}$ = CH_2)
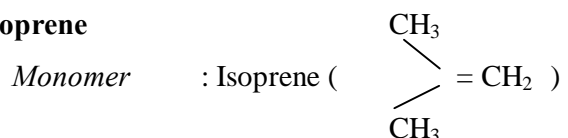
Polymerization: Ziegler-Natta catalyzed chain polymerization

Uses   : Car tires (55%), mechanical goods, sporting goods, footwear, sealants and caulking compound

(vii)   Poly isobutylene

Monomer   : Isobutylene ($CH_2 = \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}$)
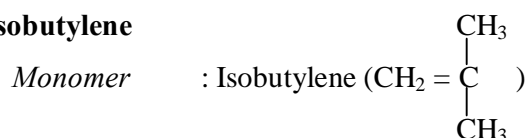
Polymerization: Cationic-initiated chain polymerization

Uses   : Lubricating oils, sealants

(viii)   Polystyrene

Monomer   : Styrene   ($C_6H_5CH=CH_2$)

Polymerization: Free radical initiated chain polymerization

Uses   : Packing and containers (35%), house wears, toys and recreational equipment (25%), appliance parts (10%), disposable food containers (10%).

3.5 Poly vinyl chloride (PVC)

The monomer, vinyl chloride, boils at 14°C. There are two methods for the production of vinyl chloride: one is by cracking ethylene dichloride in vapour phase and the other is by reacting acetylene with hydrogen chloride, in the presence of a catalyst. Industrial polymerization of vinyl chloride is carried out either in suspension or emulsion. Limited quantities of PVC are also made by bulk polymerization.

Structurally, the PVC molecule is partially syndiotactic and dose not has a completely regular structure. This is why PVC has low crystallinity. The polymer molecules are either linear or only slightly branched. PVC is insoluble in vinyl chloride, alcohols, water and hydrocarbons. Acids and alkalis have practically no effect on PVC, at least up to 20°C. PVC, however, dissolves in ketones, chlorinated hydrocarbons and the like. A mixture of acetone and carbon-disulphide is found to be an excellent solvent for PVC.

PVC is one of the cheapest and most widely used plastics globally. It is used for the large-scale production of cable insulations, equipment parts, pipes, laminated materials and in

fiber manufacture. PVC is thermally not very stable and beyond 200°C, it degrades with the evolution of HCl.

PVC, as such, is a horn-like material and difficult to process. It is, therefore, compounded with plasticizers. Depending on the plasticizer percentage, fully rigid to highly flexible finished products can be obtained. In many cases, the plasticizers content may be up to 30% by weight of the polymer.

PVC finds extensive use in certain formulations called plastisols and organosols. These are paste-like compositions and are produced from emulsion-polymerized PVC resin particles. The plastisols are produced by dispersing PVC particles into plasticizers. The organosols, on the other hand, are produced by dispersing PVC particles in a suitable mixture of volatile organic liquid and plasticizers. Plastisols and organosols also contain other compounds such as colorants, fillers, blowing agents and stabilizers. At ordinary temperatures, the PVC particles present in plastisols and organosols do not dissolve in the liquid medium, but only remain as a dispersed system. When the temperature is raised to 150-200°C; PVC fuses with the plasticizer and forms a physically cross-linked structure in the shape of the ultimate plastic article.

The total chlorine content in PVC is around 56.8% and can be further increased to 60-65% by dissolving it in a suitable solvent such as chlorobenzene and chlorinating at 100°C. The polymer thus formed is called chlorinated PVC. It is assumed that, during chlorination, the chlorine replaces the hydrogen atoms in the óCH$_2$- units rather than in the óCH-Cl- units of the molecule. The principal advantage of chlorination is that the polymer becomes more resistant to acids and bases. However, the stability towards heat and light is found to decrease. The main use of chlorinated PVC is in the manufacture of adhesives, coatings and fibers [6].

3.6 Natural fiber

3.6.1 Definition

These fibers are naturally obtained from different types of plants. The vegetable world is full of examples where cells on groups of cell are designed for strength and stiffness. A sparing use of resources has resulted in optimization of the cell function. Cellulose is a natural polymer with high strength and stiffness per weight, and it is the building material of long fiber cells. These cells can be found in the stem, the leaves, or the seeds of plants.

3.6.2 Different types of natural fibers

🔸 **Bast fibers (flax, hemp, jute, kenaf, ramie/china glass)**

In general the bast consists of a wood core surrounded by a stem. With in the stem there are a number of fiber bundles, each containing individual fiber cells or filaments. The filaments are made of cellulose and hemi-cellulose, bonded together by a matrix, which can be lignin or pectin. The pectin surrounds the bundle, thus holding them on to the bundle. Flex delivers strong and stiff fibers and it can be grown intemperate climates. The fibers can be spun to fine yarn for textile other bast fiber are grown in warmer climates. The most common is jute, which is cheap and has a reasonable strength and resistance to rot. Jute is mainly used for packing (sacks and balsa). As far as composite applications are concerned; flax and hemp are two fibers that have replaced glass in a number of components, especially in the German automotive industries.

🔸 **Leaf fibers (sisal, abaca, banana, palm)**

In general the leaf fibers are coarser than the bast fibers. Applications are ropes and coarse textiles; with in the total production of leaf fibers, sisal is the most important. It is obtained from the agave plant. The stiffness is relatively high and it is often applied as binder twines. As far as composites are concerned, sisal is often applied with flax in hybrid mats to provide good permeability when the mat has to be impregnated with a resin. In some interior application sisal is preferred because its low level of small compared to fiber like flax. Especially manufacturing process at increased temperatures (NMT) fibers like flax can cause smell [7].

🔸 **Seed fibers (cotton, coir, kapok)**

Cotton is the most common seed fiber and is used for textile all over the world. Other seed fibers are applied in less demanding application such as stuffing of upholstery. Coir is an exception to this. Coir is the fiber of the coconut husk; it is a trick and coarse but durable fiber. Applications are ropes, meeting and brushing.

Natural fibers already have been used the first time 3000 years ago in composite systems in the ancient Egypt, where straw and clay were mixed together to build walls. Over the last decade, polymer composites reinforced with natural fibers have received ever increasing attention, both from the academic world and from various industries. There is a wide variety of different natural fibers which can be applied as reinforcement or fillers. Classification of the various fibers is presented in Fig.3.1 [8].
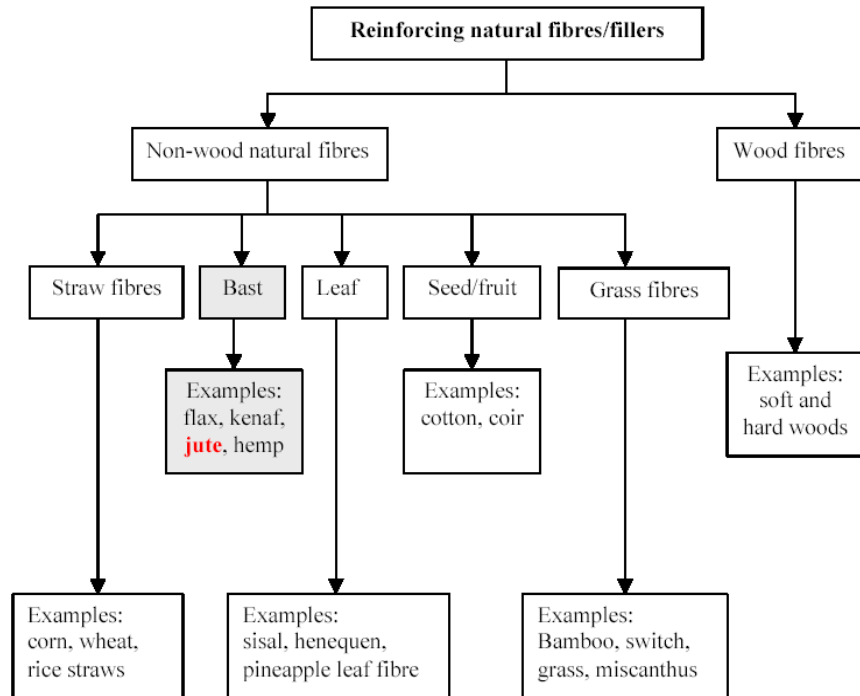
Fig.3.1: Classification of natural fiber, which can be used as reinforcement or fillers in polymers.

3.6.3 Advantages of natural fibers

The advantages of natural fibers are-

- Low specific weight, which result in a higher specific strength and stiffness than glass. This is a benefit especially in parts designed for bending stiffness.
- It is a renewable resource, the production requires little energy, CO_2 is used while oxygen is given back to the environment.
- Predicable with low investment at low cost, which makes the material an interesting, produced for low wage countries.
- Ericnally processing no wears of fooling no skin irritation.
- Thermal recycling is possible, where glass causes problem in combustion furnaces.
- Good thermal and acoustic insulating properties.

3.6.4 Disadvantages of natural fibers

The disadvantages of natural fibers are-

- Lower strength properties, particularly its impact strength.
- Variable quality, depending on unpredictable influences such as weather.
- Moisture absorption, which eases swelling of the fibers.

- Restricted maximum processing temperature.

- Low durability, fiber treatment can improve this considerably.

- Poor fire resistance.

- Price can fluctuate by harvest results or agricultural politics.

3.6.5 Important properties of natural fibers

Most important properties of some natural fibers are given below

- **Good strength:** Very good strength properties, especially tensile strength. In relation to its weight the best bast fibres attain strength similar to that of Kevlar.

- **Combustibility:** From a waste point of view, combustibility is an advantage. Products can be disposed of through burning at the end of their useful service lives and energy can simultaneously be generated.

- **Biodegradability:** As a result of their tendency to absorb water, fibres will biodegrade under certain circumstances through the actions of fungi and/or bacteria.

- **Dimensional stability:** As a consequence of the hygroscopicity of the fibres, products and materials based on plant fibres are not dimensionally stable under changing moisture conditions. This is the greatest disadvantage in relation to industrial use of plant fibres. However, if necessary, this may be controlled at an extra cost by a number of known treatments (e.g., heat treatments or chemical modification procedures such as acetylation).

- **Reactivity:** The hydroxyl groups present in the cell wall constituents not only provide sites for water absorption but also available for chemical modification (e.g., to introduce dimensional stability, durability, or improved oil/heavy metal absorption properties).

- Very good heat, sound and electrical insulating properties.

3.6.6 Structure of fibers

All plant species are built up of cells. When a cell is very long in relation to its width it is called a fiber. For example, wood fibers are mostly 50-100 times as long as they are wide. The fiber is like a microscopic tube (i.e., a wall surrounding a central void referred to as the lumen). Moreover, when the cell wall is made up mainly (85% or more) of cellulose, hemi cellulose and lignin, we talk about lignocellulosic fibers, and this includes woody species, scrubs and most agricultural crops.

3.7 Classification of fibers

3.7.1 Economic classification of fibers

It is possible to classify fibers in six groups based on their utilization, as follows:

Textile fibers: The most important use of fibers at the present time is in connection with the textile industry, which is concerned with the manufacture of fabrics, netting, and cordage. In making fabrics and netting, flexible fibers are twisted together into thread or yarn and then oven, spun, knitted, or otherwise utilized. Fabrics include cloth for wearing apparel, domestic use, awnings, sails, etc., and also coarser materials such as gunny and burlap. The fabric fibers are all of commercial importance. Netting fibers, which are used for lace, hammocks, and forms of net, include many of the commercial fabric fibers and a host of native fibers as well. Both commercial and native fibers used for cordage. For this purpose of the individual fibers are twisted together rather than woven. Twine, binder twine, fish lines, rope, hawsers, and cables are among the many kind of cordage.

Brush fibers: These are tough and stiff fibers, or even twigs and small stems, which are utilized in the manufacture of brushes and brooms.

Plaiting and rough weaving fibers: Plates are flat, pliable, fibrous strands which are interlaced to make straw hats, sandals, basket, chair seats and the like. More elastic strands are roughly woven together of mettings and thatched roofs of houses, while supple twigs or woody fibers are used for basket, chairs etc.

Filling fibers: These fibers are used in upholstery and for stuffing mattresses, cushions, etc.; for caulking the seams vessels and in casks and barrels, and stiffening in plaster; and as packing materials.

Natural fibers: These are usually tree basts, which are extracted from the bark in layers or sheets & pounded in to rough substitutes for cloth or lace.

Paper making fibers: Paper making fibers include wood fibers, textile fiber utilized in either the raw or manufactured state, or many other kinds. It is obvious that any one plant cannot be restricted absolutely to any single group in this economic classification, since the same fiber may be used for different purposes and since the plant may yield more than one kind of fiber.

3.7.2 Classification of organic fibers

In view of the fact, the chain covalent carbon-carbon bond is a very strong one. It is expected linear chain polymers such as polyethylene to be potentially very strong and stiff.

Organic

Natural fibers

Man-made fibers

Vegetable origin

Animal origin

Natural paper

Synthetic

Wood fiber

Bast fiber

Leaf fiber

Seed and fruit fibers

Cellulose (Rayon)

Cellulose esters

Protein

Miscellaneous

Wood and Hair fibers

Silk and other filaments
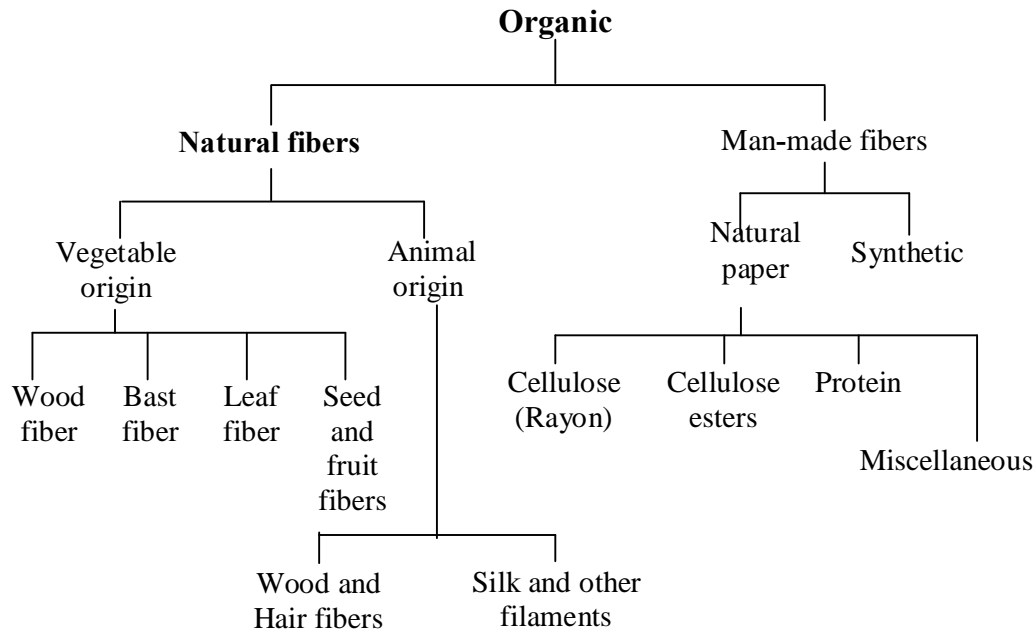
Fig.3.2: Fibers classification chart

Their chemical nature and the processing route control the orientation of these polymer chains with respect to the fiber axis and the manner in which they fit together. There are two ways of achieving molecular orientations, one without high molecular extension and the other with high molecular extension. Organic fibers are divided into two main groups, natural fibers and man-made fibers. Fibers classification chart is given Fig.3.2.

3.8 Chemical composition of the natural fibers

The properties of natural fiber largely depend on the chemical composition of the fiber and the properties of composites made from natural fibers are strongly influenced by these fiber properties.

Table.3.1: The chemical compositions of some natural fiber are shown below:

Constituents	Amounts (percentage dry basis)		
	Palm Fiber	Banana Fiber	**Jute Fiber**
α-Cellulose	38.4	63-64	**60**
Hemi cellulose	30.9	19	**22**
Lignin	27.3	5	**12**

It is evident from the composition of natural fiber that the main constituents are α-cellulose hemi cellulose, and lignin and the rest are very little influence to the structure of natural fiber.

Cellulose: Cellulose pertains to the class of carbohydrates. It contains 44.4 % of carbon, 6.2 % of hydrogen and 49.4 % of oxygen [9]. Cellulose is the principal constituent of all plant life. It is a linear polymer of anhydroglucose units linked in 1 and 4 position by a β-glucoside links. The empirical formula of cellulose $(C_6H_{10}O_5)_n$ corresponds to a polyanhydride of glucose. The two terminal glucose residues of a cellulose molecule contain two different end groups; one contains a reducing hemiacetal group in the position C_1, and is therefore, known as the reducing end group, where as the other contains an extra secondary hydroxyl group in the position C_4 and is known as the non-reducing end group. There are two secondary and one primary alcoholic hydroxyl groups in each basic anhydro-D-glucose unit $(C_6H_{10}O_5)n$, which are arranged in positions 2, 3 and 6 respectively, on the basic unit. The reactivity of the hydroxyl groups varies in different reactions. In many reactions (mainly esterification) the primary hydroxyl groups have a greater reactivity. The two secondary hydroxyls, at the second and third carbon atoms, differ somewhat in their reactivity. The chemical structure of cellulose is given in Fig.3.3.
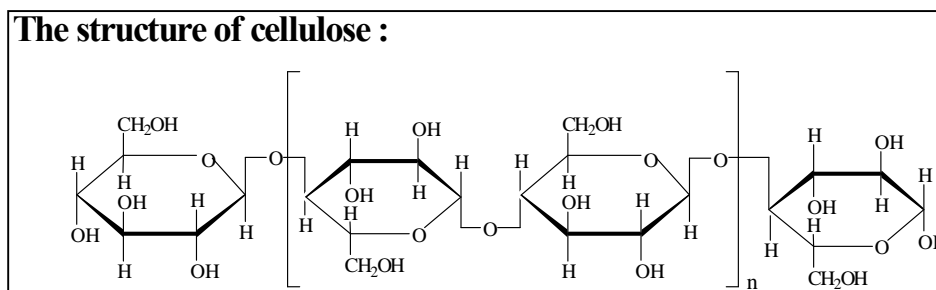
Fig.3.3: Chemical structure of cellulose

The primary hydroxyls of cellulose elementary units are responsible for the dye ability of cellulose materials. Cellulose is highly stereo specific. The high hydroxyl content of cellulose might suggest high water solubility. This is because of stiffness of the chains and hydrogen bonding between hydroxyl groups of adjacent chain as shown in Fig.3.4 [10]. Besides hydrogen bonding, another type of linkages called "Semiacetal linkages" is present between the adjacent chain molecules of cellulose [11]. From X-ray diffraction diagram, it has been concluded that cellulose has two regions: crystalline and amorphous. In the amorphous region the polymer chains end to be folded, and consequently, they will have rather different properties the crystalline region. It is in disordered regions that the most of the chemical reactions take place with cellulose. Again, polymeric fibers are never completely crystalline. This interconnection of crystalline and amorphous regions enhances the strength of the polymer [10].
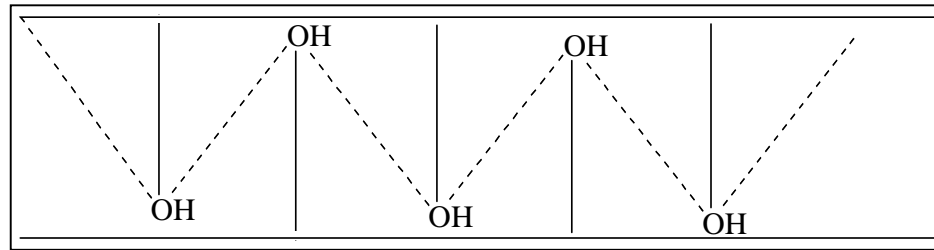
Fig.3.4: Hydrogen bonding in adjacent chains.

As early as 1920, Herzog and Janeke recognized that cellulose from such widely different sources as cotton, ramie, wood, jute and flax gave identical X-ray diagram and concluded that the fibers had identical crystalline structures.
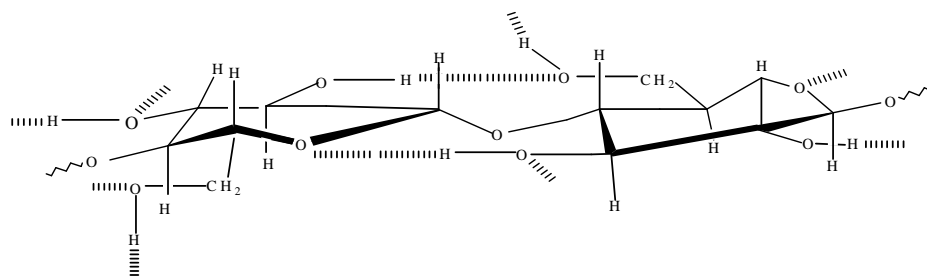
Fig.3.5: Hydrogen bonding of cellulose.

