Studies On The Effects Of Additives On The Physico-Mechanical Properties Of Jute Reinforced Composites

by

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THESIS APPROVAL

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TO MY

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ABSTRACT

In this research work, different types jute reinforced polypropylene (PP) composites were prepared by injection moulding technique. To prepare improved jute-PP composites, different types chemical treatments were carried out. The effects of these treatments on the physico-mechanical properties of the composites were studied. Reaction parameters such as time, temperature, pH and concentration of coupling agents were investigated for all chemical treatments. Unbleached raw jute fibers were modified by sodium periodate oxidation and the effects of oxidized jute on the performance of oxidized jute reinforced PP composites were studied comparing with the raw jute-PP composites. Coupling reactions were carried out using urea and urotropine with the oxidized jute-PP composites by post-treatment processes. FT-IR spectroscopic analyses were done for all chemical treatments and the results showed the evidence of positive reactions. The effects of urea and urotropine on the physico-mechanical properties of the composites were studied. Maleic acid treatment was carried out on the raw jute-PP composites. The effect of maleic acid on the physico-mechanical properties of the composites was also studied. The effects of fiber content on the physico-mechanical properties of composites were studied by preparing the composites with different percentage of fiber loading (from 20 wt% to 35 wt%) for each type of composites. Mechanical properties (tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, charpy impact strength and hardness were measured for all treated composites and raw jute-PP composites. Improved mechanical properties were obtained for all the treated composites over untreated raw jute reinforced PP composites. Scanning electron micrograph of the composites were taken to investigate the interfacial adhesion and bonding between the fiber and PP matrix resulting from the various chemical treatments. Improved interfacial interactions were found for treated composites than untreated composites.

Water absorption tests were carried out of all composites to investigate the effect of chemical treatment on the moisture absorption characteristic of hydrophilic jute in the jute-PP composites which has direct effect on the dimensional stability of the composites. Reduced water absorption was found for oxidized jute-PP composites, urotropine treated oxidized jute-PP composites and maleic acid treated raw jute-PP composites. All the findings are reported in details in this thesis.

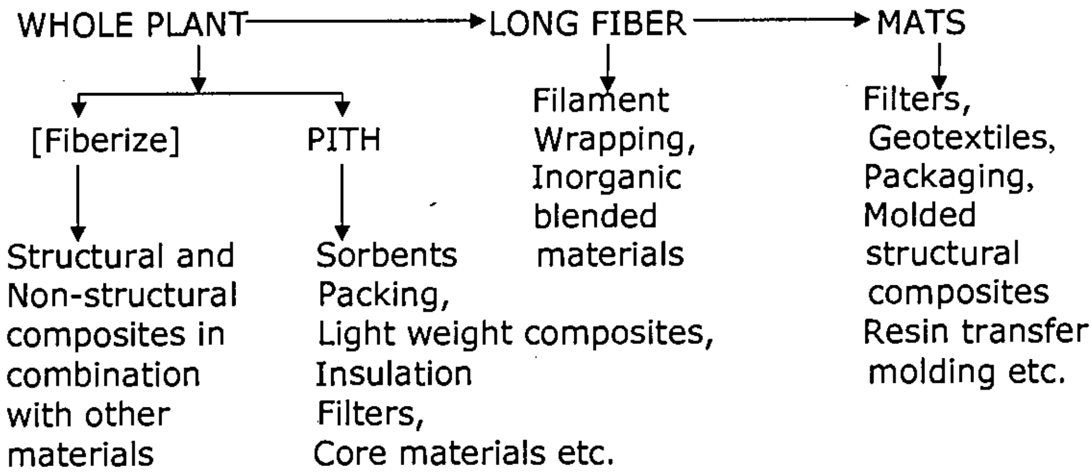
CHAPTER 1: INTRODUCTION

1.1 Introduction

The word 'composite' means "a substance, which is made up by mixing two or more distinct different substances". In most cases mixing is done by physical process. In a few case it is also done partly by chemical reaction. Polymer composites consist of one or more discontinuous phases embedded in a continuous-phase polymer matrix. The discontinuous phase is usually harder and stronger than the continuous phase, and is called reinforcement. The matrix can be classified as thermoplastic (capable of being separately hardened and softened by the decrease and increase of temperature respectively) or as thermoset (changing into a substantially infusible and insoluble material when cured by the application of heat, or through chemical means). [1]

Typical reinforcements for plastics are various synthetic fibers such as glass, graphite (carbon), boron, organic, metallic, and ceramic. These materials are heavy, expensive and harmful to the environment. Lignocellulosic fibers offer many advantages over these most commonly used synthetic fibers as filler reinforcement in thermoplastic matrix. The replacement of inorganic fillers with comparable lignocellulosic fibers provides less weight and decreases the cost without reducing the mechanical properties of the composites.[2] Any substance that contains both cellulose and lignin is a lignocellulosic material. Lignocellulosic materials include wood, agricultural crops like jute, kenaf, sisal etc.; agricultural residues such as bagasse, corn stalks,rice husk etc. and also other plant materials. In general, what is true for wood is also true for lignocellulosic materials even though they may differ in chemical composition and matrix morphology.[3] The use of lignocellulosic fibers as the reinforced materials in thermoplastics has received a lot of interest due to their low densities, low cost, and non-abrasive nature.[6] The advantages of using lignocellulosic materials also include high specific stiffness and mechanical strength,[7] ease availability, lower cost on unit-volume basis, low hardness, which minimizes the wear of processing equipment, renewability, recyclability, non-hazardousness, biodegradability, and so forth.[8-9] The use of lignocellulosic materials with thermosetting polymeric materials, like phenol- or urea-formaldehyde, in the production of composites has a long history. Disadvantages stemming from the use of thermosets include brittleness, lengthy cure cycles and inability to repair and/ or recycle damaged or scrapped parts. These disadvantages led to the development of the thermoplastic matrix composite system. Compared with thermosets, composites fabricated from thermoplastic materials typically have a longer shelf life, higher strain to failure, faster to consolidate and retain the ability to be repaired, reshaped and reused as need arises.[10] The processing temperature of the lignocellulosic fibers in thermoplastics is limited due to fiber degradation at higher temperatures. Thus the plastics that can be used with it are limited to those with low melting temperatures. In general, no deterioration of properties due to fiber degradation occurs when processing temperatures are maintained below 200^{0}C for short periods.[6] These thermoplastics include polypropylene (PP), polystyrene, vinyls, low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The most common polyolefin used to prepare composites is polypropylene (PP), a commodity polymer.[11] Polypropylene provides most of the advantages with regards to economic (price), ecological (recycling behavior) and technical requirements (higher thermal stability like HDPE).[12] In this research polypropylene polymer was used as the matrix material to prepare injection moulded fiber-reinforced polypropylene composites. Polypropylene is a semicrystalline polymer and its property and classification depends on its percent of crystallinity. The melting temperature of commercial polypropylene lies in the range 160-170^{0}C, with purified polymer reaching 176^{0}C.[13] Commercial isotactic polypropylene was used in this research and its melting point was found 160^{0}C. Isotactic structure of this PP was confirmed by FT-IR spectroscopy. In this research jute fiber was used as a reinforcing material to prepare composites. Recent research on the use of jute and kenaf fiber suggests that these fibers have high potential for being used as reinforcing fillers in thermoplastics. Experimental results indicate that kenaf-fiber-polypropylene (PP) composites have significant advantages over conventional inorganic filled/reinforced PP systems for certain applications.[6]