Fig.3.5 shows the hydrogen bonding system in cellulose i.e. the main constituent of the natural fiber. The thinner lines means the in-plan, the thicker lines denotes above plan and the dashed line signifies the position of atoms of cellulose molecule. Two types of hydrogen bonding have been identified in cellulose namely intermolecular and intramolecular type. These differences in hydrogen bonding mean that the surface chains have some freedom to move. The lack of intramolecular hydrogen bonding in the surface chains also means that they can form more hydrogen bonds to water or adjacent polysaccharides. It is an anomaly that cellulose   and   , with more intramolecular hydrogen bonding, cannot form as many hydrogen bonds from chain to chain as the surface form of cellulose, yet the chains within a crystalline unit are held together with spectacular tenacity.

Hemicellulose: Hemicellulose is a group of cell wall polysaccharides. The isolated hemicelluloses are amorphous substances. The cellulose and lignin of plant cell walls closely interpenetrated by a mixture of polysaccharides called hemicellulose. It is soluble in dilute alkali and they are readily hydrolyzed to pentose and hexose with some ureic acids. Sarker and others showed xylose linked with methyluronic acid formed the basic building units of hemicellulose in jute. It appeared that six xylose units are linked with 1-methyl glucuronic acid units.
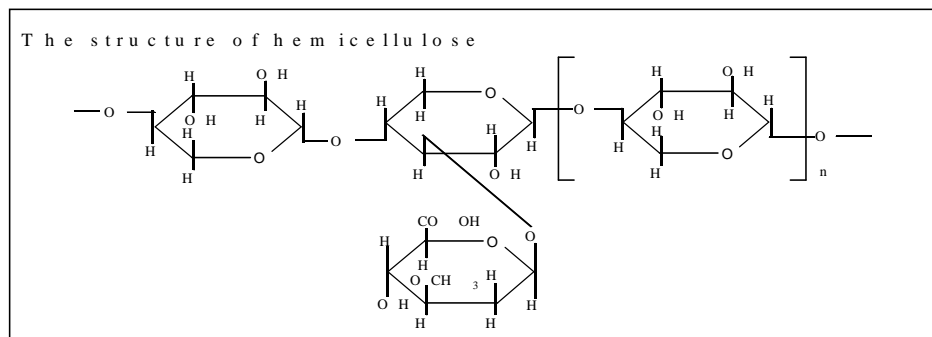
Fig.3.6: The structure of the repeating unit of jute hemicellulose 3-methylxy galactouronic acids linked with xylose units.

The structure of the repeating unit of jute hemicellulose 3-methylxy galactouronic acid linked with xylose units. The hemicellulose is relatively short chain compounds and, therefore, occupies longitudinally the same space as the anhydroglucose unit in cellulose chain. The short chain polysaccharides would, therefore, pack rigidly into the oriented cellulose structure between which some cross bridging or looping may also occur shown in Fig.3.6.

Lignin: Most plant tissues contain, in addition to carbohydrate and extractives, an amorphous polymeric gummy material is called lignin [12, 13]. The nature of lignin and its relationship to cellulose and other constituents of fiber are still uncertain. Unlike cellulose and hemicellulose, lignin gives a series of color reactions, which indicate the presence of compounds for which these reactions are typical. Isolated lignin is generally an amorphous material having average high molecular weight. Lignin is an insoluble, resin like substance of phenolic character. It is built up to a large extent, of phenyl propane building stones, often having a hydroxyl group in the para position and methoxyl group/groups in meta position/positions to the side chain. Besides, there may be carbon to carbon or carbon to oxygen bonds joining the aromatic ring to the portions of structure.
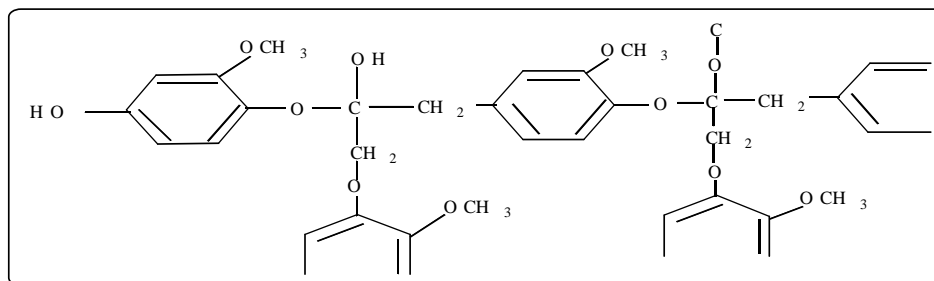
Fig.3.7: Overall structure of lignin

The lignin molecule, thus being polyfunctional due to the presence of alcoholic and phenolic hydroxyl groups, may exist in combination with two or more neighboring chain molecules,

cellulose or hemicellulose, serving the function of a cross-linking agent is shown in Fig.3.7. Postulated monomer in lignin is shown in Fig.3.8.

Structural unit of lignin:
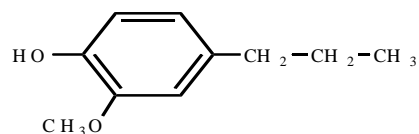
4-hydroxy-3-methoxy phenyl propane.

Fig.3.8: Structural unit of lignin

The alkali sensitive linkage is an ester type of combination existing between hydroxyl groups of lignin and carboxyl groups of ironic acids of hemicelluloses. The other one is being lived to be of ether or similar types occurring through the hydroxyl grouped of lignin.

3.9 Association of cellulose, hemicellulose and lignin

There is no conclusive proof with regard to the chemical union of hemi cellulose with cellulose in the jute fiber. The opinion is that hemi cellulose, except xylan, can not enter into cellulose crystallites due to spacing difficulty. The cellulosans, mainly xylan, associated with the true cellulose in the cellulosic structure, are relatively short chain compounds, and occupy longitudinally the same space as the glucose units in the cellulosic chains. Xylan and cellulose are laid as a mixed crystallite structure probably with incrusting cement consisting of lignin and hemicellulose [14]. It was elsewhere reported that a trisaccharide "gluco-xylo-arabinose" was isolated from delignified jute holocellulose supporting some chemical bonding affinity between cellulose and hemicellulose. But physical data from x-ray study do not appear to justify any chemical union between cellulose and hemicellulose. Regarding the possibility of cellulose-lignin combination, the view is that the lignin can not enter the cellulose crystallite due to the same spacing difficulties, but a small amount of lignin is intimately associated   at the cell   wall boundaries of cellulose [15]. Chemical union exists between lignin and hemi cellulose and it is the ester type linkage between the alcoholic hydroxyl group of lignin and the carboxyl group of polyuronic acid of hemi cellulose, and the ether type linkage between phenolic hydroxyl group of lignin and hydroxyl group of hemi cellulose [16].

Hemi-COOH + OH-Lignin $\longrightarrow$ Hemi-COO-Lignin;   ester linkage

Hemi-OH + OH-Lignin $\longrightarrow$ Hemi-O-Lignin;   ether linkage

3.10 Physical properties of natural fiber

Physical properties of fiber such as breaking strength, extensibility, flexibility and moisture absorption etc. all depend on a number of factors of which the length of the fiber molecules, the mode of alignment amongst them and the nature and intensity of inter chain cohesive forces are important. In pure cellulose fiber the lateral cohesive forces including hydrogen bonds have maximum intensity in the crystalline regions, where the chain molecules are arranged in a more organized manner. The crystalline portions contribute in the strength and rigidity of fibers, while amorphous portions, which allow a better freedom of movement of the chain molecule account for extensibility, flexibility and moisture affinity. The non-crystalline region of cotton tree is contributed to a considerable extent to its strength by the cross-linkages of incrustants, which are distributed entirely in the amorphous regions. If these cross-linkages are ruptured, appreciable loss of wet strength of the fiber results [17].

3.11 Chemical properties of natural fiber

Natural plant fiber like jute, sisal, banana, palm fiber is a lingo-cellulose or leaf fiber which properly speaking, compound of cellulose with lignin. Unlike pure cellulose fiber, it is highly reactive towards various chemical reagents such as acids alkalis and oxidizing reagents and the higher reactivity arises mainly from the non-cellulosic constituents of the fiber, namely hemi cellulose and lignin. Lignin is unhydrolysable by acids readily oxidizable and soluble in hot alkali while strong mineral acids to water soluble sugars are relatively resistant to oxidizing agents easily hydrolyze carbohydrates. This fiber is highly susceptible to the action of light, the main features of the photochemical changes being loss of tensile strength and development of a yellow or brown color. The degradation caused by light to this fiber has been found to the greatest amongst all natural cellulose fibers. The reactions involved in photo-chemical degradation of textiles are mainly oxidative in nature and on prolongs exposure to light the constituent chain molecules are gradually oxidized in all possible manners and ultimately broken down to smaller fragments as a result the tensile strength of the fiber is adversely affected. It has been observed that all the main fiber components including cellulose superior degradation and the components lignin and hemi cellulose is much reactive to light. Due to the influence of light ligneous residues (phenolic group) are into color quinoid derivatives resulting in yellow or brown color. It is established that lignin is responsible for yellowing of fibers. In absence of moisture or atmospheric oxygen it is claimed, this photochemical action of light on fiber is minimum.

3.12 Jute fiber

The most important types of natural fibers used in composite materials are flax, hemp, jute, kenaf, and sisal due to their properties and availability. Jute is an important bast fiber with a number of advantages. Jute has high specific properties, low density, less abrasive behaviour to the processing equipment, good dimensional stability and harmlessness. Jute textile is a low cost eco-friendly product and is abundantly available, easy to transport and has superior drapability and moisture retention capacity. It is widely being used as a natural choice for plant mulching and rural road pavement construction. The biodegradable and low priced jute products merge with the soil after using providing nourishment to the soil. Being made of cellulose, on combustion, jute does not generate toxic gases.

Due to low density of jute combined with relatively stiff and strong behaviour, the specific properties of jute fiber can be compared to those of glass and some other fibers (Table: 3.2).

Table.3.2: Properties of jute fiber in comparison with other fibers:

Fiber	Density (g/cm^3)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)	Specific Tensile Strength (MPa/ g.cm^{-3})	Specific Young's Modulus (GPa/g.cm^{-3})
Jute	**1.3-1.45**	**393-773**	**13-26.5**	**1.16-1.5**	**286-562**	**9-19**
Flax	1.5	345-1100	27.6	2.7-3.2	230-773	18
Ramie	1.5	400-938	61.4-128	1.2-3.8	267-625	41-85
Sisal	1.45	468-640	9.4-22.0	3-7	323-441	6-15
Coir	1.15	131-175	4-6	15-40	114-152	3-5
E-glass	2.5	2000-3500	70	2.5	800-1400	28
S-glass	2.5	4570	86	2.8	1828	34

Jute is the least expensive of fibers in large-scale use. It is available in a wide variety of weights, wide and constructions and may be dyed rot-proofed, coated, laminated or blended with other fibers, to meet special requirements. Modules of elasticity of jute fiber are about 5.87N/Tex. It is varied up to 30%. Tex means weight in gm per thousand meter of yarn. Specific gravity of jute fiber is much less than that of glass fiber. Jute fibers are weaker than those of linen. The fibers are very short but lustrous and smooth. Because jute is affected chemical bleaches, it can never be made pure white. It is not very durable and is very much weakness by dampness. Like cotton it is attacked by light.

3.12.1 Advantages of using jute fiber as reinforcing materials

- It is lower in cost.

- Since the specific gravity of jute fiber is much less than that of glass fiber. The cost advantages per unite volume is further enhanced.

- The save weight. The specific gravity of a jute/polyester laminate can be up to 25 percent less than that of a glass/polyester construction.

- The use of woven material ensures uniformity of reinforcement thickness throughout the area of the laminate.

- Jute /polyester laminate and a glass/polyester laminate of the same dimensions will have equal stiffness, but the jute /polyester laminate will be lighter and will cost less.

Jute reinforcement is therefore a means of providing structural rigidity with low weight and low cost. The natural fibers can be used to reinforce both thermosetting and thermoplastic matrices. Thermosetting resins, such as epoxy, polyester, polyurethane, phenolic, etc. are commonly used today in natural fiber composites, in which composites requiring higher performance applications. They provide sufficient mechanical properties, in particular stiffness and strength, at acceptably low price levels. Compared to compounds based on thermoplastic polymers, thermoset compounds have a superior thermal stability and lower water absorption. However, in the case of the demand for improved recycling and in combination with new long fiber reinforced thermoplastic processing, thermoplastic polymers have been expected to substitute the thermoset polymers.
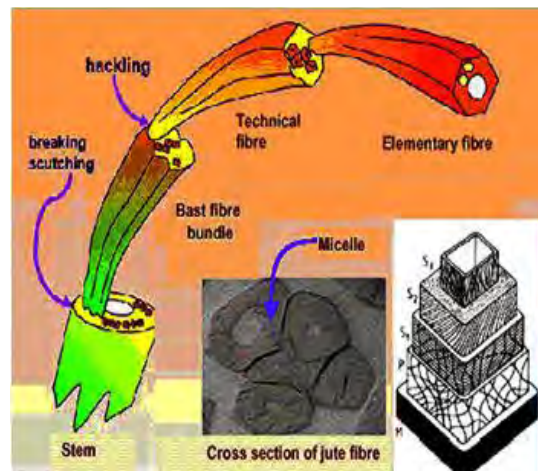

Fig.3.9: Jute plant.   Fig.3.10: Scheme of jute fiber structure.

Jute fiber is obtained from two herbaceous annual plants, white *Corchorus capsularis* (white jute) originating from Asia and *Corchorus olitorius* (Tossa jute) originating from

Africa. Next to cotton, it is the second most common natural fiber, cultivated in the world and extensively grown in Bangladesh, China, India, Pakistan, Nepal and Myanmar [18]. The Jute plant (Fig.3.9) grows six to ten feet in height and has no branches. The stem of the jute plant is covered with thick bark, which contains the fibers. In two or three-month time, the plants grow up and then are cut, tied up in bundles and kept under water for several days for fermentation. Thus, the stems rot and the fibers from the bark become loose. Then the cultivators pull off the fibers from the bark, wash very carefully and dry them in the sun.

Jute is multi-celled in structure (Fig.3.3). The cell wall of a fiber is made up of a number of layers: the so-called primary wall (the first layer deposited during cell development) and the secondary wall (S), which again is made up of the three layers (S1, S2 and S3). As in all lignocellulosic fibers, these layers mainly contain cellulose, hemi cellulose and lignin in varying amounts. The individual fibers are bonded together by a lignin-rich region known as the middle lamella. Cellulose attains highest concentration in the S2 layer (about 50%) and lignin is most concentrated in the middle lamella (about 90%), which, in principle, is free of cellulose. The S2 layer is usually by far the thickest layer and dominates the properties of the fibers [19].

Cellulose, a primary component of the fiber, is a linear condensation polymer consisting of D-anhydro-glucopyranose units joined together by ß-1; 4-glucosidic bonds [20]. The long chains of cellulose are linked together in bundles called micro-fibrils are shown in Fig.3.10.

Hemicelluloses are also found in all plant fibers. Hemicelluloses are polysaccharides bonded together in relatively short, branching chains. They are intimately associated with the cellulose micro fibrils, embedding the cellulose in a matrix. Hemicelluloses are very hydrophilic and have lower molecular masses than both cellulose and lignin. The degree of polymerization is about 50ό200. The two main types of hemicelluloses are xylans and glucomannans. Lignin is a randomly branched polyphenol, made up of phenyl propane (C9) units. It is the most complex polymer among naturally occurring high-molecular-weight materials with an amorphous structure [21]. Of the three main constituents in fibers, lignin is expected to be the one with least affinity for water. Another important feature of lignin is that it is thermoplastic (i.e., at temperatures around 90°C it starts to soften and at temperatures around 170°C it starts to flow) [19].

The jute fiber is polygonal or oval in cross section with a lumen as shown in Fig.3.9. Climatic conditions, age and the fermentation process, which influence also the chemical

composition; influence the structure of the jute fiber [22]. The jute fiber possesses moderately high specific strength and stiffness. Therefore, it is suitable as reinforcement in a polymeric resin matrix. However, it exhibits considerable variation in diameter along with the length of individual filaments. The properties of the fiber depend on factors such as size, maturity and processing methods adopted for the extraction of the fiber. Properties such as density, electrical resistivity, ultimate tensile strength and initial modulus are related to the internal structure and chemical composition of fiber [23, 24].

3.12.2 The acidic behavior of jute fiber

It is well known that jute fiber when suspended in water gives acidic reactions. Sarker and co-workers have shown that although the major portion of the óCOOH occurring in jute fiber are combined with basic ions such as calcium, magnesium etc, a small fraction exists in the free state and it is this fraction which is responsible for the acidic reaction of the fiber. It has acidic nature when suspended in water. Like tensile strength, the other properties of fibers such as extensibility and flexibility are also influenced to a great extent by the cross-linkages in the amorphous regions usually, the low inter cohesion in the amorphous region permits a better freedom of movement to the chain molecules as a result of which these regions impart the above useful qualities to the fiber. In natural fiber, however, due to the presence of cross-linkages the relative movement of the carbohydrate chains in much restricted, which ultimately affects both flexibility and extensibility. It has fairly high affinity for moisture and high hydroscopicity of the fiber compared to other pure cellulosic fibers is attributable to its low crystalline/ non-crystalline ratio.

3.13 Fiber-reinforced polymer composite

Technologically, the most important composites are those in which the dispersed phase in the form of a fiber. Design goals of fiber-reinforced composites often include high strength and/or stiffness on a weight basis [25]. These characteristics are expressed in terms of specific strength and specific modulus parameters, which correspond respectively, to the ratios of tensile strength to specific gravity and modulus of elasticity to specific gravity.

3.13.1 Principles of fiber reinforcement

The mechanical properties of a composite can depend on many factors, as alluded to in the introduction basically; these factors include the specific properties of the matrix and the

reinforcing agent, their respective volume fractions, the shape, size distribution, and orientation of the reinforcing phase and the bond between the reinforcement and its matrix. Let us examine in more detail the relationships between these factors and their influence on the mechanical behavior of composite materials.

3.14 Applications of polymer composite materials

Composites are one of the most widely used materials of their adaptability to different situations and the relative ease of combination with other materials to serve specific purposes and exhibit desirable properties. In surface transportation, PVC is the kind of composite used because of their huge size. They provide ample scope and receptiveness to design changes, materials and processes. Their stiffness and cost effectiveness Offered apart from easy availability of raw materials, make them the obvious choice for applications in surface transportation in heavy transport vehicles, the composites are used in processing of component parts with cost- effectiveness [26].

Good reproductively, resilience handling by semi-skilled workers is the basic requirements may not justify the savings obtained in terms of weight visa- a visa vehicle production, carbon fibers reinforced epoxies have been used in racing cars and recently for the safety of cars [25].

Polyester resin with suitable fillers and reinforcements were the first applications of composites in road transportation. The choice was dictated by properties like low cost, ease in designing and production of parts etc. Using a variety of reinforcements, polyester has continued to be used in improving the system and other applications.

Reinforced plastics do not cost too much to tool and they are now extensively used for automobile parts, indicator and signal lamp parts and other accessories. Truck bodies and trailers use assemblies and parts made from reinforced plastics to a great extent. The use of light metals, which lends itself to simple shapes and extricable forms, is also found to be economical. The low heat transfer confident of composites enables their use in refrigerated units. Glass reinforced polyester has all the properties that make it ideal for this purpose and it has become the standard material.

Commercial aircraft applications are the most important uses of composites [27, 28]. Aircraft, unlike other vehicles, need to lay greater stress on safety and weight. They are achieved by using materials with high specific properties. A modem civil aircraft must be so designed as to meet the numerous criteria of power and safety. Weight has been chief

problem in the minds of technologist involved in developing improved and more suitable structural concept for aircraft manufacture. Long service life is main characteristic of civil aircrafts. It dependence of the rate of utilization, which varies considerably, structural repairs need longer time period and they are the factors to be considered before initiating maintenance schedules. In commercial aircraft, fatigue corrosion is the chief problems to contend with.

Fiber epoxy composites have been used in aircraft engine to enhance performance of the system. The pilotøs cabin door of aircraft has also been made with fiberglass resin composites and these are now used in other transport systems. The boron-graphite materials were initially designed for fighter aircraft components and their use in commercial aircraft has been very less. There are a few instances of applications of these composites in wide use current! Although experimental applications are several. They are presently limited to secondary structures which can be used in commercial aircraft with considerable safety. The data from such experimentation on the long-term effects of load and stress on the structure provides input for design. Both dynamic and static conditions are combined in the turbojet engine and research has always been directed towards this. These applications involve lightweight materials and this combination offers advantages.

Aeronautical engineering comprises of various distinct area that produces vehicles capable of performing distinct flight programmers. Initially importance was given to weight, speed and power, but other parameters that influence market acceptance of the aircraft should also be considered during design. These conditions call selection of materials that give less than optimum efficiency in terms of structure and systems. Hence, it important to consider performance needs as well as service properties. Airframe design starts with evaluation of flight conditions, which the aircraft will encounter. In recent designs, wind tunnel tests and analysis are being done to determine the lift and drag forces. Once determined, they are used to develop various related factors of structural engineering. The section of material, it follows, enters naturally into the picture at early stage of design itself. The high strength of composites allows designing of higher aspect ratio wings in aerofoil sections.