Bangladesh is an agriculture based country. It produces huge amount of jute every year. Jute is the cheapest lignocellulosic, long vegetable bast fiber and abundantly available here. It was called as the 'Golden Fiber' of Bangladesh as it earned huge foreign currency for the economic growth of the country by exporting jute and jute products. Jute (including kenaf) was an important foreign exchange earner of the then Pakistan during '60s. Even during the '70s, jute was an important commodity of Bangladesh. However, during the '80s, bulk handling techniques and synthetic substitutes entered the market and jute started losing its predominant position in the market.[15] In Bangladesh jute is traditionally used for making hessian clothes, ropes, gunny bags, shopping bags, backing of carpets, floor mats etc. Nevertheless jute fibers have many drawbacks. Jute fibers are woody, coarse, contain high percentage of lignin and are not spinable to fine fabrics. Its elasticity and compressibility are quite low. The color of jute and jute products changes from yellow to brown on exposure to light. It has poor crease resistance, lack of thermoplasticity and poor dimensional stability which are requirement for manufacturing fabrics. For these drawbacks jute and traditional jute products are gradually replaced by artificial fiber and synthetic products. In order to overcome the declining market of jute products, new technologies have been developed for bulk use of jute, as a raw material in the production of high value added and price competitive products. These products for new, alternative and non-traditional use of jute are generally termed as diversified Jute Products .[15] Among the various diversified jute products, jute reinforced composites have high potential for wider use and application. The interest in using jute fibers as reinforcing agent in plastic composites has increased dramatically during the last few years. Production of jute reinforced composites using thermosets and thermoplastics can replace a variety of products including carbon- and glass-fiber composites. Processing system of jute-based composites is simple and highly cost effective. So the diversified use of jute in composites has a bright future to increase the economic stability and growth of our country. It can be used for such products as doors, windows, furniture, gaskets, ceiling tiles, partition boards, automotive interior parts, packaging, molding etc. So the aim of this present research is to find out a cost effective technology of using of jute fiber as a reinforcing material in thermoplastic composites. The used jute fibers in this research were collected from BJRI, known as "Tossa jute". Its scientific name is *Corchorus Olitorius*, genus Corchorus and family Tiliaceae.[16] The scheme shown below gives possible use of different fractions of jute plant.[17]



Scheme 1.1: Possible use of each plant fraction

Natural fiber reinforced composites are inferior to synthetic fiber reinforced composites in tensile strength and modulus, but they exhibit significantly higher elongation, which provides better tolerance to composite damage. However, a major problem of natural fiber reinforced composites is their susceptibility to fungal and insect attack and to degradation by moisture.[1] The high moisture absorption of the natural fibers and their low microbial resistance are disadvantages that need to be considered, particularly during shipment and long-term storage as well as during processing of the composites.[12] In addition, their hydrophilic behavior affects the properties of the fibers themselves as well as the properties of their composites.[12] These limitation in performance of the natural fiber reinforced composites can be greatly improved through chemical modification techniques. The main difficulty of natural fibers is their tendency to entangle with each other and form fiber agglomerates during processing. The formation of fiber agglomerates prevents complete fiber dispersion, and affects the properties and appearance of the finish products. The wide polarity differences of the surface of cellulosic fibers (hydrophilic) and thermoplastic matrix (hydrophobic) prevents efficient fiber-matrix bonding.[2] In these respects, surface modification of the fibers with coupling agents is generally needed because it will facilitate the fiber dispersion and induce bond formation between the fibers and the polymer. Coupling agents are able to react chemically (on both ends during processing) with the fibers on one side and the polymer on the other side, thus forming a chemical bridge/ coupling at the interface. Coupling is believed to be the utmost importance for perfect adhesion. Efficient coupling is usually not so simple. The lack of reactive groups in polymers prevents direct coupling of the components.[18] Thus the modification of the matrix is often required. It is relatively easier for a modified polymer to introduce itself into the composite. Sufficient coupling is often achieved by chemical interaction and inter-diffusion.[18] The nature of the bond formed between a specific coupling agent and the fibers depends mainly on the characteristics of the fiber surface to which the coupling agent is adhered. Lignocellulosic fibers are complex in structure. The chemical composition of jute and other allied fibers are given in Table 2.6. Cellulose content of jute is (59-61)%.[19] Since a surface can be characterized by its chemical composition, the investigation on the chemical composition of fiber surface before and after the treatment would be very useful for the study of adhesion. In other words, an understanding of the fundamental mechanism by which the coupling agents form bonds either to the fibers or to the matrix, would be necessary to predict adhesion.[2] In this work, experimental studies on the interfacial adhesion and probable reaction bonding mechanism of pre-treated and post-treated jute fiber reinforced polypropylene composites by FT-IR spectroscopic analyses and SEM analyses have been carried out. The results of surface modification and their effects on interaction in cellulose-polymer systems may lead to an increased number of applications for cellulose fibers in combination with polymers in our daily life.