Now a day, composites are used in peripheral structures of aerodromes. Conventional constructions of composites ought to cost much less in future and will not be a constant. Automation along with high standard for filament and matrix materials will also decrease fabrication costs, as the rejection on grounds of quality will be less. Future designs may also

include a combination of new aircraft, for instance, some parts of the structure may be fully metal or some may be composites. Graphite-epoxy or boron-aluminum may be used in some portions and the manufacturer will have a large range of materials to choose from. Future designs will composites on a very large scale. Performance, reliability and efficiency of operators alone can assure the success of any programmed and the space program in particular. The potential and application of high performance composites has revolutionized space structural technology. High performance composites are highly reliable materials, which have strength to weight rations higher than other materials. Depending on the type of matrix and reinforcement used, the properties of such composites vary. The properties are altered to meet specific design requirement rather than design being made according to material limitations.

The high cost of material has restricted the use of fiber-reinforced plastics in freight cars. Composite materials, however, have been used for component parts such as fasteners, levers, hatch covers in hopper cars etc. Glass fiber reinforced plastic, used for containers, is also used for paneling in rail cars. Fiberglass has been the flexible insulation material of choice for these vehicles.

3.15 Deformation of materials

3.15.1 Deformation

When an engineering material (as composite) is subjected to forces, such as those typically imposed by service loads, its atoms may be displaced from their equilibrium positions. Any displacement from the position or separation results in an energy increase. This requires work, with is supplied by the forces creating the displacement. Thus it is clear that this premise holds whether the material is stretched, causing the atoms to separate, thus bringing attractive forces into play, or compressed, bringing the atoms closer together and causing repulsion.

3.15.2 Effects of deformation

3.15.2.1 Elastic deformation

The displacement of atoms from their equilibrium positions constitutes deformation. Such deformation is termed elastic if the atoms can resume their equilibrium positions when the imposed forces are released. Elastic deformation then is recoverable and indicates the relative resilience of a material. For example, a rubber band can be stretched quite far yet

snap back to its original dimensions upon being released. A slightly different manner of stating this concept of elasticity is that it is the property of a material to return to its initial form and dimension after the deforming force is removed.

The process of elastic deformation is presented schematically in the figure. Here the atoms are repented as õhardö spheres on a lattice, when no forces are applied, the assume equilibrium separation (a). A relatively small tensile force tends to pull the atoms apart producing elastic deformation (δ_E). Their separation is now slightly larger than a_0. However, when the force is released, the atoms resume their equilibrium positions and no deformation or displacement remains. The material is restored to its initial condition. This process is illustrated in Fig.3.11.
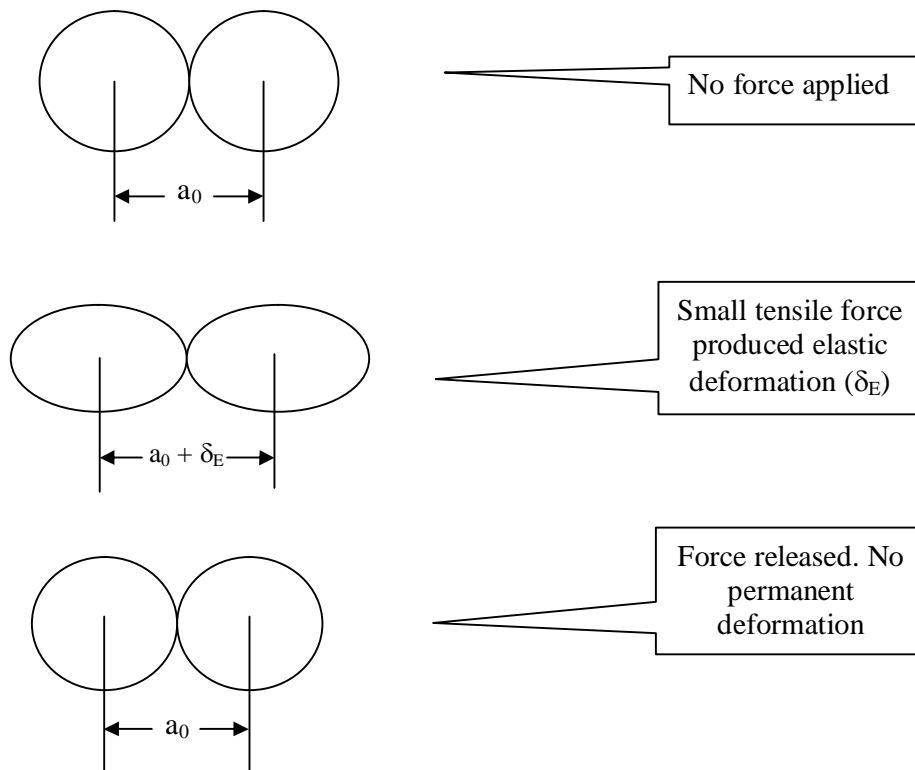
Fig.3.11: Schematic illustration of elastic deformation (δ_E).

3.15.2.2 Plastic deformation

On the other hand, if the engineering material undergoes deformation, which exceeds the elastic, capability (elastic limit) to restore the atoms to their equilibrium positions, the deformation is permanent and termed plastic. Plastic deformation is non-recoverable and leaves the atoms permanently displaced from their original positions where the forces are released. Deformation of materials may be entirely elastic, or elastic plus plastic.

The total deformation may then consist of the combined elastic and plastic portion. In this case, removal of the load or forces producing the deformation results in recovery of the elastic portion, while the plastic portion remains. Plastic deformation of engineering materials is permanent in that work or energy must be supplied to restore the atoms to their original equilibrium positions. For instance, the effect of this type of deformation can be alleviated by thermal treatments, when necessary. This process is illustrated in Fig.3.12.
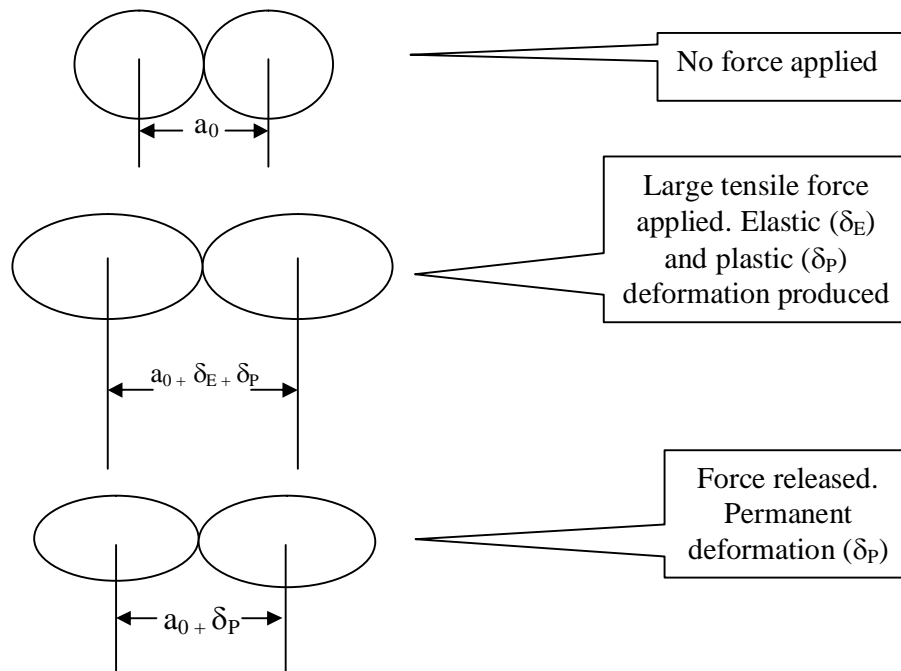
Fig.3.12: Schematic illustration of plastic deformation (δ_P).

3.16 Stress

The response of am engineering material to forces imposed on it has been discussed in terms of deformation and strain.

Now let us analyze the resistance of a material to deformation. We know that, the net force. On an atom is zero only for the equilibrium position. Displacement in either direction produces on increase in the forces (tensile or compressive) that oppose the deformation. This resistance is due to the interatomic attractive and repulsive forces that operate in a particular material. ÷Stressø is the result of the internal response that a material exhibits when forces are imposed on it. To simplify matters at this point, we will assume that the forces acts uniformly over a certain area, Then we can state that the internal espouse, the stress, is a force per unit area.
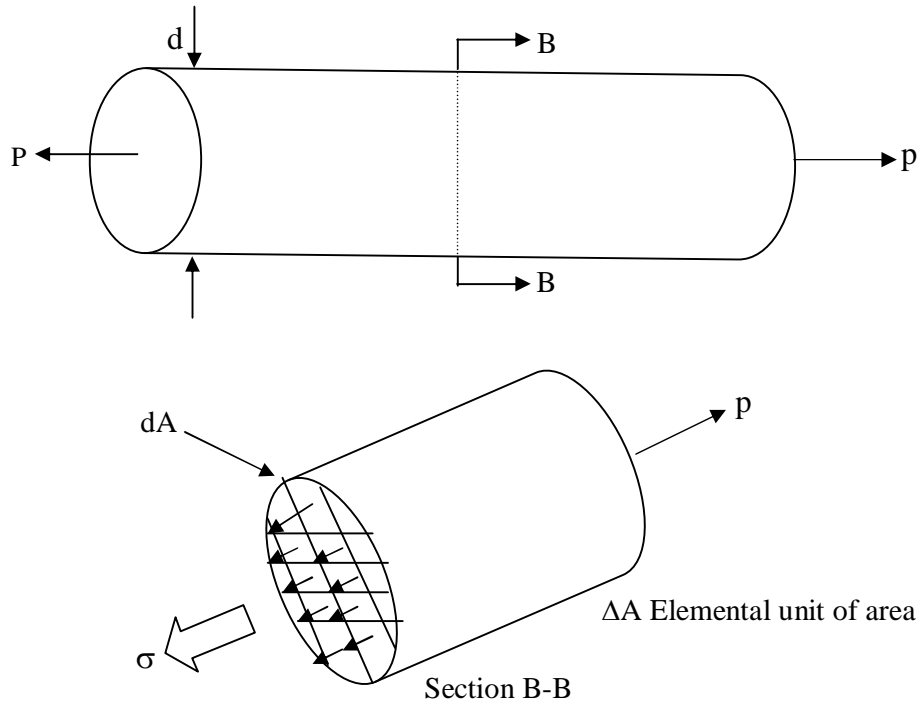
Fig.3.13: Response of cylindrical bar to applied load. Cross-sectional cut way shows
uniform resistance balancing (P).

Consider the load (P) applied to the cylindrical bar in Fig.3.13**.** The bar remains intact, indicator that the external force is balanced internally by a response of the material. If we section this bar at any particular location (normal to the axis of the applied load) P must be opposed by the stress produced in each elemental area (ΔA). It these increment of area become smaller and smaller in the limit-

$$P = \sigma dA$$

Since it previously assumed that the force uniformly applied over the cross section, the summa of stress over the entire area may be expressed a follows:

$$P = \sigma \int_{0}^{A} dA$$

Or, $P = \sigma A$

Therefore, the stress (σ) can be expressed as-

$$\sigma = \frac{P}{A} \qquad \text{...   ...   .} \qquad (3.1)$$

Where, σ = average stress

P = load or force

A = cross sectional area over which the force act

Stress is commonly denoted in unitsø lb/in^2 (psi), or in international units (SI) of Pascal (Pa). Since the Pascal is a rather small value of stress, it is customary to express stress values in mega Pascal (MPa), where the prefix M stands for 10^6.

3.16.1 Engineering stress

A common application of the stress concept is termed the engineering stress. This particular expression, which is used in many design calculations and analyzes is given as follows: [3]

$$\sigma = \frac{P}{A_0} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (3.2)$$

The only modification to our basic stress equation is A_0, which represents the original area; therefore, engineering stress treats cross sectional area as a constant.

Although this is not completely accurate, for elastic striations in the loading direction the corresponding changes in cross sectional area are generally small.

Furthermore, most design and structures are based on service conditions in the structures, are based on service conditions in the elastic range, thus the engineering stress is very useful parameter.

3.16.2 True stress

The concept of engineering stress treats the area under consideration as a constant (A_0). In reality, however, the area does not remain constant and in the case of an axially loaded tensile bar, gradually decreases as the stress (and corresponding manifestation of Poissonøs ratio effect.

The true stress therefore can be expressed as follows:

$$\sigma_{tr} = \frac{p}{A_i} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (3.3)$$

Where A_i is the actual instantaneous area over which the force is acting.

Ordinarily, the true stress in larger than the engineering stress. However, in the elastic region, change in area is usually inconsequential and the engineering stress in sufficiently accurate. When the elastic timid is exceeded and plastic strain come into play the discrepancy between engineering strain and true strain becomes more significant. From a design standpoint, however, this condition (Plastic deformation) is typically avoided in service.

The true stress (σ_{tr}) is related to the engineering stress in the following manner:

$$\sigma_{tr} = \frac{P}{A_i} \frac{A_0}{A_o}$$

$$= \frac{P}{A_o} \frac{A_0}{A_i}$$

$$= \sigma \frac{A_O}{A_i} \qquad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \qquad (3.4)$$

In this type of analysis the volume of matron is constant (even thought the dimensions may change). Therefore the following relationships also applied.

Initial volume (V_0) = instantaneous volume (V_1)

$$V_0 = V_1$$
$$\text{or, } A_o l_o = A_i l_i$$

$$\text{or, } \frac{A_0}{A_i} = \frac{l_i}{l_o} \qquad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \qquad (3.5)$$

Substituting above gives us-

$$\sigma_{tr} = \sigma \frac{l_i}{l_o} \qquad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \qquad (3.6)$$

But from the section on strain, since t is any instant in time it is equivalent to l_f, we can substitute for l_i / l_o as follows:

$$\sigma_{tr} = (e + 1) \qquad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \quad \text{...} \qquad (3.7)$$

Thus, the true stress equals the engineering stress times the quantity engg. strain plus 1.

3.17 Strain

3.17.1 Engineering strain

We have just briefly examined the response of atoms to deformation by mechanical forces. It this concept of atomic displacement is extended to bulk engineering materials, we can define the deformation in terms of the original dimensions of the material under consideration in other words, the ratio of the dimensional change to the original dimension. For example, consider a bar of length (l_0) as shown in the Fig.3.14.

Under the action of an applied load (p) this bar experiences deformation and elongates to a new length (1_f). The ratio of this change in length (l) to the original length (l_0) is the õaverage linear strainö (e) and can be expressed as follows:

$$e = \frac{\Delta l}{l_o}$$

$$= \frac{l_f - l_o}{l_o} \qquad ... \quad ... \quad ... \quad ... \quad ... \quad ... \qquad (3.8)$$

$$l_0$$

$$P \longleftarrow \qquad \longrightarrow P$$
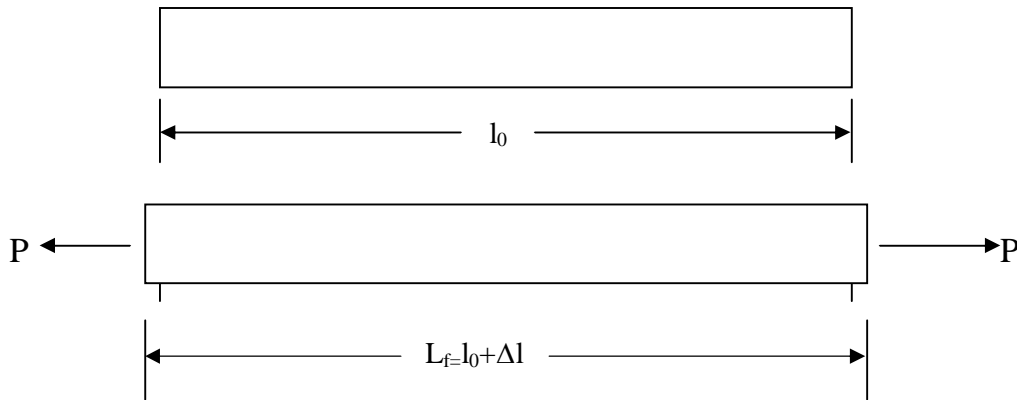
$$L_{f=l_0+\Delta l}$$

Fig.3.14: Deformation of a bar produced by axial load.

This quantity is referred to as the average linear strain because only the dimensional change in the axial direction is considered and it is considered over the entire length of the sample. In reality, because its volume remitters constant, the bar diameter does decrees slightly, resulting in a decrease in the cross-sectional area, but for small strains this response in usually in significant. Average strain (e) is commonly referred to as the engineering strain and expressed in units of in/in or mm/mm. However, stern may also be treated as a dimensionless quantity because these units cancel.

3.17.2 True strain

Since a material undergoing deformation is continuously changing its dimension (i.e. length and width or diameter), a more precise definition of strain is given by the ratio of the change in dimension to the instantaneous dimension. In the case of round bar, this may be viewed as the change in length (dl) with respect to the instantaneous length (t) at any point in the process. This ratio is actually the true strain (E) and is expressed as follows.

$$E = \frac{dl}{l} \qquad ... \quad ... \quad ... \quad ... \quad ... \quad ... \qquad (3.9)$$

A more specific expression for E is obtainer by placing some limits on the above equation. For example, if the initial length is to and the final length is t_f. We can integrate this equation as follows:

$$E = \int_{l_0}^{l_f} \frac{dl}{l}$$

$$= [\ln l]_{l_o}^{l_f}$$

$$= (\ln l_f) - (\ln l_o)$$

$$= \ln \frac{l_f}{l_o} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad \ldots \qquad (3.10)$$

The engineering strain (e) is related to the true strain and this relationship can be demonstrated as follows:

$$e = \frac{l_f - l_o}{l_o}$$

$$\text{or, } e = \frac{l_f}{l_o} - 1$$

$$\text{or, } \frac{l_f}{l_o} - e = 1 \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad \ldots \qquad (3.11)$$

Then substituting these results we obtain

$$E = \ln(e + 1) \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad \ldots \qquad (3.12)$$

3.17.3 Shear strain

In addition to linear strain, an engineering material can experience shear strain (γ), this type of strain is due to the displacement of parallel planes through a certain angle ( ) as shown in the Fig.3.15.
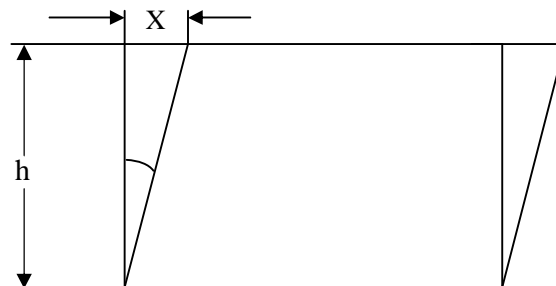
Fig.3.15: Shear displacement on parallel planes of a solid material.

The shear strain is therefore defined as the ratio of the displacement (x) to the distance (h)

between the planes, expressed as: $\gamma = \dfrac{x}{h}$ ...   .   (3.13)

3.18 Poisson's ratio

Because of the constancy of volume when a material is deformed in one direction there is a

corresponding displacement or deformation in a direction perpendicular to it. For example,

consider the bar in fig. If axial load (P) is applied, the bar elongates in the direction shown

in Fig.3.16.
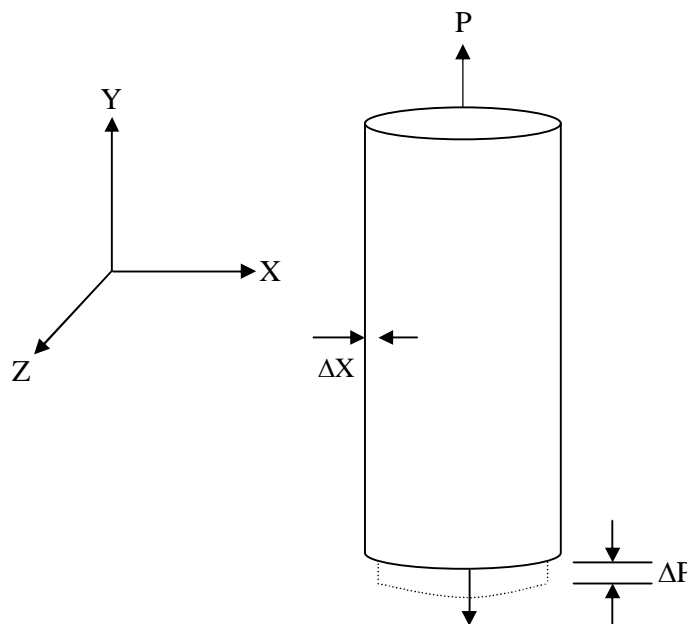
Fig.3.16: Deformation in x direction due to axial load (P) applied in y direction

The ratio of the strain in the x direction to the strain in the y direction is termed poison's

ratio (v) and expressed as follows:

$$\frac{e_x}{e_y} = v$$ ...   .   (3.14)

Since this example is symmetrical shape and the strains have been assumed to be uniform,

the strain in the z direction (e_z) equals e_x. So ÷v÷ is equivalent in the x and z directions. This

relationship is important, because ÷v÷ is a constant for elastic strains and can be used to

compute strains in directions other than the direction of the applied force.