Sufficient mechanical properties and resistance to moisture absorption of natural fibres have been achieved by various surface treatments. M. Andersson et al[20] reported that modification of jute with liquid acetic anhydride made it much more hydrophobic than raw jute and greatly improved the resistance to fungal attack. P. Chow et al[21-22] investigated the acetylation effect on aspen, southern pine, hemlock fibers and observed that acetylation reduced the hygroscopicity of these fibers. A comparative study on the improvement of physico-mechanical properties of jute fibre by the treatment with alkali and diazonium salt was studied by M.M Huque et al.[23] Improved physico-mechanical properties of 3-(trimethoxysilyl) propylmethacrylate monomer grafted and 2-hydroxy ethyl methacrylate (HEMA) grafted jute fibers were investigated by M. M. Hassan et al[24] and M. B. Ahmad et al.[25] Effect of alkali treated jute fibers, hemp fibers and wood fibers on composite properties were investigated by D. Ray et al[26], G. W. Beckermann et al[27] and M. D. H. Beg et al.[28] A .K. Mohanty et al[29] has studied the effect of different surface modifications of jute fibers (e.g. dewaxing, alkali treatment, cyanoethylation, and vinyl monomer grafting) and the properties on modified jute reinforced composites. They observed that fiber/matrix interactions for compatibilized systems are superior to those for the uncompatibilized system. Oxidation of pure cellulose and cellulose in cotton (where principal component is 88-96% cellulose) were carried out by periodic acid and periodate salts.[6] In this thesis oxidation of unbleached raw jute fibers with sodium periodate has been reported. The conversion of cellulose into dialdehyde cellulose in jute was confirmed by FT-IR spectroscopy. The performance of oxidized jute fiber reinforced polypropylene composites comparing with untreated raw jute fiber reinforced polypropylene composites have been investigated and reported.

The effect of silane treated wood and jute fiber reinforced composites were studied by B.V. Kokta et al[30], T. G. Rails et. al[31] and M. A. Khan et al.[32] The effect of compatibilizer and additives on the physico-mechanical and degradable properties of jute reinforced polypropylene (PP) composites was studied by A.K. Rana et al[33] and M.M Hassan et al.[34] The improvement of mechanical properties of jute fibre reinforced epoxy composites by chemical treatment was studied by J.Gassan et al.[35] In this thesis another two studies have been submitted on the effects of some new coupling agents (urea and urotropine) treatment on the injection moulded oxidized jute fiber reinforced polypropylene composites by post treatment processes. Proper reaction conditions of the post treatment processes have been carried out to get highest mechanical properties of the composites. Improved physico-mechanical properties have been observed and reported.

Various investigations have been carried out on esterification of lignocellulosics. Maleic anhydride grafted polypropylene (MAPP) has been widely used as coupling agent to improve the interfacial adhesion between fiber and thermoplastic matrix. Improvement of physico-mechanical properties of cellulose fiber polypropylene composite by grafting maleic anhydride was studied by Bledzki et al.[36] Improved physico-mechanical properties of jute and hemp fiber reinforced polypropylene composites were obtained by addition of MAPP as coupling agent.[37-38] M. Kazayawoko et al[39] elucidated the interaction between anhydride groups of maleated polypropylene and hydroxyl groups of wood fiber and explained the mechanisms of the interfacial adhesion between wood fiber and polypropylene matrix. R. Karnani et al[40] reported the improved adhesion and enhanced polar interactions at the fiber/ matrix interface by modification of PP matrix with maleic anhydride and modification of fiber surface with silane. L.M. Matuana et al[2] reported on esterification of cellulosic fibers with phthalic anhydride and maleated polypropylene. FTIR spectroscopy results showed that anhydride moieties of both phthalic anhydride and maleated polypropylene entered into the esterification reaction with the hydroxyl groups of the cellulosic fibers. The treatment procedures were followed using solvent system.[2] M. L. Hassan et al[41] reported on esterification of bagasse fibers in absence of solvent to modify mainly the thermoplastic matrix of bagasse, that is to modify mainly hemicelluloses and lignin, and to keep cellulose as a reinforcing element. They proved the occurrence of thermoplasticization of the esterified bagasse fibers using SEM and supported by the absence of reversible swelling of some esterified bagasse composites. J. A. Murshidi et al[42] also showed that lignocellulosic material oil palm emty bunch (EFB) acquired plastic properties by the modification with benzyl chloride. Several methods have been expressed to combine lignocellulosic materials with thermoplastics.[43] These methods have been discussed in the literature review chapter of this thesis. Rowell et al[44] reported that only the hemicelluloses and lignin have been modified in thermoplasticization using maleic and succinic anhydriedes. Matsuda et al[46] also extensively investigated the esterification of wood in order to make a totally thermoplastic material. They esterified wood without a solvent by simply heating wood meal with succinic anhydride in a mixer for 3 h at temperatures greater than 60^{0}C. The uses of MA or MAPP as coupling agent to prepare composites were investigated by various methods.[36-46] Significantly improved mechanical properties have been obtained using MAPP as a coupling agent.[36-46] In this thesis a new method for the study of the effect of maleic acid on untreated raw jute fiber reinforced polypropylene composites has been presented. In this method aqueous maleic acid was used as coupling agent without using any solvent. The post treatment processes have been carried out at different reaction conditions to get the highest mechanical properties of the composites. Improved physico-mechanical properties have been observed and reported in this thesis.

In this work all chemical modification of jute and composites by pre and post treatment respectively were carried out in aqueous solution instead of using any inert or toxic solvents. Chemical modifications were characterized by FT-IR spectroscopic analyses and SEM analyses. Water absorption behaviors of all composites were carried out and reported in this thesis.

1.2 Objective

In the literature lot of work has been found on natural fiber-polypropylene composites. However, very limited works have been reported on pre- and post-treatment together on the natural fiber-polypropylene composites. The aim and objective of the present work is to investigate and prepare some improved injection moulded jute-PP composite materials using some new coupling agents by chemically pre-treatment and post-treatment methods. The specific aims and objectives of this research are:

1. to modify raw jute fibers (unbleached) by sodium periodate oxidation process which will make the jute fiber more active to the coupling agent to form positive coupling reaction.
2. to prepare jute-PP composite materials followed by extrusion and then injection moulding process using both the treated and untreated jute.
3. to investigate the effect of oxidation of jute fibers on the performance of oxidized jute fiber reinforced PP composites comparing with the untreated jute reinforced PP composites.
4. to improve physico-mechanical properties of the jute reinforced polypropylene composites by suitable coupling reaction.
5. to search for suitable coupling agents for better quality jute-PP composite.
6. to find out the properties of the composites according to fiber loading variation.
7. to find out some new and ease coupling reaction techniques on the injection moulded jute fiber reinforced polypropylene composites by post treatment process.
8. to characterize the chemically modified jute and jute-polymer composites by FT-IR spectroscopic analyses.

9. to characterize the interfacial bonding between PP matrix and fiber in the composites by morphological SEM analyses.
10. to increase the water repellent properties of the jute-PP composites.

CHAPTER 2: LITERATURE REVIEW

This chapter presents a brief review on the literature related to the composite materials, raw materials used in this research work (PP and jute), preparation composites and about the chemical modification of composites that are related to this work. The details of different chemical treatments of natural fibers and their effects on the properties of composite materials are also discussed.