3.19 Hook's law

The elastic limit of an engineering material is the highest stress that can be produced without experiencing any plastic (Permanent) deformation. We alluded to the concept of elastic limit easier in the discussion of plastic deformation. In most materials for values of stress below the elastic limit, stress is proportional to strain as follows:

$$\sigma = Ee \qquad ... \qquad ... \qquad ... \qquad ... \qquad ... \qquad ... \qquad (3.15)$$

This relationship is known as Hooke's law and the proportionality constant (E) is the modulus of elasticity (Young's modulus).

3.20 Elastic modulus

The elastic modulus (E) is a measure of the stiffness of an engineering material. Examination reveals that for a given stress; greater values of E result in smaller elastic strains, meaning that the higher the elastic modulus, the smaller elastic strains, meaning that the higher he elastic modulus, the smaller the response of the structure to a particular stress, this parameter is important for design and amylases purpose, especially in computing the allowable displacements and deflections of engineering components or structure.

Although the modulus of elasticity is a structure insensitive property, it is intended by temperature. As temperature is increased E decreases, thereby reducing the stiffens of a material. This reduction in elastic behavior is due to an inverse relationship between the modulus and the interatomic or interionic distance in metals and ceramics respectively. Therefore as we increase and E gradually decreases.

3.21 Stress-Strain relationship for the case of fiber

In order to analyze the stress strain behavior of a composite will consider a simple situation where a matrix containing continuous cylindrical fibers is deformed in direction prattle to the long axis of the fibers, as illustrated in the following Fig.3.17.

If we can assume that no slippage occurs at the interface between the fibers and matrix, the elongation is the same in both phases.

Therefore, the engineering strain in the composite may be expressed as-

$$E_c = e_f = e_m = \frac{\Delta l}{l_o} \qquad ... \qquad ... \qquad ... \qquad ... \qquad ... \qquad (3.16)$$

Where, e_f = strain of fibers
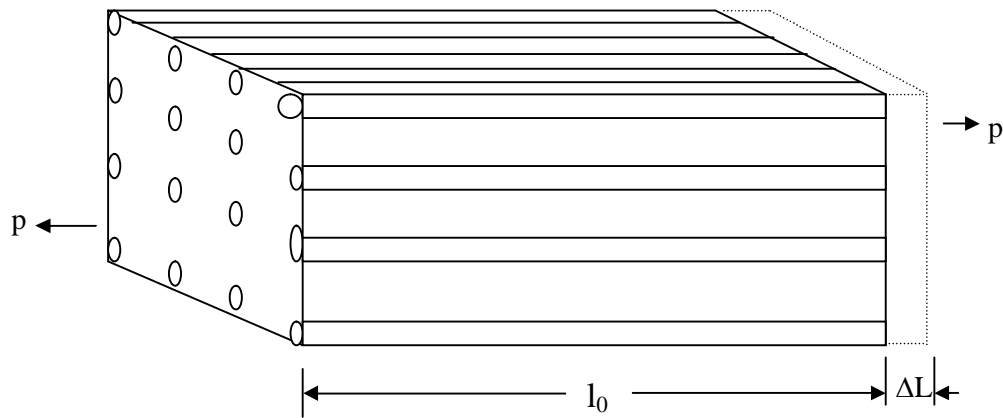
e_m = strain of matrix.

Fig.3.17: Axial deformation due to the load (p) in a composite reinforced with continuous cylindrical fibers.

Furthermore, when these strains are elastic the engineering stress in the respective composite can be determined by applying Hook's law as follows:

$$\sigma_f = E_f.e_f \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (3.17)$$

$$\sigma_m = E_m.e_m \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (3.18)$$

Where, σ_f = stress in fiber

σ_m = stress in matrix

E_f = elastic modulus of fiber

E_m = elastic modulus of matrix

In most cases, the modulus of the fiber is greater than that of the matrix, for a given strain the stress in the fiber is greater than the matrix stress. Although this is a bray simplified analysis it serves to illustrate the extremely important concept fiber reinforcement. Generally, the fibers are more highly stressed than the matrix when a load is applied to the composite. The mechanism permits transfer of the stresses from the matrix to the reinforcing phase. As a result, the composite can sustain greater stresses them the unreinforced matrix material. This concept of utilizing the advantages of one material such as high modulus or high strength, in conjunction with the advantages of another, such as low density or corrosion resistance, is the very essence of composite material.

3.22 Fiber orientation

The alignment of fibers in reinforced composites is also a very important factor, Misalignment of fibers occurs during fabrication simply because short fibers and slender filaments are difficult to align. Orientation of the fibers with respect to the direction of applied loading affects the tensile strength of a composite, small angle of disorientation (up to about-8) the strength of the composite is unaffected. But when the fibers are misaligned and are greater than this critical value (ϕ_{crit}), the strength of the composite decreases precipitously.

3.23 Interfacial bond

In addition to the aspect ratio and the orientation of the fibers, the strength and the bond between the fiber and matrix is a prime factor in determining the mechanical behavior of a composite. A strong bond between these constituents is necessary for them to act together during loading or service. To develop this bond, it is essential that the matrix wet the surface of the fiber during fabrication. Such wetting is necessary in obtaining good molecular atomic interaction between the constituents. If the matrix material does not readily wet the fiber, special finishes called coupling agents can be used to promote mounding between the matrix and its reinforcement. Such finishes are usually applied to the fiber reinforcement- prior to fabrication of the composite during the process referred to as õsizingö. Surface roughness of the fiber phase another important consideration in promoting bonding between the constituents of the composite: If the surface is very rough containing many minute asperities, the matrix material may not penetrate the depressions and a poor interfacial bond will result [29ʹ30].

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CHAPTER-FOUR

MATERIALS AND METHODS

4.1 Raw materials

It was discussed earlier that jute fibers are obtained from jute plants that were shown in Fig.3.8 of chapter 3. The plants are cut at the base and kept under water for some days to scrape away mushy fibers. The mushy fibers are washed with clean water and then dried under the sunlight. This gives golden colored fibers as shown in Fig.4.1.

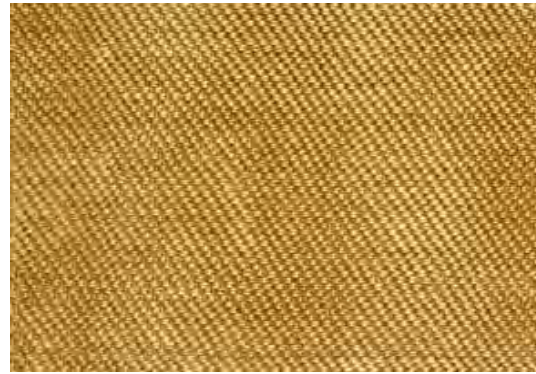Fig.4.1: A photograph of raw jute fiber.   Fig.4.2: A photograph of raw jute mat.

One of the principal raw materials used in this investigation are JM (JM) as shown Fig.4.2, obtained from the jute fiber. It's scientific and family names are *Corchorus olitorius* and *Malvaceae* or *lime* respectively. The JMs were collected from local market. The other main material used is polyvinylchloride (PVC) sheet, purchased from local market. These two materials were combined to produce PVC-JM composites.

4.2 Equipment

4.2.1 Equipment used in composite fabrication

Several equipments were used in the fabrication of PVC-JM composites. The main equipments are as follows:

(a)   Electric balance

(b)   Water bath

(c)   Heating mental

(d)   Hot plate with stirrer

(e)   Sample die

(f)   Weber-Pressen hydraulic press

Brief descriptions on the used of equipment for the sample preparation are given below:

(a)   Electric Balance

An electric balance (HP 200) was used for measurement of weight of the sample (Fig.4.3). The balance is sensitive and has a measuring capacity of 0.001 gm.

Fig.4.3: A photograph of an electric balance

(b)   Water bath

The water bath is used for surface modification of JM.

(c)   Heating mental

The heating mental is used for bleaching the JM.

(d)   Hot plate with stirrer

The hot plate with stirrer is used for scouring and bleaching of JM sample.

(e)   Sample dryer

The sample dryer is used for removing moisture from the processed JM.

(f)   Weber-pressen hydraulic press

The compression-molding process is a very widely used method for fabrication of articles from polymer materials. Fig.4.4 shows a typical mold employed in this study for compression molding. The mold is made of two halves- the upper and the lower halves or the male and the female. In most cases, the lower half contains a cavity when the mold is closed. The gap between the projected upper half and the cavity in the lower one gives the shape of the molded article.
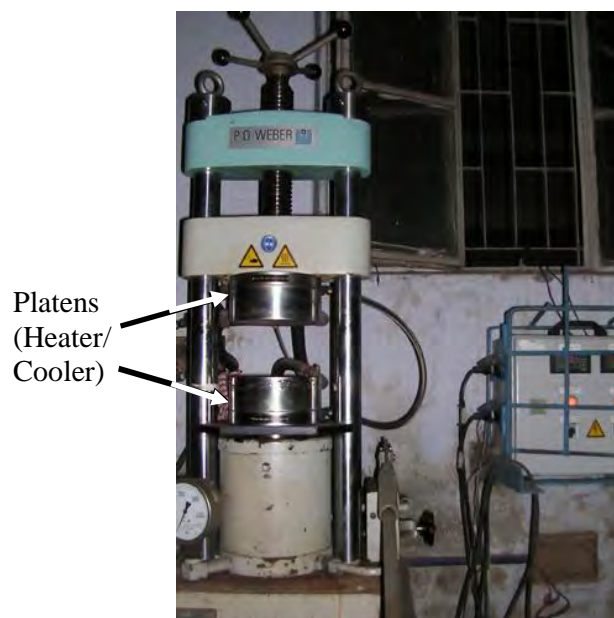
Fig.4.4: A Weber-pressen hydraulic press machine

The mold used in this research work had both the upper and lower halves but had no cavity in any half in the mold. These two halves are completely plane with smooth surface platens, which also acts as heater and cooler simultaneously. In this molding process, one has to make die for casting with his desired size. A die used in this study had a ring of inside diameter 14.6 cm and outside diameter 15.8 cm and have two disc (or plates) on each side, each of 0.75cm in thickness. This die with the raw samples is placed in between the platens.

4.2.2 Equipment used for the characterization of the sample
4.2.2.1 Fourier-transform infra-red spectrometer

Fig.4.5: A photograph of an FTIR spectrometer.

Fig.4.5 shows the picture of a Fourier-transform infra-red (FTIR) spectrometer. This instrument consists of a far-IR, near-IR and mid-IR light sources and detectors. This

apparatus was used to determine the formation of new chemical bonds in the composites. A brief description of the apparatus and its working principle is discussed below:

Light from the source is split into two beams. One of the beams is passed thorough the sample under examination and is called the sample beam. The other beam is called the reference beam. When beam passes thorough the sample, it becomes less intense due to the absorption of certain frequencies. Let I_0 be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively. The absorbance of the sample at a particular frequency can be calculated as:

$$A = \log (I_0/I)$$

Also transmittance, $T = I/I_0$

So that, $A = \log (1/T)$ í   í   í   í   (4.1)

Various techniques can be employed for placing the sample in the path of the infra-red beam depending upon whether the sample is a gas, a liquid, or a solid. The intermolecular forces of attraction are most operative in solids and least in case of gases. Thus, the sample of the same substance shows shifts in the frequencies of absorption as we pass from the solid to the gaseous state. In some cases, additional bands are also observed with the change in the state of the sample. Hence, it is always important to mention the state of the sample on the spectrum which is scanned for its correct interpretation. Solids for the infra-red spectrum may be examined as an alkali-halide mixture. Alkali metal halides, usually sodium chloride, which is transparent thorough out the infra red region is commonly used for the purposes. Potassium bromide (KBr) also serves the purpose well. The most popular method of FTIR spectral studies is KBr pellet method.

In this method, the solid sample is finely pulverized with pure, dry KBr, the mixture is pressed in a hydraulic press to form a transparent pellet, and the spectrum of the pellet is measured. It is important that the solids be extremely finely divided and well mixed. The pellet is usually pressed in a special die that can be evaluated in order to avoid entrapped air, which causes cloudiness in the pellet. A major advantage of this method is that KBr has no absorption in the IR above 250 cm^{-1}, so that an unimpeded spectrum of the compound is obtained. A disadvantage of the method for co-ordination compounds is that Br from the KBr can often replace lagans in the compound whose spectrum is desired. If this is not realized by the experimenter, misinterpretation of the spectrum will result. The substance under investigation should be absolutely dry as water absorbs strongly at about 3710 cm^{-1} and also near 1630 cm^{-1}. The particle size of the ground mixture should be less than 2 m   to

avoid scattering. Potassium bromide is transparent to the infra-red region (2.5 m-15 m) and thus, a complete spectrum can be scanned by mixing 1ó2% of the solid sample with it and then grinding it to the desired particle size.

4.2.2.2 Universal Testing Machine

A universal testing machine (UTM) was used for measuring the mechanical properties such as, tensile and flexural strength, tensile and flexural strains, Youngøs modulus and tangent modulus of the composites. A photograph of the Hounsfield UTS 10 kN (H10KS) is shown in Fig.4.6. This machine contains grips to hold a sample, which is stretched by the application of a continuously increasing load to measure the tensile properties. The gap between the grips is maintained according to ISO standard. The maximum load that can be employed in this machine is 10 kN. Flexural measurements of a sample can also be performed by this apparatus. For flexural measurements a three-point loading to fracture the sample is employed. The present setup of the Fig.4.6 shows an arrangement of flexural test. The measuring conditions are input by the programmed software. The data acquisition and analyses can be performed by the software.

Fig.4.6: A UTS machine with related accessories

4.2.2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to observe the microstructure and the surface morphology of the composites [1]. Fig.4.7 shows a SEM apparatus that consists of

two linked electron beam devices. It has the following main components: electron gun, condenser lens, objective system (lens, stigmator, scan coils), specimen stage and detector (secondary electron detector, CRT screen) (Fig.4.8).
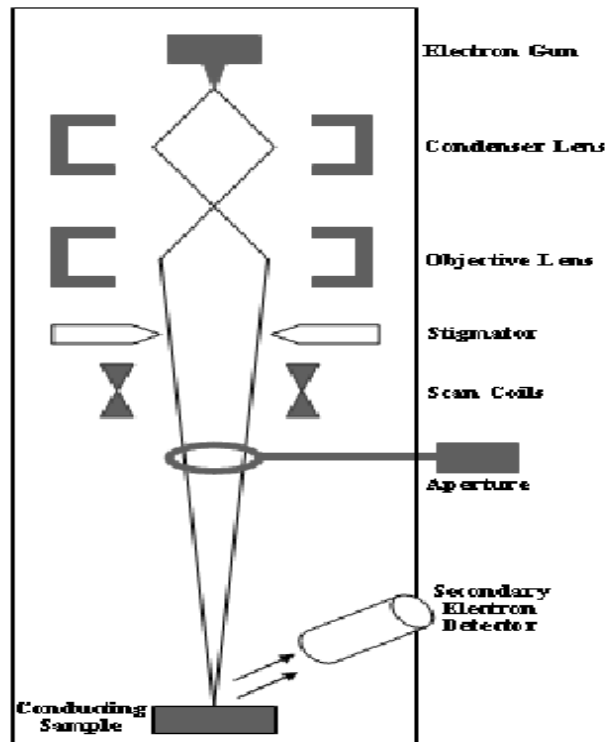

Fig.4.7: A photograph of SEM apparatus.

Fig.4.8: Block diagram of a SEM component.

In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission. Tungsten is used because it has the highest melting point

and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which can be detected to produce an image.

4.2.2.4 Thermo Gravimetric Analyzer and Differential Thermal Analyzer

Fig.4.9 illustrates a photograph of a thermo gravimetric analyzer (TGA) coupled with a differential thermal analyzer (DTA) [Seiko-Ex-STAR-6300, Japan], which was used in this study. TGA is used primarily for determining thermal stability of polymers [2] and TGA method is based on continuous measurement of weight on a sensitive balance (called thermo balance) as sample temperature is increased in air or in an inert atmosphere. This is referred to as non-isothermal TGA. Data are recorded as thermograms of weight versus temperature. Weight loss may arise from evaporation of residual moisture or solvent at lower temperatures, but at higher temperature it results from polymer decomposition.

Fig.4.9: A coupled differential thermal analyzer and thermogravimetric analyzer.

Fig.4.10 shows a sample-balance-beam and a reference-balance-beam that are independently supported by a driving coil/pivot. When a weight change occurs at the beam end, the movement is conveyed to the opposite end of the beam via the driving coil/pivot, when optical position sensors detect changes in the position of a slit. The signal from the optical position sensor is sent to the balance circuit. The balance circuit supplies sufficient feedback current to the driving coil so that the slit returns to the balance position. The current running to the driving coil on the reference side is detected and converted into weight signals.
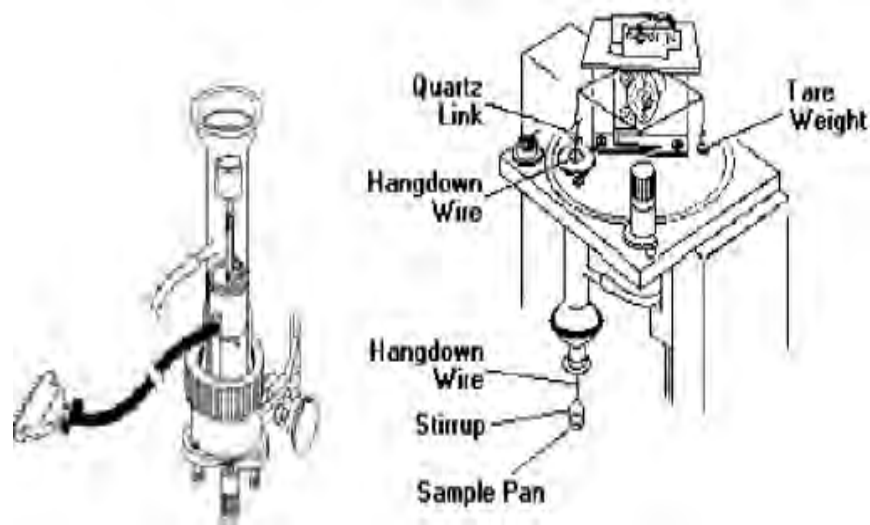
Fig.4.10: Schematic picture of a furnace and a micro balance of a TGA.
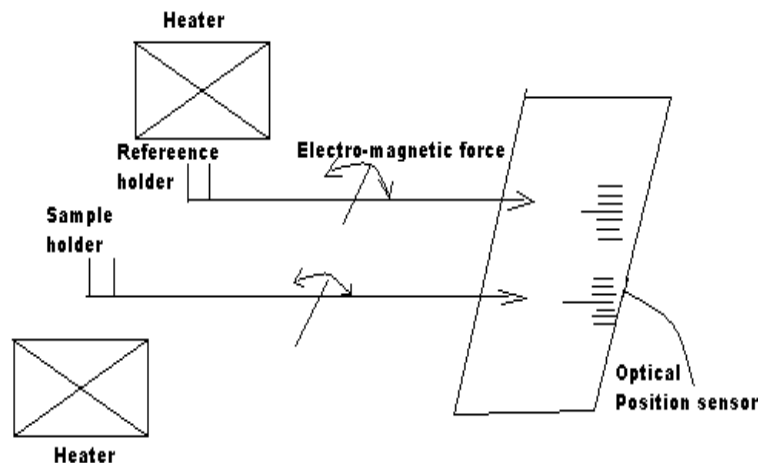

Fig.4.11: Principle of TGA measures

Fig.4.11 illustrates a scheme of the principle of TGA measurements.

Fig.4.12 illustrates the schematic diagram of a DTA. It is an important tool to study structural and phase changes occurring in solid and liquid materials during heat treatment. Thus changes may be due to dehydration, transition from one crystalline from to another, destruction of crystalline structure, melting, oxidation, decomposition, degradation temperatures, etc.

DTA is a process of accurately measuring the difference in the temperature between a thermocouple embedded to a sample and a thermocouple in a standard inert material such as aluminum oxide while both are being heated at a uniform rate [3].

Any physical or chemical change in the test sample at a specific temperature, which is a characteristic feature of the material under study, is usually associated with a thermal transition leading to an enhanced difference of temperature ΔT, between the test and reference sample. ΔT is recorded as a function of temperature T. For no transition in the shape, ΔT remains nearly constant. In DTA, the correlation between ΔT and energy change ΔE for a transition is unknown, thereby making an uncertain conversion of endothermic or exothermic peak areas to energies.

4.2.2.5 Differential Thermogravimetry

DTG stands for differential thermogravimetry. If not the weight itself rather the first derivative of the sample weight with respect to time at constant temperature or with respect to temperature at constant value of heating is determined then this procedure is termed as DTG. Basically DTG is the differential of TGA data with respect to temperature.
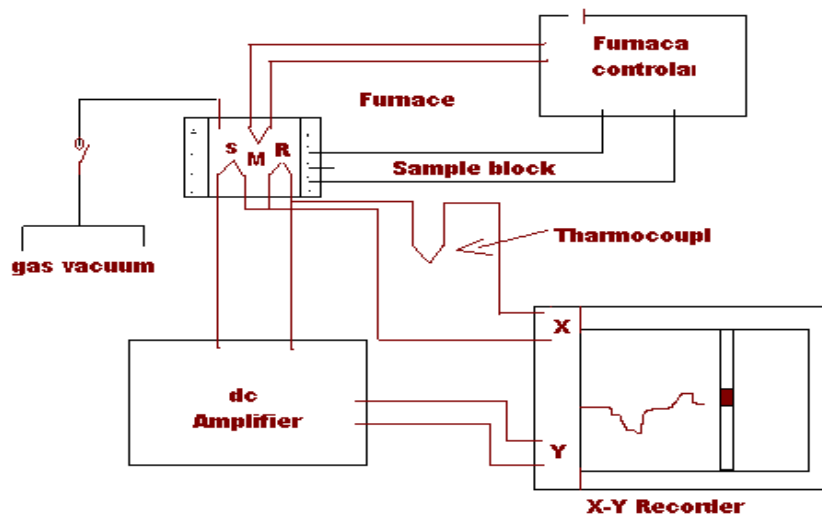

Fig.4.12: Schematic diagrams showing different part of a DTA apparatus.

4.3 Methods

4.3.1 Sample preparation

4.3.1.1 Mat cutting

JM were cut in a size of 12×12 cm^2, equal to the size of two die with the help of a scissor. Each mat was kept in an oven for 24 hours for the partial removal of moisture.

4.3.1.2 Acetylation

One simple method that can be used to increase the roughness of fiber surface is acetylation. The effect of acetylation on natural fibers at different reaction times and reaction temperatures imparts different surface characteristics. The extents of moisture regain by the fibers and stability of fibers can be improved by this treatment. The increase of surface roughness of fiber can result in a better adhesion with the polymer matrix. The thermal stability of acetylated natural fiber can also be improved by surface treatment [4]. Acetylation is a rather attractive method of modifying the surface of natural fibers and making it more hydrophobic. It has been studied more than any other chemical reaction of lignocellulosic materials. The main principle of the method is to react the hydroxyl groups (OH) of the fiber with acetyl groups (CH$_3$CO), therefore rendering the fiber surface more hydrophobic. The hydroxyl groups that react are those of the minor constituents of the fiber, i.e. lignin and hemicelluloses, and those of amorphous cellulose [2].

Procedure of acetylation: 2 gm of glacial acetic acid (CH$_3$COOH) was dissolved in 98 gm of distilled water to prepare 2 wt% acetic acid solutions. JMs were soaked in the solution kept at 30°C maintaining a liquor ratio of 1:20 (1 gm JM in 20 gm solution).The mats were immersed in the acid solution for 1hr. The mats were removed from the solution and washed several times with fresh water to remove acetic acid from the mat surface. The mats were then dried at room temperature for 24 hours and then at 105°C in an oven for 6 hours. Reaction of JM with acetic acid is shown in Fig.4.13 [5].
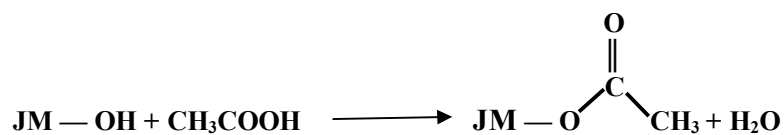
$$JM-OH + CH_3COOH \longrightarrow JM-O-\overset{\overset{\textstyle O}{\|}}{C}-CH_3 + H_2O$$

Fig.4.13: Reaction of JM with acetic acid.

4.3.2 Composite preparation

The PVC-JM composites were prepared by the following ways:

 (a) Mat placing

Mat placing is an important part for this experimentation, because if the JM and PVC matrix are not combined homogeneously, the quality of the products obtained will be poor. Considering this, JMs were carefully placed on PVC sheets.

 (b) Casting

A special molding device is made by steel to very close tolerance for the molding process. The mixture of JM and matrix is cast by simply pouring the mixture into the mold and leveling it to the desired thickness. Only slight stamping or hammering on the mold is required for sufficient compaction. However, a vibration table or such will give a more efficient compaction and does a denser matrix.

 (c) Curing and controlling

On pouring the mat or matrix mixture into the special molding device, sufficient initial pressure of 50 kN is applied at first to get the desired shape and possible homogeneity. The applied pressure is measured by using a pressure gauge, set in the device. Heating is done electrically and the final temperature set at 160° C for PVC. Only 30ꞌ40 minutes is required to reach the temperature to 160^0C. The temperature was kept for 3 min at final pressure of 100 kN. After completion of heating the initial pressure was set zero and an additional pressure of 100 kN was applied to avoid the formation of voids. This additional pressure was kept for 10ꞌ15 minutes.

 (d) Cooling

Cooling is essential throughout the curing operation in order to get the ultimate composites. Cooling was done by tap water through the outer area of the heating plates of the hydraulic press machine. Cooling time was 15 minutes.

 (e) Demolding

When the composite is pressed in the die by the hydraulic press, the composite is got intact into the die through fast cooling. As a result, a demolding device is made to separate the composites from the die.

Thus, a series of JM reinforced PVC composites were prepared with and without acetylated fibers. In the fabricated composites, PVC sheet and JM are embedded and heat pressed. The

ratio of PVC:JM are maintained as 1:2, 2:1, 2:2, 3:2 and 3:3. For example, when one PVC sheet is sandwiched with two JMs, the resulting ratio is PVC:JM=1:2.

The finally obtained samples are the neat PVC sheet, the PVC-JM composites without treatment of JM and the PVC-JM composites with acetylated JM.

Fig.4.14: A photograph of prepared PVC-JM composite.

4.3.3 Characterization of composite materials

The resulting composites were characterized in various ways. These include physical test, mechanical test, surface morphological test, structural test and thermal test. The properties characterized under these tests are as follows:

- A. *Physical test*
    - I.   Water intake
- B. *Mechanical test*
    - I.   Tensile test
    - II.   Flexural test
- C. *Surface morphological observation*
- D. *Chemical bonding test*
- E. *Thermal test*
    - I.   Weight loss
    - II.   Melting temperature
    - III. Thermal degradation temperature

4.3.3.1 Methods of measuring physical properties

I. *Water intake or absorption*

Water intakes of the composites were performed according to ASTM Designation: C 67691 [6]. The test specimen was cut in a size of 6 cm length, 2 cm width and 0.2 cm to 0.4 cm thickness (Fig.4.15).

Fig.4.15: A sample for water intake measurement.

The cut sample was kept in a woven at 80°C for 24 hr. It was taken out from the woven and immediately weighed. Let this weight be W_i. The sample was then immersed in distilled water of 23°C and kept for 24 hr. It was taken out from the water, wipe by a cloth, dried in air and then weighed. Let this weight be W_f. Then the amount of water intake was calculated by the following formula:

$$\text{Water intake } (\%) = \left[\frac{W_f - W_i}{W_f}\right] \times 100 \qquad í \qquad í \qquad í \qquad í \qquad (4.2)$$

The above procedures were repeated for 48, 72 and 96 hr with other samples. It is noteworthy that the cut sides of the samples were coated with araldite to prevent from penetrating water into the sample.

4.3.3.2 FTIR spectroscopic measurements

At first the JM was dried at 105^0C for 24 hours and then powdered in a mortar. The JM compounds for IR analysis were frequently obtained by mixing and grinding a small amount of the powdered JM materials (1 mg) with dry and pure KBr (200 mg). Through mixing and grinding were accomplished in a mortar by a pestle. The powdered mixture was then compressed in a metal holder under a pressure of 8-10 tones to produce a pellet. The pellet was then placed in the path of the infrared beam of wave number in the range of 50064000 cm^{-1}.

4.3.3.3 Methods of measuring mechanical properties

The mechanical properties such as tensile strength, tensile strain, elongation-at-break, Youngøs modulus, flexural strength, flexural strain and tangent modulus of the prepared samples were evaluated by a universal testing machine (Fig.4.5).

4.3.3.3.1 Measurements of tensile properties

I. Tensile strength

Diagram of the size and shape of the specimen used in measuring stress ( ), strain ( ), tensile stress (TS), elongation-at-break [EB (%)] and Young's modulus (*Y*) is shown in Fig.4.16.
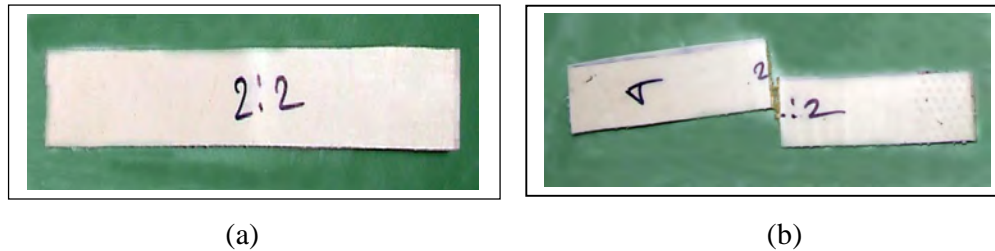

(a)   (b)

Fig.4.16: A sample for tensile test a) before test, b) after test.

Specimen for tensile measurement was prepared according to ASTM standard [7]. Crosshead speed of 2 mm/min and a gage length 48 mm were maintained. The load was continuously applied to the sample till it is fractured. The loads and corresponding extensions were recorded by the computer. Calculations of tensile properties are described below:

II. Tensile stress

Tensile stress was evaluated using the following formula:

$$\sigma = \frac{F}{A} \qquad í \qquad ... \qquad í \qquad í \qquad í \qquad í \qquad (4.3)$$

Where, *F* = Applied load to the sample

A = Cross sectional area of the test sample

The value of *F* was obtained from the UTM. The value of *A* was obtained by a slide calipers by measuring the width and thickness at least three points in the narrow zones of the samples.

III. Tensile strain

Tensile strain was calculated by the relation given below:

$$\varepsilon(\%) = \left(\frac{\Delta L}{L_0} \right) \times 100\% \qquad ... \qquad ... \qquad ... \qquad ... \qquad (4.4)$$

Where, *ΔL* = Extension due to applied load

L_o = Gage length or original length of the sample

The value of *ΔL* was obtained from the UTM.

IV. Tensile strength

Tensile strength was estimated by the following formula:

$$TS = \frac{F_{max}}{A} \qquad ... \qquad ... \qquad ... \qquad ... \qquad ... \qquad (4.5)$$

Where, F_{max} = Maximum load applied to the sample

A = Cross sectional area of the sample

V. Elongation-at-break

Percentage of elongation-at-break was obtained by the following relation:

$$EB(\%) = \left(\frac{\Delta L_b}{L_0} \right) \times 100\% \qquad ... \qquad ... \qquad ... \qquad ... \qquad (4.6)$$

Where, ΔL_b = Extension at break point of the sample

L_o = Gage length or original length of the sample

The value of ΔL_b was obtained from the UTM.

VI. Young's modulus

Young's Modulus (YM) is one of the basic parameters in characterizing the mechanical properties of solids. The bigger the YM, the stiffer the material is. For example it is bigger for steels than that for aluminium. For all material it is determined through tensile test. Within elastic limit, the stress-strain variation is linear in a material. Fig.4.17 shows a typical stress-strain curve of a polymeric material. The stress increases linearly with the strain up to the yield point.
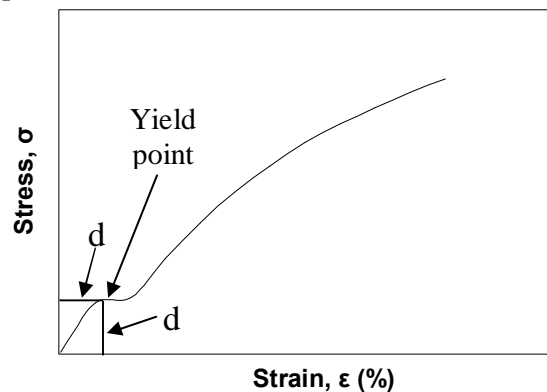
Fig.4.17: A typical stress-strain curve.

The slope of the linear portion gives the Young's modulus and determined as:

$$Y = \frac{d\sigma}{d\varepsilon} \qquad í \qquad í \qquad í \qquad í \qquad í \qquad ... \qquad (4.7)$$

Where, $d\sigma$ = Stress at yield point

$d\varepsilon$ = Strain at yield point

4.3.3.3.2 Measurements of flexural properties

A bar shaped specimen with a rectangular cross section was prepared for flexural measurement. The flexural test applies only to a freely supported beam, loaded at mid-span [1]. The dimension of flexural test specimen is shown in the attached Fig.4.18. The specimen dimension was 6 cm length, 1 cm width and 0.2 cm to 0.4 cm thick. Flexural measurement was performed according to ASTM standard (D790-98) using 3-points loading method as shown in Fig.4.19 [8]. *A & B* are two support spans on which the sample was placed. Continuously increasing load *P* was applied in the middle of the sample at *C*. the loads *P* and corresponding deflections *y* were recorded by the computer. The loading speed was 2 mm/ min and support-span was 48 mm.

| (a) | (b) |
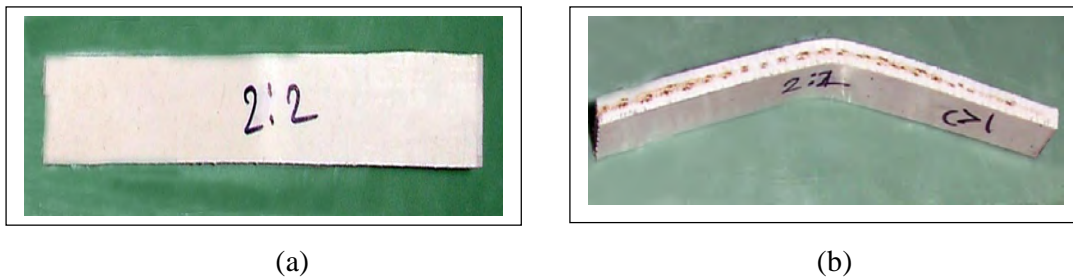
Fig.4.18: A sample for flexural test a) before test, b) after test

I. Flexural stress

The load applied on the mid-span was taken from the UTM and then the following equation was used to calculate the flexural stress of the samples:

$$\sigma_f = \frac{3PL}{2bd^2} \qquad \ldots \qquad í \qquad í \qquad í \qquad í \qquad (4.8)$$

Where, P = Load applied on the mid-span

L = Distance between support Span

b = Width of the specimen

d = Depth of the specimen

II. Flexural strain

The mid-span deflection was taken from the UTM and it may be able to calculate flexural strain of the samples using the following equation:

$$\varepsilon_f (\%) = \frac{6yd}{L^2} \times 100\% \qquad í \qquad í \qquad í \qquad í \qquad (4.9)$$

Where, y = Mid-span deflection

d = Depth or thickness of the specimen
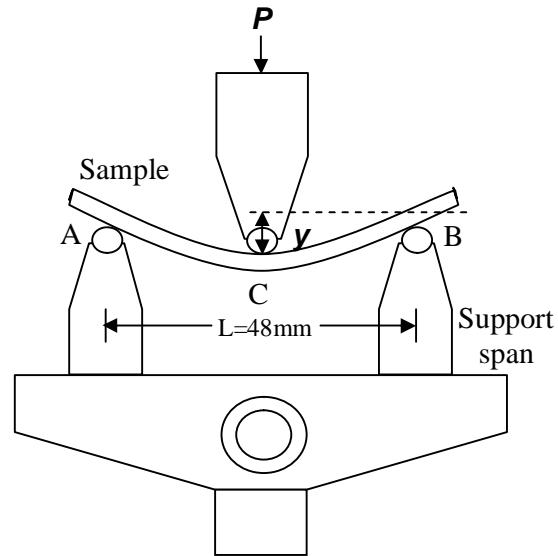
L = Distance between support spans

Fig.4.19: 3-point (A, B, C) loading arrangement for flexural measurement.

III. Percentage of flexural strain

The mid-span deflection at break or maximum deflection, y_{max}, was taken from the UTM and was used in the following equation to calculate maximum flexural strain:

$$FB(\%) = \frac{6y_{max}d}{L^2} \times 100\% \quad ... \quad ... \quad ... \quad ... \quad (4.10)$$

Where, y_{max} = Mid-span deflection at maximum flexural stress

d = Depth or thickness of the specimen

L = Distance between support spans

IV. Flexural strength

The maximum load applied on the mid-span was taken from the UTM and then the following equation was used to calculate the flexural stress of the samples:

$$FS = \frac{3P_{max}L}{2bd^2} \quad ... \quad ... \quad ... \quad ... \quad ... \quad ... \quad (4.11)$$

Where, P_{max} = Maximum load applied on the mid-span

L = Distance between support spans

b = Width of the specimen

d = Depth or thickness of the specimen

V. Tangent modulus

At first, load-deflection curves were plotted from the data of the UTM. A typical y-P curve is shown in Fig.4.20. The slope, $K = P/y$, of the initial straight-line portion of the load-deflection curve was estimated and introduced into the following equation to calculate the tangent modulus of the samples:

$$E = \frac{KL^3}{4bd^3} \qquad í \qquad í \qquad í \qquad í \qquad í \qquad (4.12)$$

Where, K = Slope of the initial straight-line portion of the load-deflection curve

L = Distance between support spans

b = Width of the specimen

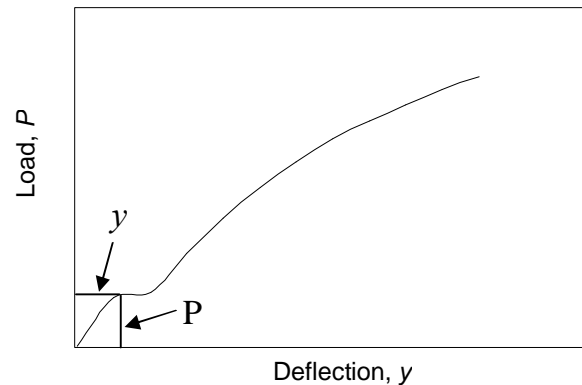d = Depth or thickness of the specimen

Fig.4.20: A typical load-deflection curve.

4.3.3.4 Surface morphology test

Surface morphology of the neat PVC sample and the PVC-JM composites of different ratios were studied by a scanning electron microscope (SEM) [Philips XL 30, Netherlands]. Each sample was cut with an appropriate size for the study of surface structure by a SEM. Two series of samples were prepared in this investigation. Both of series were cut from the end side of fracture surfaces. The sample surface was coated with a thin layer of gold by sputtering prior to SEM measurement. Then the surface micrographs of the sample were taken at a magnification of 100X or 200 m with a maximum operating voltage of 30 kV. The apparatus used in this study is shown in Fig.4.7.

4.3.3.5 Thermal Measurements

Thermal properties of the samples were monitored by a coupled differential thermal analyzer (DTA) and thermogravimetric analyzer (TGA) [Seiko-Ex-STAR-6300, Japan] (Fig.4.9). The measurements using DTA and TGA were carried out from 37 to 600°C at a heating rate of 20°C/min under nitrogen gas flow. While the DTA traces give the crystallization, melting and degradation temperatures as determined from the exotherm versus temperature curves, the TGA runs exhibit the weight-loss of the sample with temperature.

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CHAPTER-FIVE

RESULTS AND DISCUSSION

The ultimate samples obtained for different characterizations are neat PVC, a series of untreated PVC-JM composites and a series of treated PVC-JM composites. Before measuring structural, physical, mechanical and thermal properties, the moisture content from all samples were removed by heating them in an oven. Results and discussion on these properties of the neat PVC and the composites are presented in this chapter in details.

5.1   Water absorption

Water absorption (WA) has been estimated using equation 4.2 of chapter 4. The effect of soaking time on WA of the neat PVC and the PVC-JM composites prepared with various ratios of PVC and JM is shown in Figs.5.1ó5.4.