2.1 Introduction and classification of composite materials

The term composite material is used to describe macroscopic combinations of two or more materials. The fundamental goal in the production and application of composite materials is to achieve a performance from the composite that is not available from the separate constituents or from other materials. The concept of improved performance is broad and includes increased strength or reinforcement of one material by the addition of another material.[11] The modern interest in composite materials can be traced in the development of Bakelite, or phenolic resin, which was synthesized by Backeland a Belgium scientist, in 1906.[11] Bakelite was a hard, brittle material that had a very few mechanical applications of its own. However, the addition of a filler, (the earliest applications used short cellulose fibers) yielded Bakelite molding compounds that were very strong and tough and found several applications in mass-produced automobile components. The wood flour additives improved Bakelite's processibility, physical, chemical, and electrical properties, as well as reducing its cost.[11]

Polymer composites are now an important class of engineering materials. The properties of composites are largely influenced by the properties of their constituents and the distribution and interactions among them. The constituents usually interact in a synergistic way, providing properties that are not accounted for by a simple volume-fraction sum of the components. Along with the volume fraction and the distribution of discrete units in the discontinuous phase, the interfacial area plays an important role in determining the extent of interaction between the reinforcement and the matrix and –in this way –the final properties of the composite. The fabrication technology of composites, as well as some of their physical properties, is dominated by the chemistry and rheology of the matrix resin and by the type and physical form of the reinforcement.[1]

The use of reinforcing agents makes it possible for any thermoset- or thermoplastic-matrix property to be improved or changed to meet varying requirements. Thus most polymer composites have been developed or fabricated to improve mechanical properties such as strength, stiffness, or toughness. The strengthening efficiency of the discontinuous phase plays the most important role in these products, and the strengthening mechanism depends strongly on the geometry of the reinforcements. Therefore, polymer composites can be classified according to geometry of reinforcement materials. The three major classes of polymer composites are fibrous, laminar, and particulate. The commonly accepted classification scheme for polymer composites is presented in Figure2.1.[1]

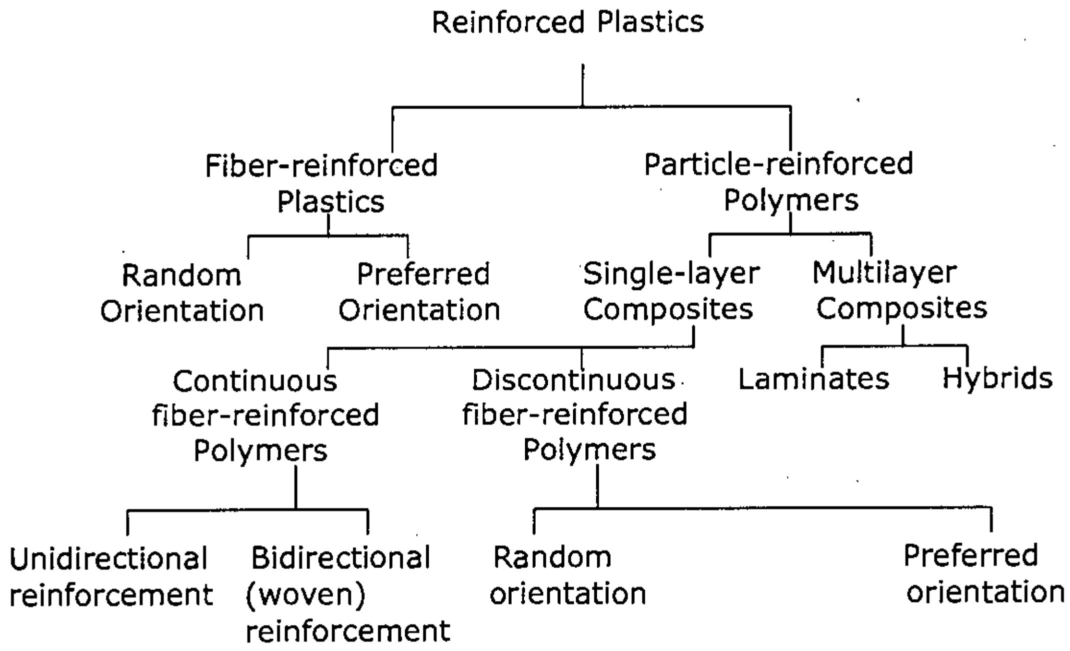


Figure 2.1: Classification of polymer composites.

2.1.1 Matrix materials

The mechanical properties of composites based on the fibers depend not only on the characteristics of the fibers but also on the matrix itself as well as on the fiber-matrix interface. The matrix in a polymer composite serves both to maintain the position and orientation of the fibers and to protect them from potentially degrading environments. Polymer matrices may be thermosets or thermoplastics. Thermosetting polymers are rigid, cross-linked materials that degrade rather than melt at high temperatures. Thermoplastic polymer are linear or branched molecules that soften upon heating. Thermoset-based composites are somewhat less expensive than thermoplastic-based composites, but have lower heat distortion temperatures and poorer toughness when tested in an interlaminar mode. Thermosetting polymers, includes unsaturated polyesters, epoxies, and phenolic resins. Whereas thermoplastic polymers are polyamides, polyolefin's, polycarbonates and saturated polyesters.[11]

Many of the thermoplastic-based composites offer excellent resistance to impact loading and are thereby suitable for use in high performance engineering applications. Other interesting aspects of these composites include the possibility of thermoforming and shaping at elevated temperature and the potential for thermal joining and repair, as well as recycling.[11]

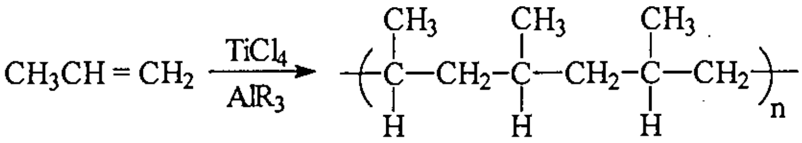
2.1.2 Thermoplastic polymer

Thermoplastic resins have received considerable attention in the past few years as the matrix material in organic resin-based composites.[11] Whereas, thermosetting materials date back 5000 years, when Egyptians used a straw-reinforcing agent in a clay matrix to form bricks. So, thermoplastic composites are relatively new development. Although their use in advanced composites is not widespread, thermoplastic composites are used extensively in commercial applications ranging from automobiles to durable goods.[11]