Fig.5.1 shows the variation of WA on soaking time for untreated and treated PVC-JM composites with ratio 2:1. In this case, WA increases rapidly at the initial stage for the composites while the neat PVC does not show any water intake with time. The neat PVC and JM are hydrophobic and hydrophilic in nature, respectively. For this reason, the neat PVC practically shows no WA with time. On the other hand, due to the hydrophilic nature of JM water intake is higher in untreated composites. WA is slower in the treated composites as compared to the untreated ones and is saturated after 96 hr, suggesting a development of hydrophobic nature of the acetylated composite.
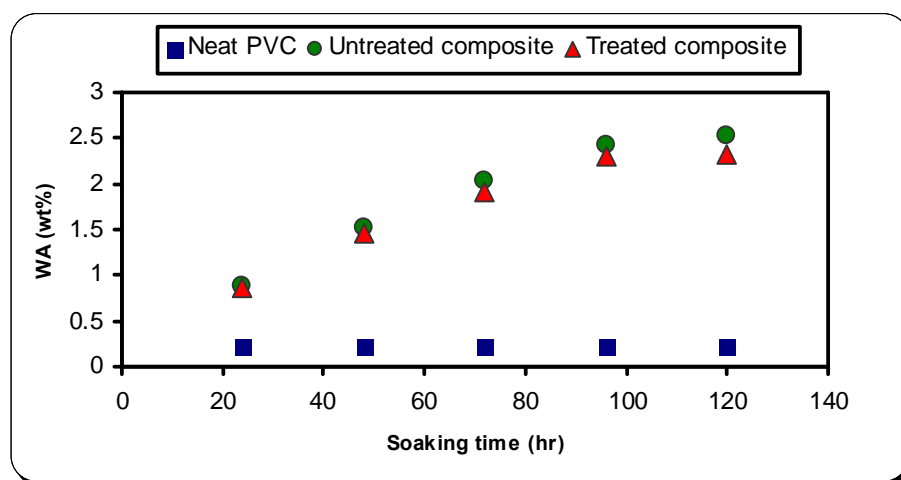
Fig.5.1: Variation of water absorption with soaking time for the neat PVC and the untreated and treated PVC-JM composites with ratio 2:1.
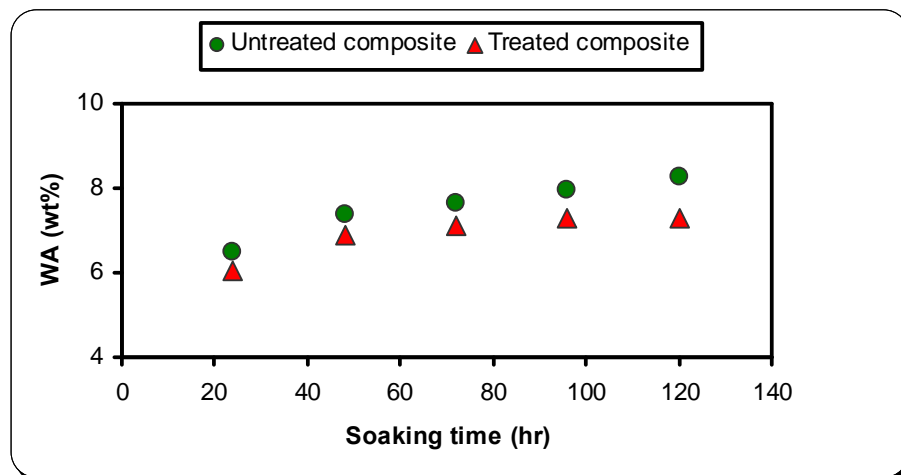
Fig.5.2: Dependence of water absorption on soaking time for the composites with ratio 1:2.

Fig.5.2 shows the dependence of WA on soaking time for untreated and treated PVC-JM composites with ratio 1:2. For this ratio, WA with the increase of time duration is less in treated composites than the untreated ones. After 96 hr the treated composites show saturation properties. WA for treated composite is found lower than that of untreated composite because of the increased hydrophobic nature of JM by acetylation.
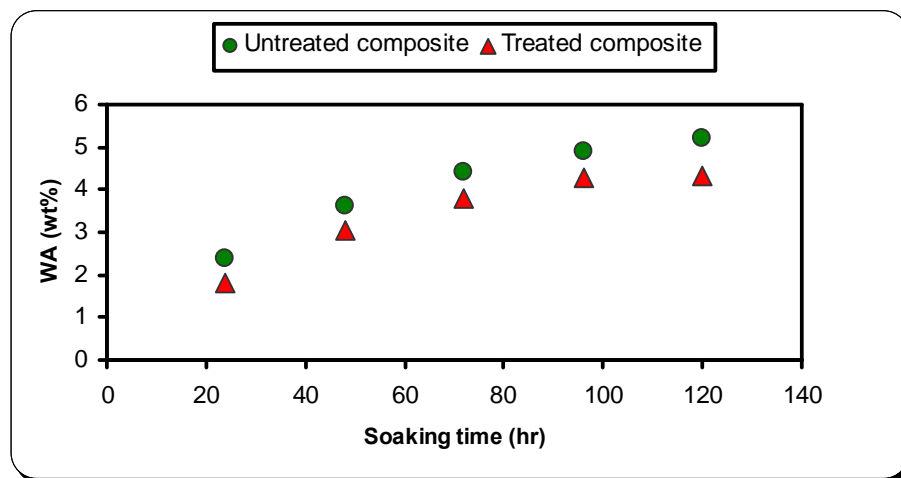
Fig.5.3: Effect of soaking time on water absorption of the composites with ratio of 2:2 for the untreated and treated composites.

In case of PVC:JM=2:2 (Fig.5.3), WA increases with the increase of time duration in both treated and untreated PVC-JM composites. The amount of WA of treated composite is less than that of untreated composite. After 96 hr, the value of WA of treated composite seems to be saturated.

In case of PVC:JM=3:2 (Fig.5.4), WA increases with the increase of time duration up to 96 hours in both treated and untreated PVC-JM composites and the water intake levels off from 96 hours to above for treated sample. The amount of WA of treated composite is less than that of untreated composite.
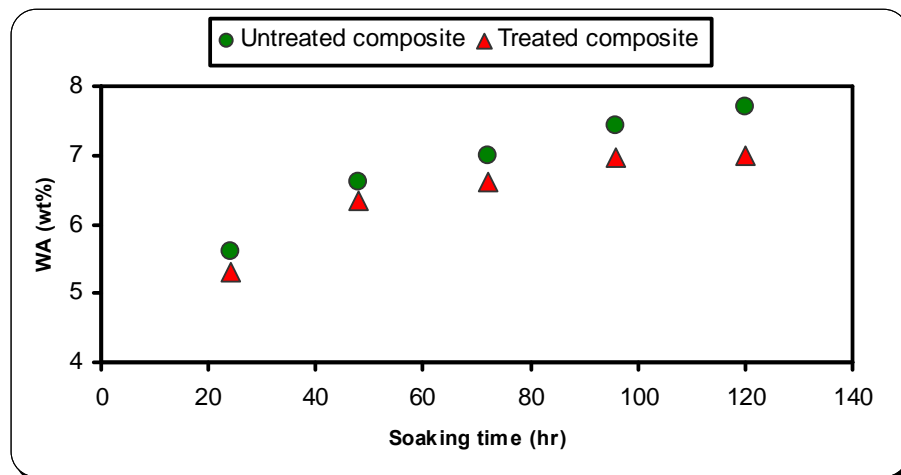
Fig.5.4: Variation of water absorption with time for the untreated and treated composites with the ratio of 3:2.

In the initial stage, water intake shows a rapid increase and after 96 hr it becomes saturated. The maximum WA obtained in this study is 8.5 wt%. The results are in agreement with those of published report [1].

5.2   FTIR structural analysis

Fig.5.5 shows the FTIR spectra of the neat PVC, the untreated PVC-JM composite and the treated PVC-JM composite, recorded as a transmittance versus wave-number in the range of 500-4000 cm^{-1}. The profiles are newly presented in Figs. 5.6 and 5.7 in order to observe the spectra more clearly. Interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for understanding the types of bonds. Identities of the source of an absorption band are intensity (weak, medium or strong), shape (broad or sharp), and position (cm^{-1}) in the spectrum.

For neat PVC, two wide bands appear at 600 cm^{-1} and 1100 cm^{-1}; two peaks appear at 2379 cm^{-1} and 2900 cm^{-1}. Besides, the zigzag peaks are also present in the range 1300-1900 cm^{-1}, with noticeable variation from the zigzag peaks observed in the case of PVC-JM composites. The absorption peaks in the range 600-700 cm^{-1} may be attributed to C-Cl stretching, while in the range 900-1200 cm^{-1} may be assigned to C-C stretching of PVC molecules. The absorption peaks appearing at 1210, 1439, 1550, 1600, 1760 and 1900 cm^{-1}

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may correspond to numerous CH modes such as cis-C-H wagging, trans-C-H wagging, C-H rocking, C-H stretching, CH_2 deformation, C=C stretching of the PVC molecules. The broad band at 2900 cm^{-1} may be due to C-H stretching of alkene. The peak positions obtained for PVC agree with the published results [2-5].

In the case of untreated PVC-JM composite, the shape of the peak at 2379 cm^{-1} is different from that at 2379 cm^{-1} of neat PVC. Moreover, the peak at 1900 cm^{-1} of neat PVC does not appear in the untreated PVC-JM composites. These results suggest that some of the molecular vibrations of neat PVC are restricted after inclusion of JM.
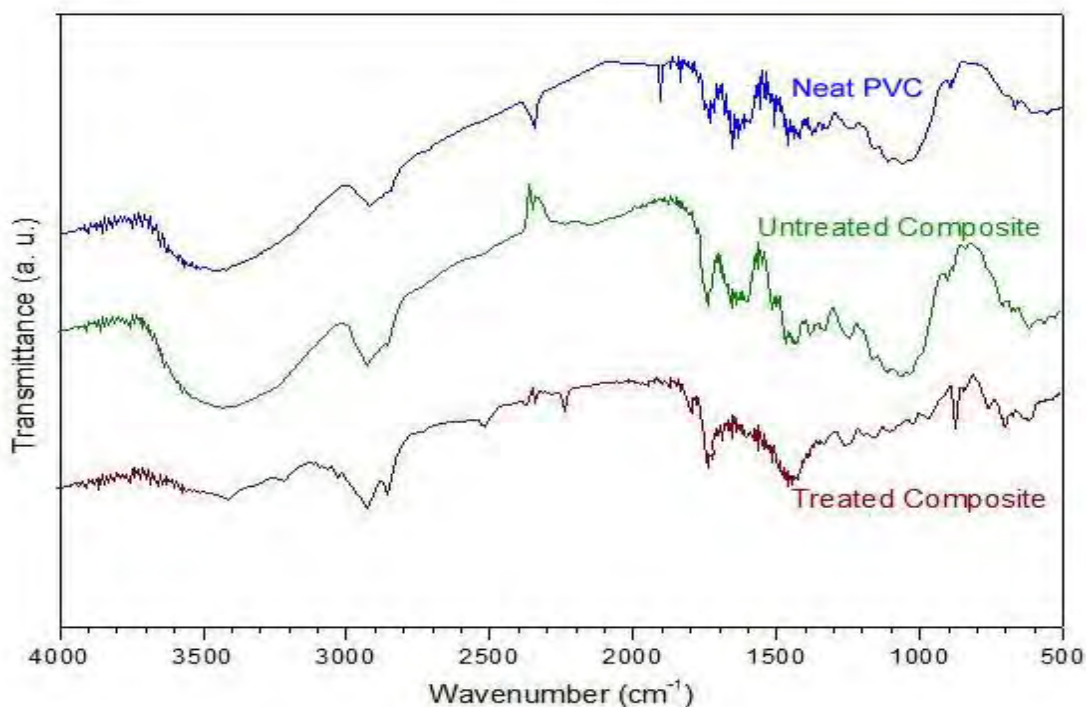
Fig.5.5: FTIR spectra of a neat PVC, an untreated PVC-JM composite and a treated PVC-JM composite.

In the spectrum of treated composite, a number of additional peaks with both broad and sharp peaks are seen. A broad peak around 2900 cm^{-1} may be due to the C-H stretching in alkene. The absorption band at 2820 cm^{-1} may be due to the presence of hydrogen bonded carboxylic acid (COO-H). The next absorption band at 2500 cm^{-1} is probably due to the presence of alkynes (C=C). The absorption band at 2360 cm^{-1} is due to the presence of carboxyl group (C=O). The absorption bands from 1300 cm^{-1} to 1800 cm^{-1} is fingerprint region. In case of composites, not only new bands appear but also peak positions of PVC are shifted, suggesting adhesion of JM with PVC. These are the additional peaks coming from JM and are similar to those reported in the literature [6-8].
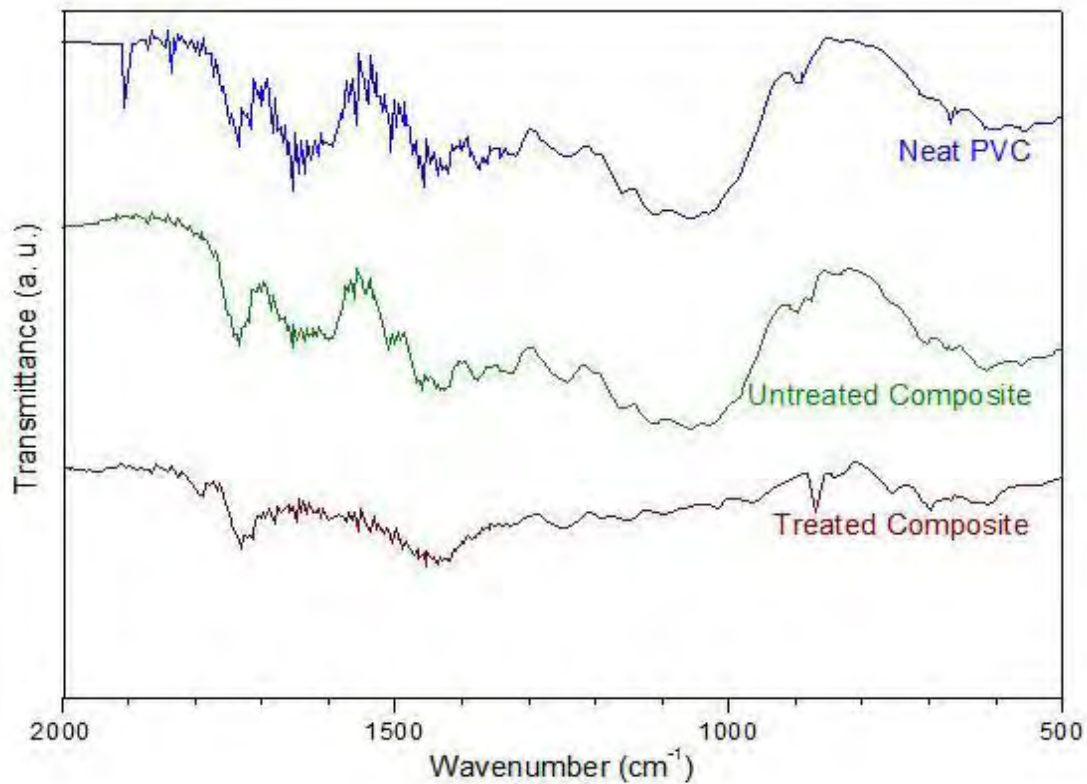
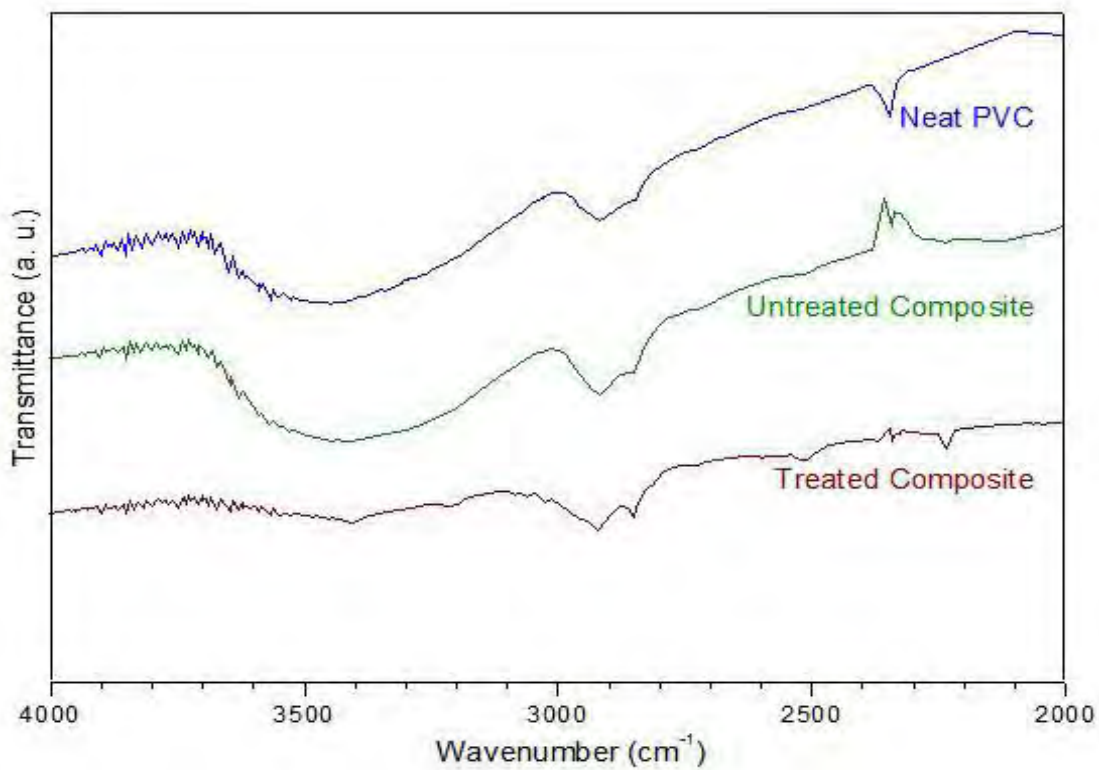Fig.5.6: FTIR spectra of neat PVC, untreated and treated composite (Wave number 500-2000 cm^{-1}).

Fig.5.7: FTIR spectra of neat PVC, untreated and treated composite (Wave number 2000-4000 cm^{-1}).

The results demonstrate that inclusion of JM fibers affects not only on the vibrational or rotational motion of the molecules but also affect on the formation of new bonds between the molecules of PVC and JM. The possible reaction between acetylated JM and PVC is shown in Fig.4.13. The chemical reaction between JM and CH_3COOH results in JM-O-C=O-CH_3 [9]. Both COOH and C=O bands are present in the spectra. Therefore, the adhesion between acetylated JM and PVC molecules is confirmed from the FTIR spectra.

5.3 Mechanical properties

Mechanical properties such as stress, strain, tensile strength, elongation-at-break, flexural strength, flexural strain, Young's modulus and tangent modulus of the neat PVC and the untreated and treated PVC-JM composite have been measured. Results and discussion of mechanical properties are presented below:

5.3.1 Tensile properties
5.3.1.1 Tensile stress-strain relation

Figs.5.8 and 5.9 illustrate the stress-strain variations for neat PVC and the untreated and treated composites with ratios 2:1 and 1:2, respectively. The stress increases rapidly at low strains, showing a linear increase. After this linear increase, the curve shows a hump, indicating yield stress. From the yield point, the stress does not increase with strain considerably and the curve becomes flat for all samples. In this region, a plastic deformation in the sample occurs. It may be mentioned here that after deforming the sample by a load the materials undergo both elastic and plastic deformation before fracture.
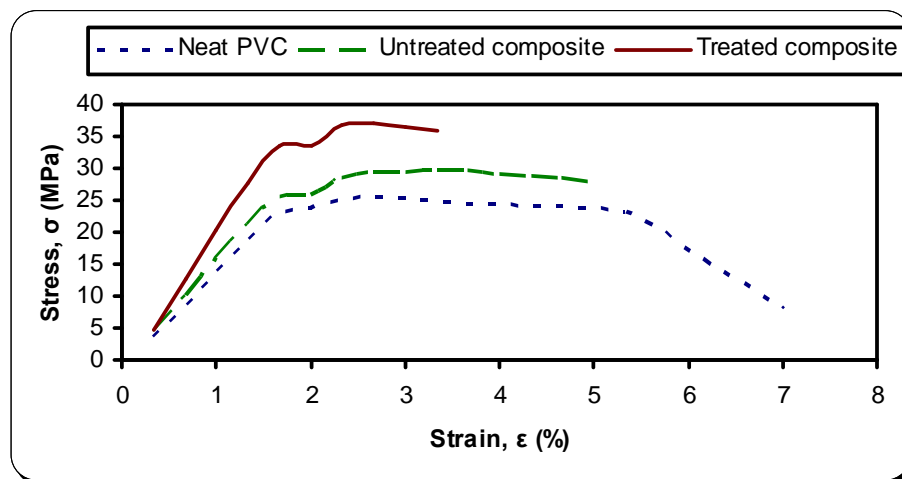

Fig.5.8: Stress-strain curves of neat PVC, treated and untreated composites with PVC:JM=2:1.
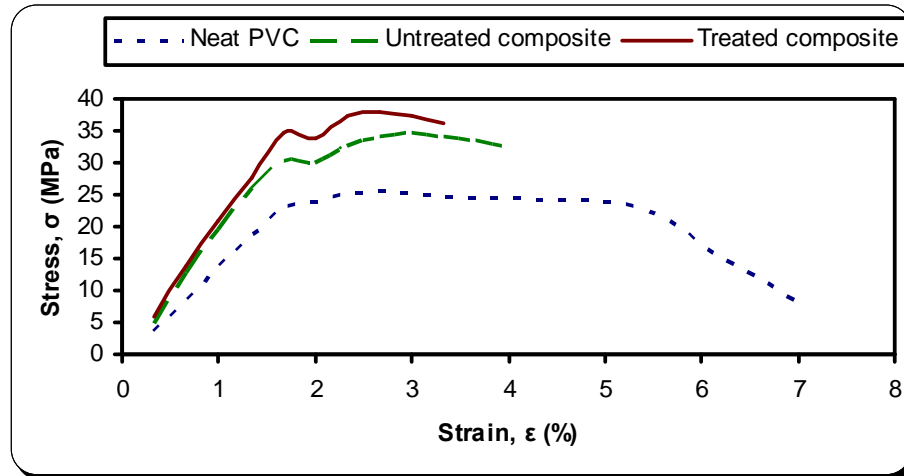
Fig.5.9: Stress-strain curves of neat PVC, treated and untreated samples with PVC:JM=1:2.

5.3.1.2 Tensile strength

Tensile strength (TS) for the neat PVC, the untreated PVC-JM composite and the treated PVC-JM composite are shown in Fig.5.10. The TS values for neat PVC, untreated jute and treated jute are found to be 26, 89 and 93 MPa. TS increases with the ratio of PVC and JM in the composite. In each ratio of PVC:JM, the TS value for treated composite is higher than that of the untreated composite. The highest TS value of 38 MPa and 40 MPa are respectively obtained in the case of untreated and treated composites with ratio 3:2. Because of the chemical treatment, the swelling behavior of the JM increases, resulting in rough surface, which helps develop better interfacial adhesion between the JM and PVC matrix. This adhesion is the origin of TS increase of treated composites.
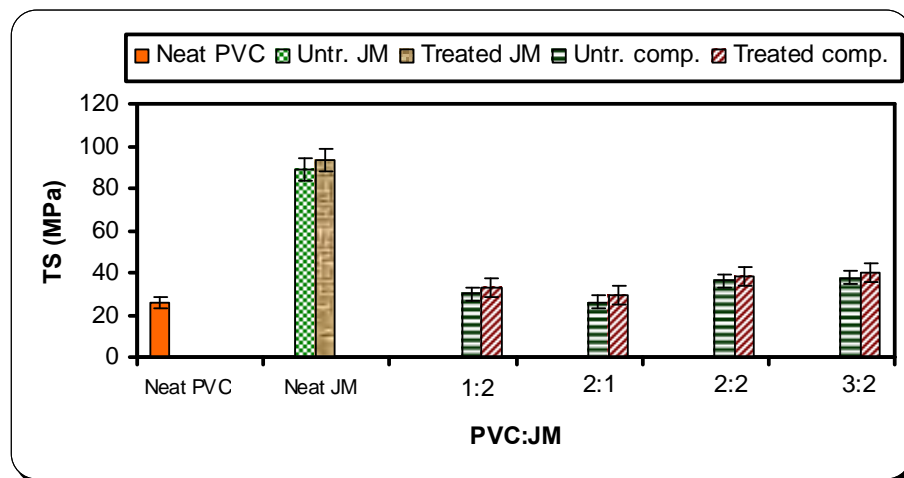
Fig.5.10: TS values for neat PVC, untreated and treated PVC-JM composites with various ratios.

5.3.1.3 Elongation-at-break

Percentage of elongation-at-break [EB (%)] for neat PVC, untreated and treated PVC:JM composites with different ratios are presented in Fig.5.11. EB (%) shows the highest value for neat PVC. For treated composite, it is lower than that of untreated composite.
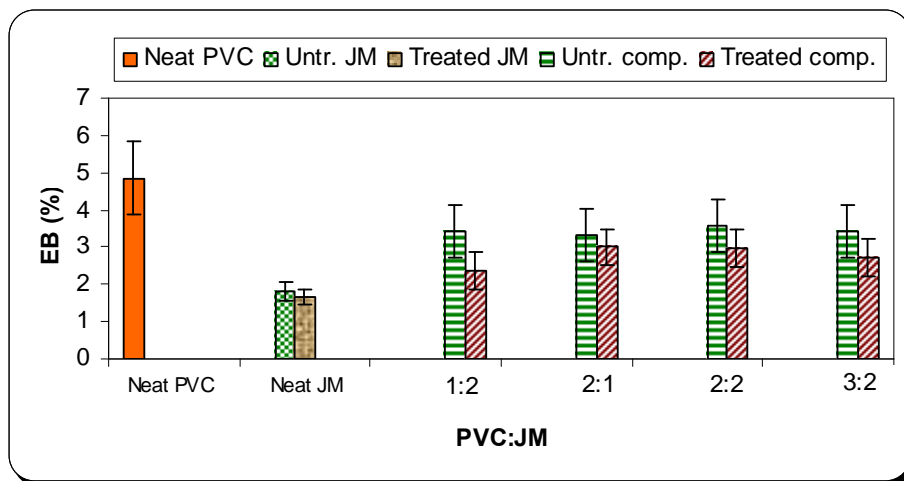

Fig.5.11: Change of EB (%) for neat PVC, and treated and untreated PVC:JM composites with different ratios.

After chemical treatment of JM and then heat-pressing of JM and PVC, a linkage among their molecules can be established. In case of neat PVC and untreated PVC-JM composite, an easy plastic deformation occurs during stretching i.e. the molecules of PVC and JM can slip past each other easily, resulting in higher strain. On the other hand, due to the linkage between JM and PVC molecules in treated composite, molecules find difficulties to slip, resulting fracture at lower values of EB (%).

5.3.1.4 Young's modulus

Young's modulus (YM) indicates the stiffness of a material. Fig.5.12 shows the YM for neat PVC and untreated and treated PVC-JM composites for different ratios of PVC and JM. The values of YM for treated PVC-JM composites are higher than those for neat PVC and untreated PVC-JM composites. A higher YM value for untreated composite than that for neat PVC arises from higher YM value of JM than PVC. Thus, the addition of fibers increases the stiffness of the resulting composite. The fiber-surface treatment enhances this stiffness. While the maximum YM for neat PVC is about 1.3 GPa, it is about 2.5 GPa in the untreated composites and even higher in the acetylated JM-PVC composites, suggesting better performance due to chemical treatment.
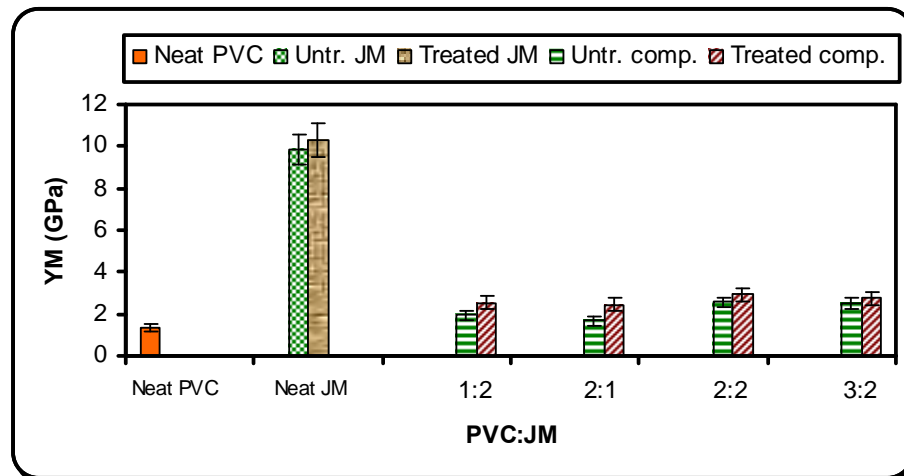
Fig.5.12: A comparison of Young's modulus for neat PVC and untreated and treated PVC-JM composites at various ratios.

5.3.2 Flexural Properties

5.3.2.1 Flexural stress-strain relation

Flexural stress versus strain variations of neat PVC, untreated PVC-JM composite and acetylated composite are shown in Fig.5.13 and 5.14. These variations resemble those of the tensile stress versus strain. In case of flexural stress-strain curve, the value of stress for treated composites is higher than those of neat PVC and untreated PVC-JM composites.

5.3.2.2 Flexural strength

The stress required to rupture a material under flexure is its flexural strength (FS). It is equal to the maximum stress in the outer samples at the moment of break. FS for neat PVC and untreated and treated PVC-JM composites are shown in Fig.5.15.
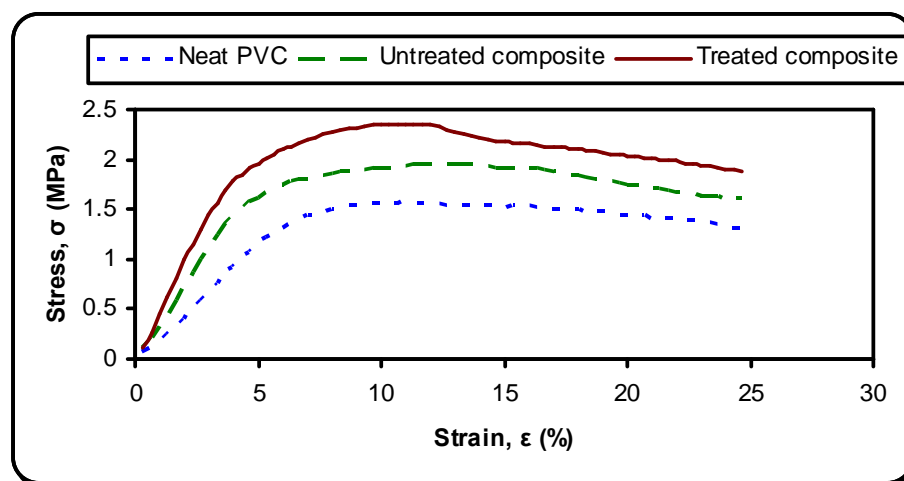
Fig.5.13: Stress-strain curves of neat PVC, treated and untreated samples for PVC:JM=2:1.
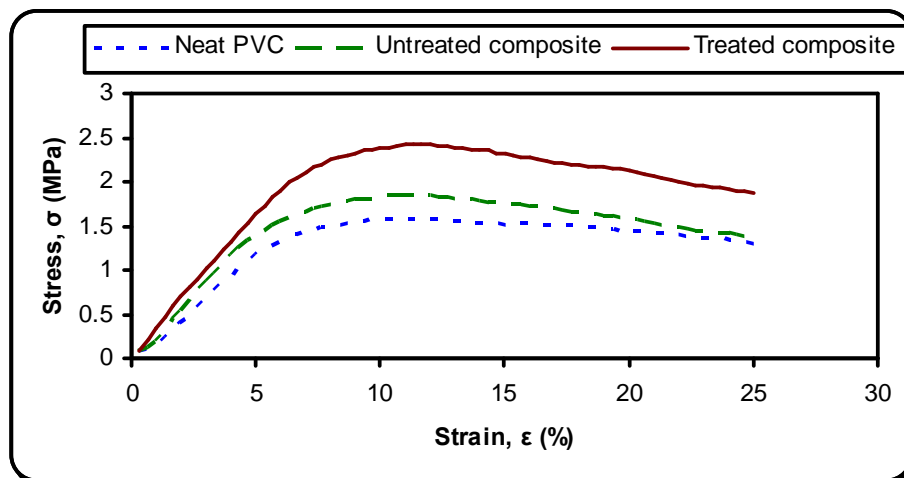
Fig.5.14: Stress-strain curves of treated and untreated samples for PVC:JM=1:2.

FS for treated PVC-JM composite is the highest as compared to that of untreated PVC-JM composite and neat PVC. Because of surface treatment, the swelling behavior of the JM increases, resulting in better interfacial bonding between the JM and PVC matrix. The reason can be explained in the same way as that explained in case of TS.
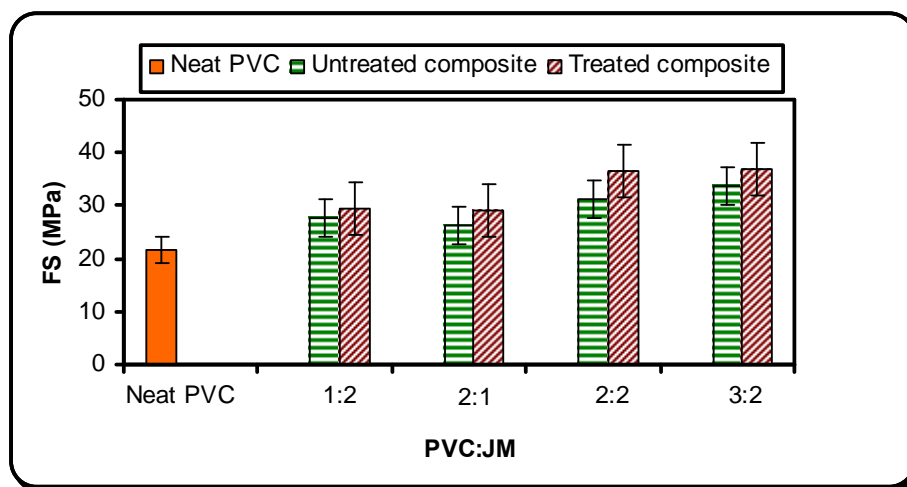

Fig.5.15: A comparison of FS values for neat PVC, untreated and treated PVC-JM composites with various ratio.

5.3.2.3 Flexural strain

Fig.5.16 shows the flexural strain [FB (%)] of neat PVC, untreated and treated PVC-JM composites for different ratios. FB (%) of neat PVC and untreated PVC-JM composites is found higher than that of the treated PVC-JM composites. This result represents that the treated composites are stiffer than that of neat PVC and untreated PVC-JM composites. In case of neat PVC and untreated PVC-JM composite, a plastic deformation occurs during stretching i.e. the molecules of JM and PVC can slip past each other easily. On the other

hand, due to the formation of chemical bonds in treated composite, molecules find difficulties to slip, resulting in lower values of FB (%).
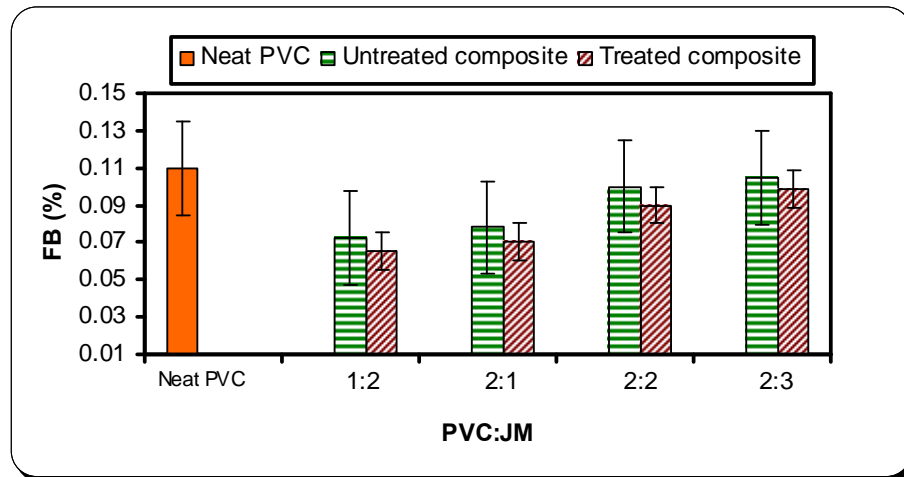

Fig.5.16: Flexural strain for different ratios of neat PVC, treated and untreated PVC-JM composites.

5.3.2.4 Tangent modulus

The tangent modulus (TM) of elasticity, often called the õmodulus of elasticityö, is the ratio, within the elastic limit of stress to corresponding strain.
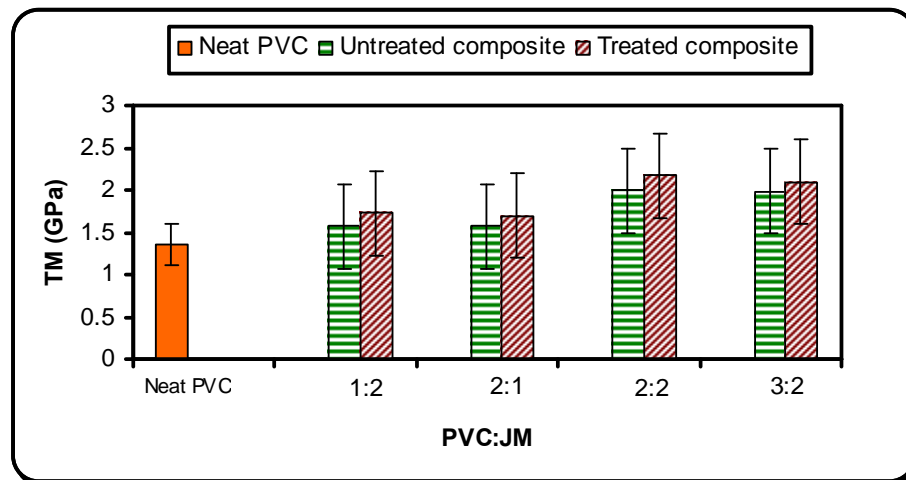

Fig.5.17: Effect of treatment and JM addition on tangent modulus of the composites with various ratios of PVC:JM.

Fig.5.17 shows the TM for neat PVC, untreated and treated PVC-JM composites for different ratios of PVC and JM. The values of TM for treated PVC-JM composites are higher than those for neat PVC and untreated PVC-JM composites, indicating that the treatment of JM by acetic acid increases the stiffness of the resulting composite. The surface treatment enhances this stiffness. While the maximum TM for neat PVC and untreated

PVC-JM composite are about 1.3 GPa and 2 GPa, it is 2.2 GPa in the treated PVC-JM composite, suggesting increase of TM values for treatment.

5.4 Surface morphology analysis

Fig.5.18 shows an SEM micrograph of the fractured surface of neat PVC. The surface is not smooth rather it contains huge number of flaws on the surface. Fig.5.19 represents an SEM micrograph of the fractured surface of untreated PVC-JM composite (PVC:JM=2:1).
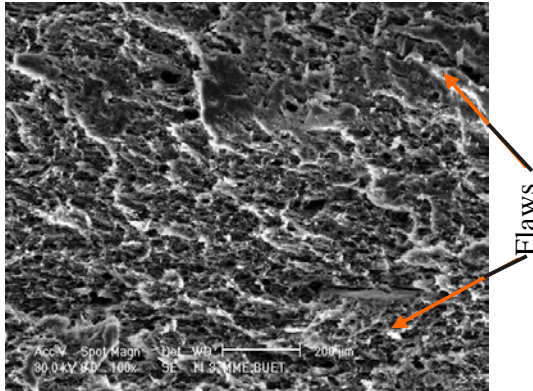

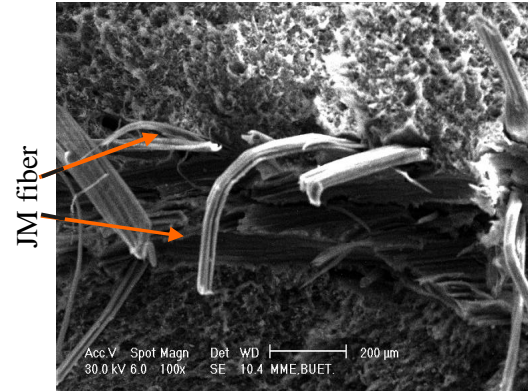Fig.5.18: An SEM micrograph of neat PVC.

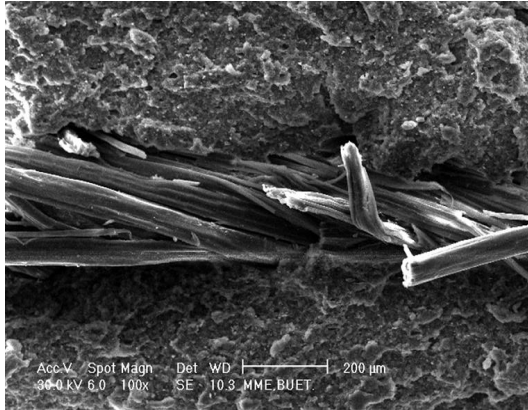Fig.5.19: An SEM image of untreated composite (PVC:JM=2:1).

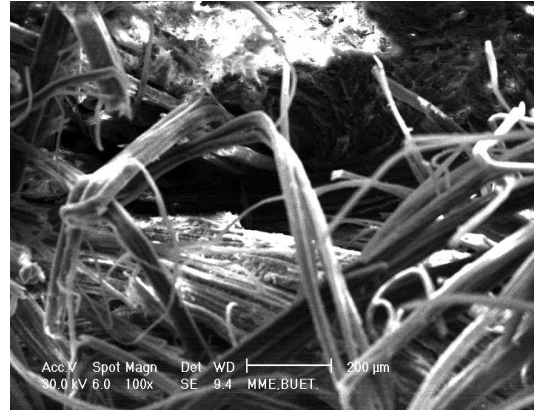Fig.5.20: An SEM photograph of treated composite (PVC:JM=2:1).