Thermoplastic polymers are usually linear molecules with no chemical linkage between the chain of the molecules. The molecules are held together by weak secondary forces, such as van der Waals or hydrogen bonding. These are readily deformed by the application of heat or pressure. Thermoplastic resins can be amorphous, that is, structureless, or semicrystalline, in which some of the molecules form an ordered array. A material is usually considered semicrystalline if as little as 5% of the polymer is in the crystalline form. Semicrystalline resins exhibit higher modulus, but amorphous materials are tougher. Amorphous materials are usually more solvent sensitive and can be processed at lower temperature. One of the most important advantage of thermoplastic resins is their toughness, that is, high impact strength and fracture resistance, which, unfortunately, is not linearly transmitted into properties of the composite. Other advantages of thermoplastic polymers include long life at room temperature; post formability, that is, thermal reforming; ease to repair by thermal welding or solvents; and ease of handling, that is, they are not tacky.[11] One of the principal advantages of true thermoplastic polymer is their ability to consolidate or flow at elevated temperature; however, this quality also limits their use at higher temperature. Amorphous materials begin to flow or creep above the glass-transition temperature, T_g, whereas crystalline resins must be heated above the melting point, Tm. As a rule of thumb, Tg is approximately 2/3 Tm (Kelvin temperature). So crystalline polymers may begin to degrade at the temperatures required for processing. Even a relatively low temperature material such as polypropylene, which melts between 168 and 175^{0}C, must be heated to approximately 180-190^{0}C to process the composite. In many instances the processing window is quite narrow owing to a lower temperature limit set by the melting point and an upper temperature limit set the rate of thermal degradation.[11]

2.1.3 Polypropylene (PP)

The most common polyolefin used to prepare composites is polypropylene, a commodity polymer that has been in commercial production for the last 40 years following its controlled polymerization by Natta in 1954.[11] Natta used a Ziegler catalyst consisting of titanium tetrachloride and an aluminum alkyl to produce isotactic polypropylene directly from propylene:



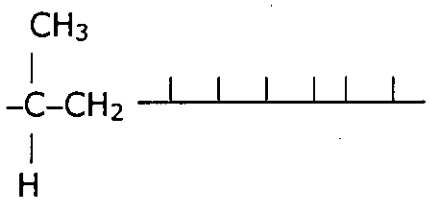
$$CH_3CH=CH_2 \xrightarrow[AlR_3]{TiCl_4} \left(\underset{H}{\overset{CH_3}{C}} - CH_2 - \underset{H}{\overset{CH_3}{C}} - CH_2 - \underset{H}{\overset{CH_3}{C}} - CH_2 \right)_n$$

Stereoregular

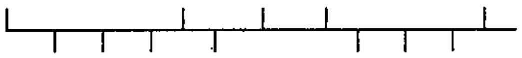
Polypropylene is available with many different reinforcing agents or fillers, such as talc, mica, or calcium carbonate; chopped or continuous strand fiber. Glass is the most common reinforcing agent used for composites. Many additives have been developed to enhance the thermal stability of polypropylene to minimize degradation during processing. One of the most important requirements of the polypropylene used in the manufacture of composites is that, it should be relatively pure and free of residual catalyst. Recent developments to form copolymers of polypropylene and polyethylene have great promise for relatively inexpensive, tough, thermoplastic composite applications.[11]

2.1.4 Molecular structure of PP

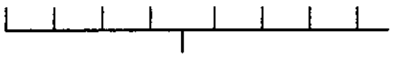
In 1955 Natta[13] first determined the molecular structures of the various types of PP and introduced the descriptive nomenclature universally used today. Commercial interest lies primarily in highly crystalline PP, together with its further modifications through copolymerization. In isotactic PP, each monomer unit in the chain is arranged in a regular head-to-tail assembly without any branching. Furthermore, the configuration of each methyl group is the same (Fig. 2.2 A). This is caused by the template type constraints of the stereospecific catalytic site. Such a regular structure is the hallmark of a good catalyst. Occasionally, some imperfect monomer insertion gives the type of fault shown in Figure 2.2 C, amounting to about 0.3-1.5 per hundred monomer units in the salable polymer. An extreme example of deffects is atactic PP (Fig. 2.2 B), with complete loss of steric control. In syndiotactic configuration, methyl groups are alternatively on either side of the carbon chain. Syndiotactic polymer is of theoretical, but not commercial importance.[13]



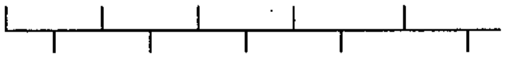
(A) Isotactic polypropylene; mp 176^{0}C



(B) Atactic polypropylene rubber



(C) Chain imperfection; mp< 176^{0}C



(D) Syndiotactic polypropylene; mp ca. 130^{0}C

Figure 2.2: PP chain structure

2.1.5 Crystallization of PP

PP is semi-crystalline, which means it always has two phases, an amorphous and a crystalline one. The useful properties of PP stem from its ability to crystallize and form rigid and tough articles. Highly isotactic polymer, with its regular structure, forms a helical coil having three monomer units per turn. These coils stack together into thin lamellar crystallites which force the chains to fold several times as they emerge and reenter lamellae.[13] Three crystalline forms are known (Table 2.1) of which the α-form is the most stable.

The more stable α-form is favored at higher temperatures and slower cooling rates. Rapid quenching yields the β-form with a lower density and melting point of 150^{0}C. Polymers of lower stereoregularity and random copolymers usually contain low-melting γ-crystallites in addition to the α-form.

Formation of crystallites from a viscous melt is hindered by chain entanglements and by the need for helics to fold as they close pack into lamellae. This, and the formation of nuclei might contribute to the low degree of crystallization even in highly steroregular polymers. Commercial articles vary from 30% crystallinity in rapidly quenched films to 50-60% in moldings. Even purified and annealed samples of very stereoregular polymer rarely achieve more than 70% crystallinity. It is to be pointed out that high helical contents are not synonymous with high crystallinities, which require three-dimensional long-range order. PP is properly regarded as a semicrystalline polymer for these reasons.[13] Crystalline properties of PP are given in Table 2.1. The most predominant and stable crystal form being the α form, having a monoclinic structure. The more stable form is favored at higher temperatures and slower cooling rates.