Fig.5.21: An SEM image of untreated composite (PVC:JM=2:2).

The micrograph shows that the adhesion between PVC matrix and JM fiber is not good, resulting poor adhesion between these two components. In SEM photograph, the most of the JM fibers seem to be pulled out from the PVC matrix. This is due to the poor adhesion between fiber and polymer matrix.

Fig.5.20 shows an SEM micrograph of the fractured surface of treated PVC-JM composite (PVC:JM=2:1). The impact between interfaces of PVC and JM is observed to be better than

untreated composite. In SEM photograph, despite a few fibers are observed to be pulled out from the matrix most of them are in good adhesion with PVC.

Fig.5.21 shows an SEM micrograph of the fractured surface of untreated PVC-JM composite (PVC:JM=2:2). In SEM photograph, it is clearly seen that the fibers are pulled out from matrix. This may be due to the poor adhesion between fiber and polymer matrix.
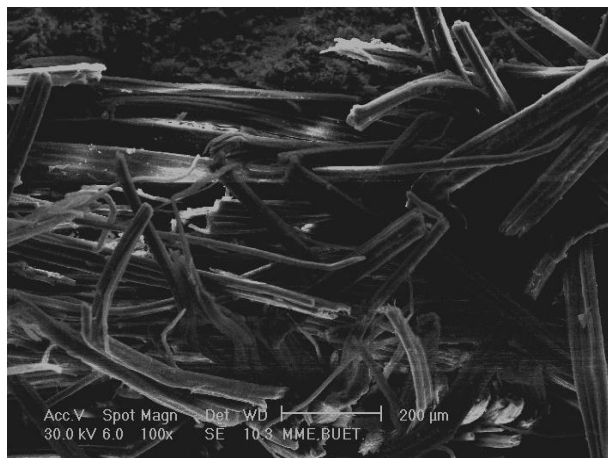

Fig.5.22: An SEM image of treated composite (PVC:JM=2:2).

Fig.5.22 shows an SEM micrograph of the fractured surface of treated PVC:JM composite (PVC:JM=2:2). It shows the interfacial adhesion between matrix and fiber in upper portion of the photograph. In SEM photograph, it is clearly seen that the fibers are pulled out with matrix from composite. This may be due to the inhomogeneous adhesion between fiber and polymer matrix.

5.5 Thermal Properties

Fig.5.23 shows the TG (upper line), DTG (lower line) and DTA (middle line) thermograms for the neat PVC obtained at a heating rate of 20ºC/min. According to the TG spectra, PVC undergoes two separate degradation steps under heating and is stable at low temperatures. The initial weight loss is found to start at 262ºC and the thermogravimetric percentage (TG %) rapidly drops to 50% from this temperature. It gradually decreases before 400ºC and then there is another rapid drop at around 410ºC. The TG% of PVC decreases to about 26% at 470ºC and do not show any decrease beyond this temperature. These results agree with the reported values [10, 11]. As the DTG means the differential of TG, the apparent changes observed in DTG are complementary to TG. DTG is the maximum when the slope of the TG-fall is the maximum.
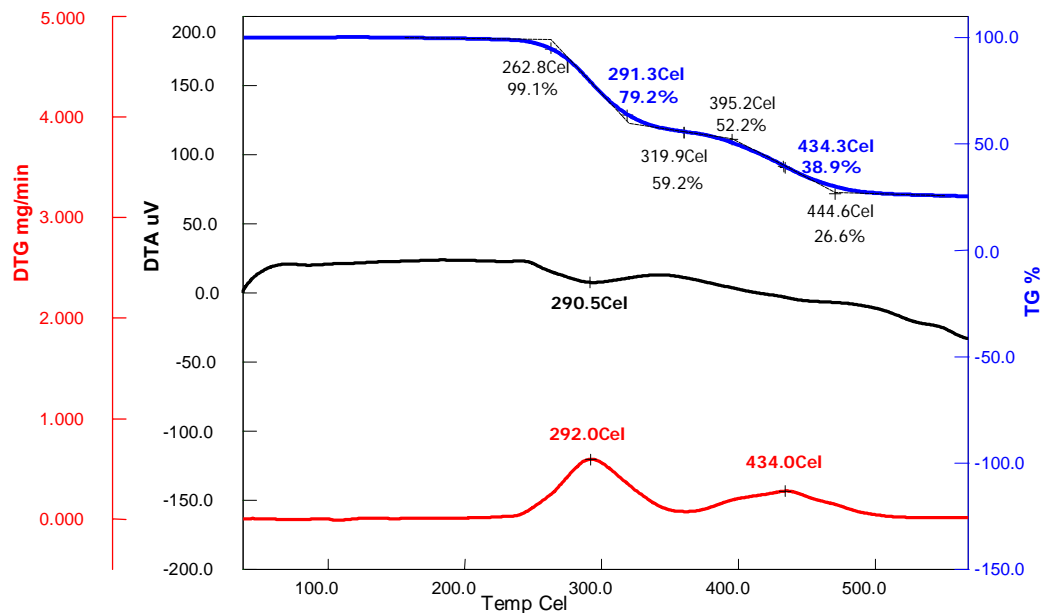
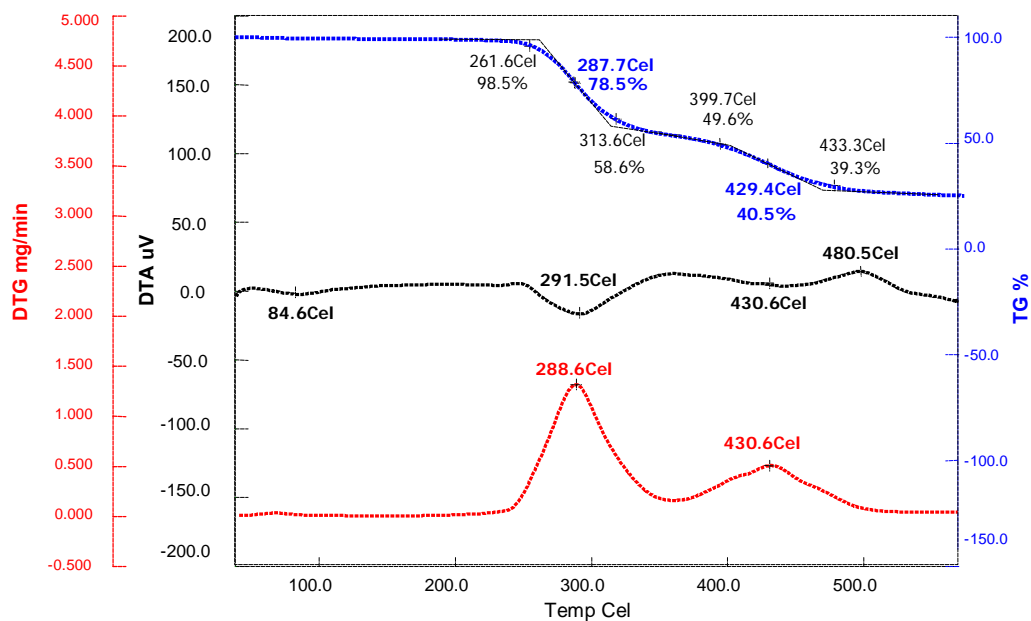Fig.5.23: TG, DTG and DTA curves for neat PVC (PVC:JM=2:0).

Fig.5.24: TG, DTG and DTA curves for untreated composites with PVC:JM=2:2.

On the other hand, DTA traces both melting and decomposition of a sample. In DTA curve, one endothermic peak starting at 230ºC and ending at 330ºC with a peak at 290ºC indicates the degradation temperature of PVC. However, the reported degradation temperature (T_d) of pure PVC is 280ºC [12]. This discrepancy of T_d may arise from the fact that processed PVC sheets are used in this study instead of PVC pellets.

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PVC is a linear polymer, synthesized from vinyl chloride (–CH$_2$–CHCl–) monomer and contains a chlorine (Cl) content of 57%. After heating, it decomposes into polyacetylene and HCl gas and its thermal degradation follows radical mechanism [13]. Evidences from studies indicate that the dehydrochlorination of PVC is due to a loss of HCl gas. The weight loss occurring at first step is more than 50%, which demonstrates that this loss is due to the emission of HCl starting at 260ºC and ending at 320ºC. It is reported that after dehydrochlorination, a conjugated polymer structure (–CH=CH–CH=CH–) called polyene is formed [13]. Next step of thermal degradation involves decomposition of polyene in the range of 325–470ºC. The ash contents obtained after complete degradation of PVC arise from the additives such as lead carbonate, lead sulphate etc., which are used as catalysts during polymerization of vinyl chloride.
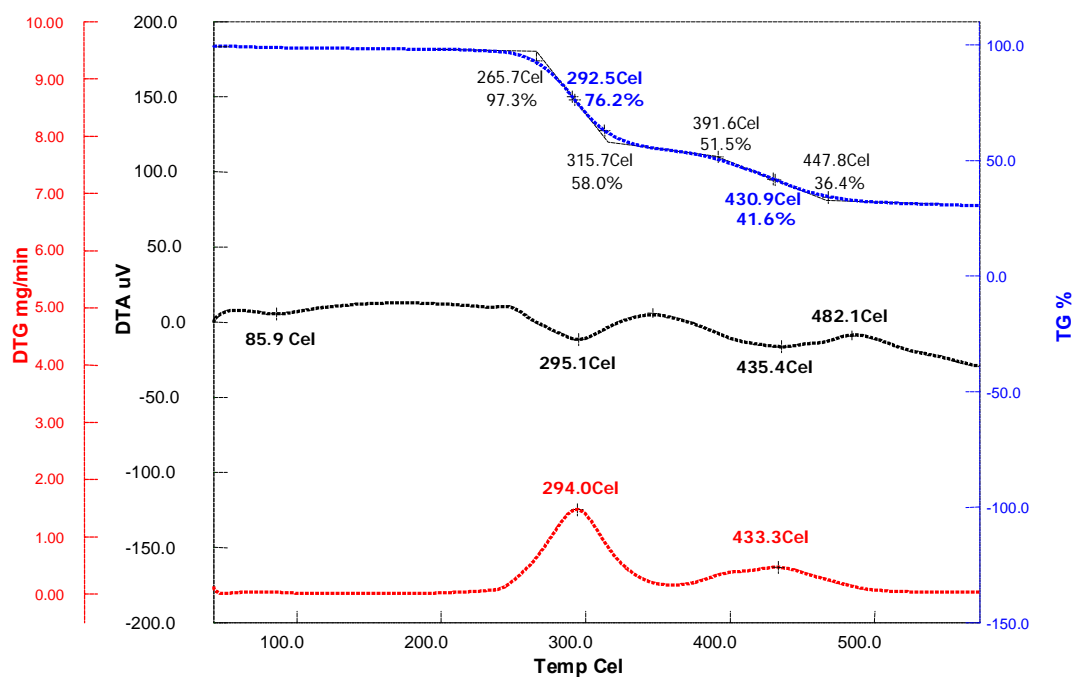

Fig.5.25: TG, DTG and DTA curves for untreated composites with PVC:JM=3:2.

Fig.5.24 shows the thermograms for the untreated PVC-JM composites with ratio 2:2. The 1st peak appears at 80ºC is endothermic. The 2nd one at 295 ºC is endothermic; the 3rd one at 340 ºC is exothermic, the 4th one at 431 ºC is endothermic and the 5th one at 490 ºC is exothermic. It has been reported that jute presents several separate decomposition procedures under heat treatment, resulting in a number of endothermic and exothermic peaks [14-17]. The first peak corresponds to the decomposition of water. The second peak is from PVC. The third one is due to the decomposition of comparatively low molecular

weight component such as lignin, hemicellulose etc. The fourth peak represents a kind of interaction between JM and PVC and the fifth one is due to the dissociation of cellulose. The thermograms of untreated PVC-JM composites (Fig.5.25) with the ratio 3:2 resemble that of the sample with ratio 2:2.
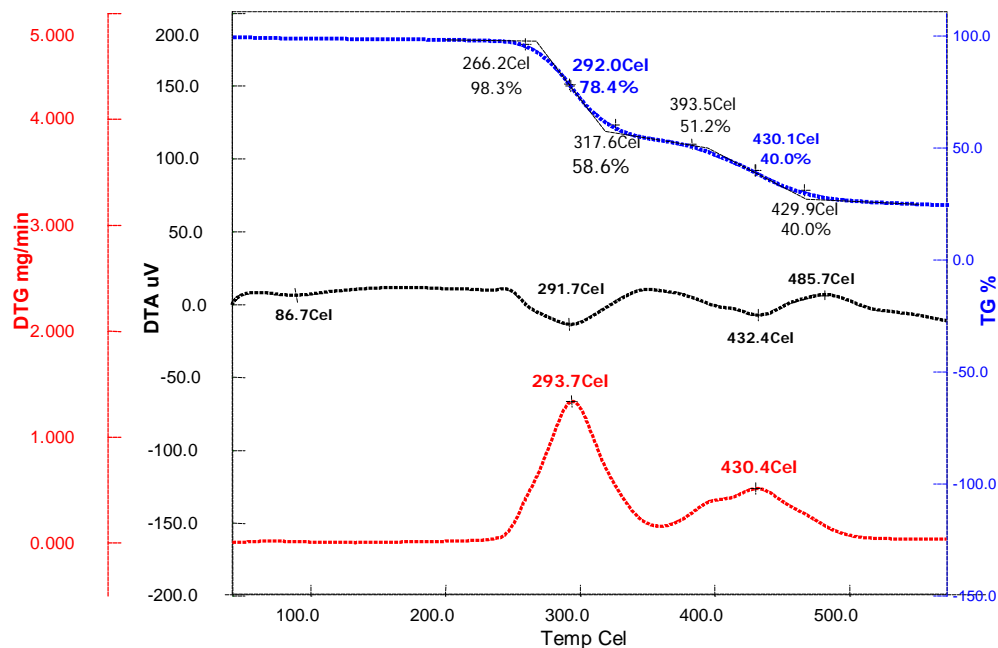

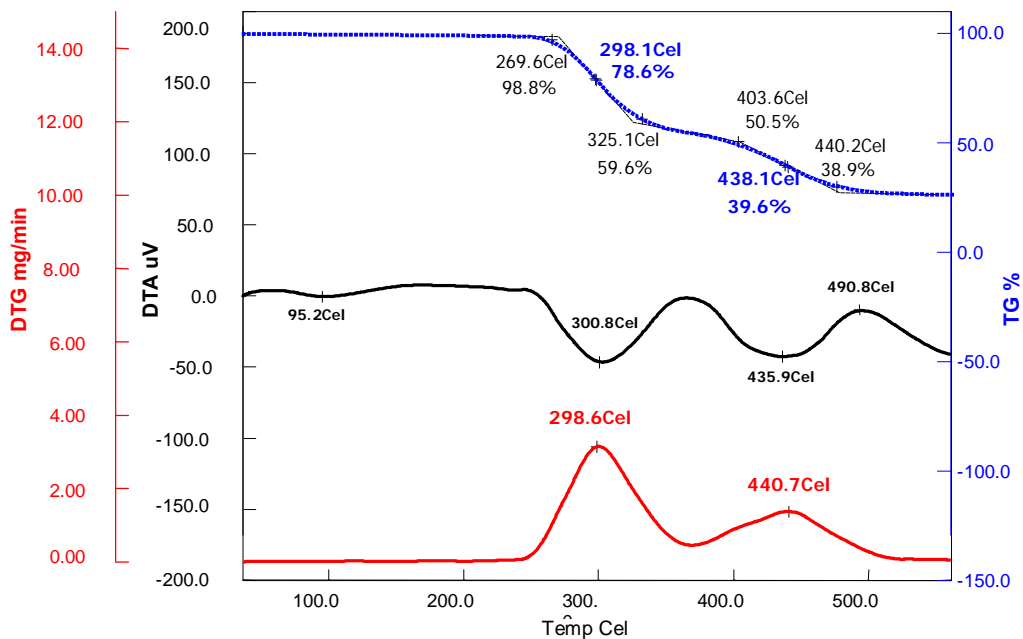Fig.5.26: TG, DTG and DTA curves for treated composites with PVC:JM=2:2.

Fig.5.27: TG, DTG and DTA curves for treated composites PVC:JM=3:2.

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Figs.5.26 and 5.27 show the thermograms for the treated PVC-JM composites with ratio 2:2 and 3:2, respectively. The thermal behaviors of the treated composites are not exactly similar to those of the neat PVC and untreated composites. In case of the sample with ratio 3:2, the 1st, 2nd, 3rd, 4th and 5th peaks appear at 95 ℃ , 370 ℃, 435 ℃ and 495 ℃, respectively. It is found a shift of the decomposing peaks toward higher temperatures, suggesting more stability of the treated composites. In addition to these, the peak area is larger in the sample of ratio 3:2. The increase of decomposing temperatures in the composites may be attributed to the interaction of hydroxyl groups of acetylated JM with PVC molecules.
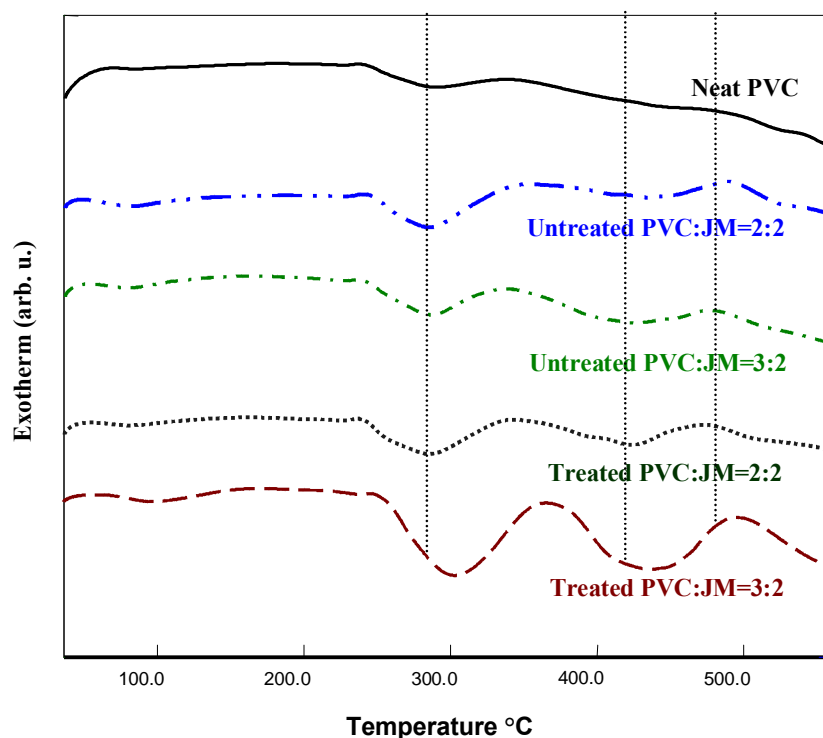

Fig.5.28: A comparison of DTA curves for neat PVC, untreated PVC:JM composite and treated composite in various ratios.

Fig.5.28 represents the comparison of DTA curves for neat PVC, untreated PVC-JM composites and treated PVC-JM composites in various ratios. From this comparison, the degradation temperature is found to shift to higher values for the reason of the better adhesion between JM and PVC.

Similar behavior as that observed in case of acetylated JM reinforced composites of the present study is also reported in the case of jute fiber reinforced shellac composites [17]. Different decomposing temperatures observed in this study are included in Table 5.1.

Table 5.1: Melting and degradation temperatures of the neat PVC and the untreated and treated composites at 20°C/min are tabulated.

Sample name	PVC:JM	Decomposing temp. of H_2O (°C)	Endothermic peak (°C)		Exothermic peak (°C)	
			1st Peak	2nd Peak	1st peak	2nd Peak
Neat PVC	2:0	ó	290	ó	ó	ó
Untreated composites	2:2	84	291	430	ó	480
	3:2	85	295	435	ó	482
Treated composites	2:2	86	292	432	ó	485
	3:2	95	300	436	ó	490

The melting temperature of the neat PVC is found to be 291°C, which increases to a maximum of 295°C for untreated JM-PVC composites and 300°C for acetylated JM-PVC composites. The increase of melting and degradation temperatures reveals a better impact of JM and PVC. Degradation of polymers at elevated temperatures does not follow any unique mechanism. Thermal decomposition of a polymer is largely dependent on the chemical structure of the chain segments. The degradation may primarily lead to chain scission or involve non-chain scission reaction [13]. During chain scission, the chain length is cut down.

In case of non-chain scission process, the side groups attached to the chain backbone are eliminated. It is reported that the jute fibers as a natural fiber does not melt but it shows degradation due to the ignition of jute fibers in the presence of nitrogen atmosphere.

From DTA analysis, it can be informed that acid treatment shows not only the development of hydrophobicity and reduction in volume fraction of the porosity but also the formation of bonds between JM and PVC.

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