Table 2.1: Crystalline properties of PP[13]

Crystal form	System	Crystal density (20^{0}C), g/cm^3	Chains per unit cell	Mp,^{0}C
Iso α	monoclinic	0.932-0.943	4	171
Iso β	pseudo Hexagonal	0.922	9	150
Iso γ	triclinic	0.939	1	131
Amorphous	-	0.85	-	-
Syndio	orthorhombic	0.93	2 (4/1 helix)	138

2.1.6 Properties of PP

Polypropylene is a linear hydrocarbon polymer containing little or no unsaturation. It is therefore not surprising that polypropylene and polyethylene have many similarities in their properties.[49] Basic mechanical properties are largely influenced by molecular mass and molecular mass distribution (MMD), chain stereoregularity, and processing conditions, which introduce orientation, structural strain, etc. Various additive packages must be tailored to the application to achieve good and durable performance. Some typical properties of PP are given in Table 2.2.The final melting point of commercial PP lies in the range 160-170^{0}C, with purified polymer reaching 176^{0}C. Within the range of commercial polymers, the greater the amount of isotactic material the greater the crystallinity and hence, greater the softening point, stiffness, tensile strength, modulus and hardness.[49] The crystalline and nonpolar nature of PP confers good resistance to a wide range of aqueous and polar media, including emulsifier solutions with their strong stress cracking abilities. Powerful oxidizing agents, highly aromatic and chlorinated solvents are too aggressive for safe storage in PP containers.[13] One disadvantage of PP is the susceptibility of its methyl groups to thermooxidative degradation.[50]

Table 2.2: Properties of PP[49, 50]

Parameters	Standard Used	Values
Specific gravity	ASTM D792	0.90-0.91
Crystallinity, %	-	82
Melting temperature, ^{0}C	-	165-171
Tensile strength, MPa	ASTM D638	31-41
Tensile modulus, GPa	ASTM D638	1.10-1.55
Elongation-to-break, %	ASTM D638	100-600
Impact strength, notched Izod,J m^{-1}	ASTM D256	21-53
Rockwell hardness (R-scale)	ASTM D785	90-95
Heat-deflection temperature,^{0}C, at 455 kPa (66psi)	ASTM D648	225-250

2.2 Lignocellulosic fibers

Lignocellulosic fibers refer to those agrobased substances which contain cellulose, hemicelluloses, and lignin as their structural molecules. Lignocellulosics include wood, agricultural residues, water plants, grasses, and other plant substances.[52] To better understand the properties of lignocellulosic fiber-reinforced composite materials, it is necessary to know the physical and chemical properties of lignocellulosic fibers. Fibers are classified as[4,5]

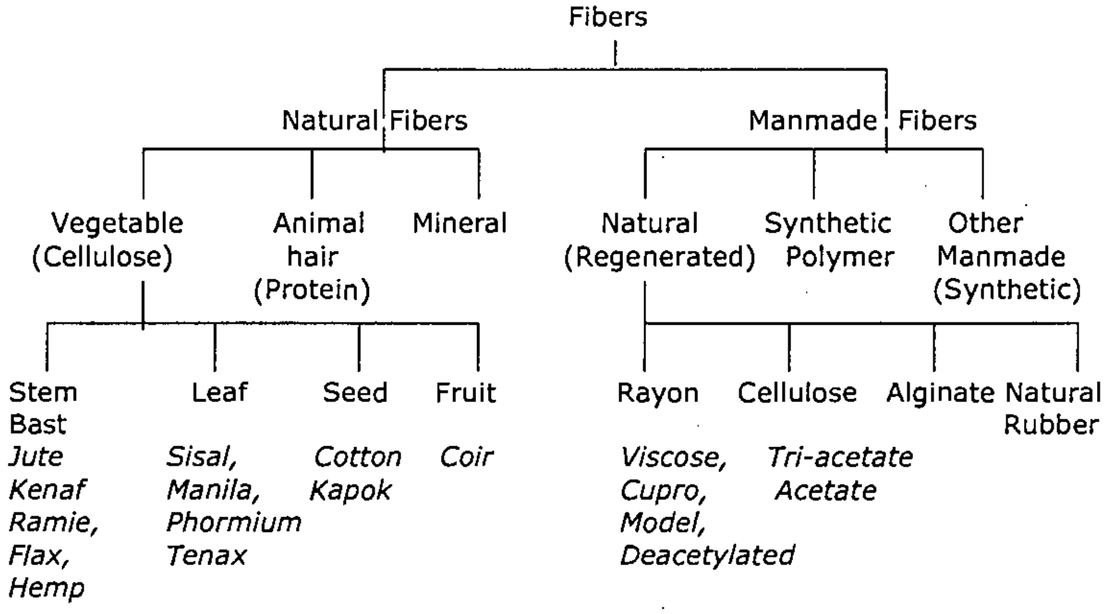


Figure 2.3: Classifications of fibers[4]

Agro-based lignocellulosic fibers are also classified on the basis of part of the plant where they store in.[17] Five different classes of fiber are: (1) bast or stem fibers, which are the fibrous bundles in the inner bark of the plant stem running the length of the stem; (2) leaf fibers, which rim the length of leaves; (3) seed-hair fibers; (4) core, pith or stick fibers, which form the low density, spongy inner part of the stem of certain plants; and (5) all other plant fibers not included above.[17] Examples of bast or stem fibers include jute, flax, hemp, kenaf, ramie, roselle, and urena. Leaf fibers include banana, sisal, henequen, abaca, pineapple, cantala, caroa, mauritius, and phormium. Seed-hair fibers include coir, cotton, kapok, and milkweed floss. Core fibers represent the center or pith fibers of such plants as kenaf and jute and can represent over 85 percent of the dry weight of these plants. The remaining fibers include roots, leaf segments, flower heads, seed hulls and short stem fiber. While individual single fibers in all of these classes are quite short (except for flax, hemp, ramie, cotton, and kapok). However, the fibers obtained from inner bark of the plant are quite long. For example, hemp, jute, and kenaf can have fiber bundles as long as 400 cm and abaca, mauritius, and phormium are about half this length. Considering all types plant fiber, there is a vast array of potential long and short fibers for composite production.[17] Table 2.3 shows a comparison of properties of natural lignocellulosic fibers and conventional man-made fibers. Jute, ramie, flax, and sisal are the most commonly used fibers for polymer composites.

Table 23: Properties of natural & synthetic fibers[51]

	Fibers	Density	Tensile strength MPa	Tensile Modulus GPa	Elongation at break, %	Decomposition Temperature, ^{0}C	Price in Euros/kg
Natural	Jute	1.3-1.5	187-540	3-55	1.4-3.1	270	0.7
	Ramie		585-900	33	2.0-3.5	260	
	Hemp fibers	1.4-1.5	580-1110	3-90	1.3-4.7	258	
	Bamboo			1.7-29	3.2		
	Flax	1.4	250-1000	12-100	1.3-40	280	0.15-0.76
	Sisal	1.4	507-855	24	2.9	270	0.7-1.02
	Cotton	1.5-1.6	350	11	2-10		0.35
	Banana fibers	1.3	791	30	2.10		0.7-0.9
	Kenaf	1.4	930	53		270	
	Coconut		544	14			0.36-0.45
	Wood fibers	0.6		12	2.90		0.31-0.35
	Cellulose fibers	1.2		2.1			
	Wood flour	0.6		10			
Synthetic	E-glass fibers	2.5	1625-3400	72	2-5	756	1.6-2.0
	C-glass fibers	2.5	2800	69		756	9.3-16
	S-glass fibers	2.5	4600	87		946	8.3-20
	A-glass fibers	2.5	2400	68		696	2.5
	Aramid (Kevlar)	1.4	2380-3100	124		496	16-67
	Carbon fibers	1.8-1.9	2090-5200	525		3647	33-166
	Zirconia fibers	5.6	700	100		2497	41.7
	Alumina fibers	2.8	1000	100		1997	

2.2.1 Jute and allied fibers and their physical properties

Jute *(Corchorus capsularis & Corchorus olitorius)*, Kenaf *(Hibiscus cannabinus)* and Roselle *(H. sabdariffa var (Altissima)* are vegetable bast fibre plants next to cotton in importance. In the trade there are usually two names of jute, White and Tossa. *Corchorus capsularis* is called White Jute and *Corchorus olitorius* is called Tossa Jute. The genus of the jute is Corchorus and the family is Tiliaceae. In Bangladesh & India Roselle is usually called Mesta. Jute fibres are finer and stronger than Mesta and are, therefore, better in quality. The natural fibre colour of white jute is white creamy and that of tossa jute is golden. Depending on demand, price and climate, the annual production of jute and allied fibres in the world remains around 3 million tonnes.[15]

Structurally the jute and allied fibre stems are composed of epidermis, cortex, large phloem, cambium, wide xylem or wood and central pith tissues. The tissue, phloem, is most important as it is connected with fibre development. Bast is another name of phloem tissue. Jute includes about 40 species mostly distributed in the tropical regions. The vegetative period of jute is about 3-5 months. At the harvest stage varieties of *C. capsularis* attain a height of about 5-12 feet and those of *C. olitorius* 5-15 feet or more. The stems of both are cylindrical. Leaves are glabrous. Flowers of both the species look yellow, are small in size and occur in condensed cymes.[16] The ribbons, fibres, leaves and stick contents of different jute and allied fiber plants vary considerably. The fibre content of *C. olitorius* jute plant is the highest and that of *H. sabdariffa* is the lowest. The green leaf content of *H. sabdariffa* plant is the highest. The dry ribbon contents of both *C. capsularis* and *C. olitorius* plants are higher than those of *H. cannabinus.* Physical compositions of different jute and allied fiber plants are given below:

Table 2.4: Physical compositions of different jute & allied fiber plants

Crop	Whole (100%)	Ribbons %		Leaf %		Sticks%		Fibers %
	Plant (t/ha)	Green	Dry	Green	Dry	Green	Dry	Dry
C. olitorius	46	38.7	11.7	11.0	2.7	50.3	16.6	6.8
C. capsularis	34	40.2	11.2	15.6	3.9	44.2	12.5	5.9
H. sabdariffa	48	35.2	9.6	16.3	3.6	48.5	15.0	4.8
H. cannabinus	36	34.0	9.5	14.2	3.3	51.8	15.9	4.9
Approx. Avg.	40	37.0	10.3	14.2	3.3	48.8	15.2	5.5

Some other physical and mechanical properties of jute are given in Table 2.5. Among jute, ramie, flax, hemp & cotton, jute has the shortest fiber length (0.5-6.0 mm) and ramie has the longest fiber length (125-126 mm). In case of jute the average length of fibers from outer parts of the wedge is 0.3-2 mm and from the inner parts about 1-5 mm only. The table is given below:

Table 2.5: Some physical properties of jute & allied fiber plants[15]

Properties	Jute	Mesta	Roselle	Ramie	Flax	Comparative value for Cotton
Ultimate Cell Length (mm)	0.5-6.0	2-11	1.5-3.5	125-126	26-65	15-60
Length x Breadth Ratio	110	140	100	3500	1700	1300

2.2.2 Chemical composition of jute fibers

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 three layers (S1, S2 and S3). In all lignocellulosic fibers these layers contain cellulose, hemicellulose and lignin in varying amounts. The individual fibers are bonded together by a lignin-rich region known as the middle lamella. Cellulose attains its highest concentration in the S2 layer (about 50%) and lignin is most concentrated in the middle lamella (about 90%) which, in principle, is free from cellulose. The S2 layer is usually by far the thickest layer and dominates the properties of the fibers.[14]

Main ingredients of jute fibers are about (59-61)% cellulose, (15-17)% pentosan or hemicellulose and (12.5-13.5)% lignin. There is a predominance of pentose sugars in the hemicellulose and hence it is convenient to refer to it as pentosan. Chemical composition of the fibers varies with plant age, retting, etc. The details of chemical composition of jute fiber and other allied fibers are given below[15]:

Table 2.6: Chemical composition of jute and other allied fibers[15]

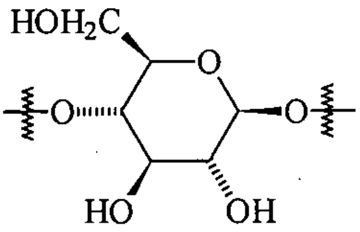
Constituent	Cellulose (%)	Pentosan (%)	Lignin (%)	Polyuronide (%)	Acetyl value	Fat & Wax (%)	Nitrogenous matter (%)	Mineral Substances (%)
Jute	59-61	15-17	12.5-13.5	4.8-5.2	2.8-3.5	0.9-1.4	1.56-1.87	0.5-0.79
Mesta	60	14.8	10.1	-	4.8	0.6	1.2	0.7
Roselle	59.7	15	9.9	-	4.8	0.6	0.8	0.5
Ramie	86.9	3.9	0.5	-	0.6	0.3	2.1	1.1

Cellulose is the basic structural component of all plant fibres. It is the most important organic compound produced by plants and the most abundant in the biosphere. The cellulose molecules consist of glucose units linked together in long chains, which in turn are linked together in bundles called microfibrils. The tensile strength of the cellulose microfibrils is very high. It is the strongest amongst the known material with a theoretically estimated tensile strength of 7.5 GPa or 1,087,500 pounds per square inch. In the S2 layer the microfibrils run almost parallel to the fiber axis. With S2 representing about 50% of the cell wall, this gives the fibers a very high tensile strength.[14]

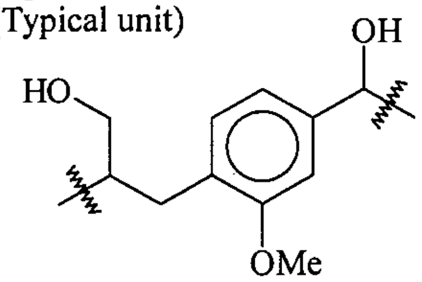
Hemicelluloses are also found in all plant fibres. Hemicelluloses are polysaccharides bonded together in relatively short, branching chains. They are intimately associated with the cellulose microfibrils, embedding the cellulose in a matrix. Hemicelluloses are very hydrophilic (i.e., containing many sites to which water can readily bond).[14]

Lignin is a Latin word for wood. Lignin is the compound which gives rigidity to the plant. Without lignin, plants could not attain great heights (e.g., trees) or the rigidity found in some annual crops (e.g., straw). Lignin is a three-dimensional polymer with an amorphous structure and a high molecular weight. Of the three main constituents in fibers, it is expected that lignin would be the one with least affinity for water. Another important feature of lignin is that it is thermoplastic (i.e., at temperatures around 90^0C it starts to soften and at temperatures around 170^0C it starts to flow).[14] Lignin in jute makes the fibre resistant to ease microbial attacks, and provides better strength along with hardness and brittleness.[15] The polymers lignin and hemicellulose are responsible for most of the physical and chemical properties such as: biodegradability, flammability, sensitivity towards moisture, thermoplasticity, degradability by UV-light, etc.[51] Some structures of the monomeric units for the major polymeric constituents of cellulosic plant fibers are given below[16]:

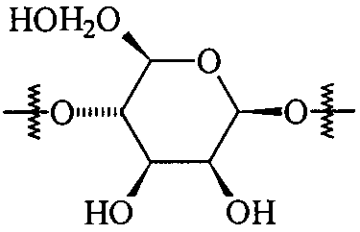
Cellulose:



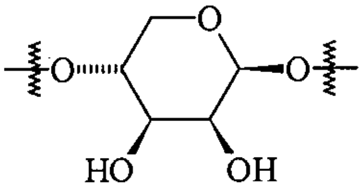
Lignin:
(Typical unit)



Hemicellulose:

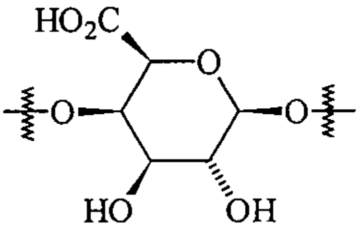


(Mannose)

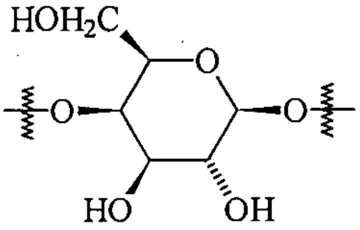


(Xylose)

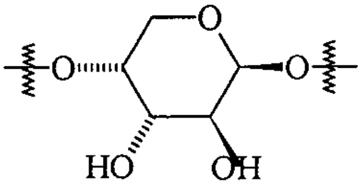
Pectin:



(Galaeturonic Acid)



(Galatose)



(Arabinose)

2.3 Lignocellulosic fiber reinforced thermoplastic composites

There is a long story of the use of lignocellulosic materials with thermosetting polymeric materials, like phenol or urea formaldehyde in the production of composites. The use of lignocellulosics with thermoplastics, however, is a more recent innovation. Lignocellulosic fibers have been incorporated in a wide variety of thermoplastic materials such as polypropylene, polyethylene, polystyrene, poly-vinyl chlordide, polyamides. Thermoplastic materials selected for use with lignocellulosic materials must melt at or below the degradation point of the lignocellulosic component, normally 200-220^{0}C.[52]

2.3.1 Lignocellulosics in combination with other materials

Combining of lignocellulosic materials with thermoplastic materials can be done in several ways.[43] In one case, thermoplastic materials are simply mixed with biobased powder or fiber (nut shell powder or wood fiber are presently used) and the mixture are heated. The plastic melts, but the wood fiber and plastic components remain as distinct separate phases. One example of this technology is reinforced thermoplastic composites, which are light weight, have improved acoustical, and heat reformability properties, and cost less than comparable products made from plastic alone. These advantages make possible the exploration of new processing techniques, new applications, and new markets in such areas as packaging, furniture, housing and automobiles.

A second way to combine wood fiber and plastics is to use a compatibilizer to make the hydrophobe (plastic) mix better with the hydrophil (wood). The two components remain as separate phases, but if delamination and/ or void formation can be avoided, properties can be improved over those of either separate phase. These types of materials are usually referred to as wood fiber/ plastic blends.[43]

A final combination of wood fiber and thermoplastics is in products that can best be described as wood-plastic alloys. In this case the wood and plastic have become one material and it is not possible to separate them. The formation of wood-plastic alloys is possible through fiber modification and grafting research. This can be done if we consider that biobased fibers consist of a thermoset polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). The glass transition temperature (GTT), however, of the thermoplastic matrix is higher than the decomposition temperature of the fiber. If the GTT were lowered through chemical modification, it should be possible to thermoplasticize the lignin and the hemicelluloses at temperatures below decomposition. If a reactive thermoplastic is used it is then reacted with the modified biobased fiber, it should be possible to form biobased fiber/ thermoplastic alloys.[43] Rowell et al[44] reported that only the hemicelluloses and lignin have been modified in thermoplasticization using maleic and succinic anhydriedes. Matsuda et al[46] also extensively investigated the esterification of wood in order to make a totally thermoplastic material. They esterified wood without a solvent by simply heating wood powder with succinic anhydride in a mixer for 3 h at temperatures higher than 60^{0}C.

2.3.2 Properties of lignocellulosic fiber- thermoplastic composites

Before 1980, the concepts of blends and alloys were essentially unknown in the plastics industry. Blends and alloys have revolutionized the plastics industry, as they offer new materials with properties that were not achieved before. These materials can be tailored for specific end uses. The jute and kenaf industries have the same opportunity to follow this trend and greatly expand markets for new materials based on blends and alloys with other resources. Newer materials and composites that have both economic and environmental benefits are being considered for applications in the automotive, building, furniture, and packaging industries. Mineral fillers and fibers are used frequently in the plastics industry to achieve desired properties or to reduce the cost of the finished article. For example, glass fiber is used to improve the stiffness and strength of plastics, although there are several disadvantages associated with its use. Glass-fiber production requires a great deal of energy–processing temperatures can exceed 1200^{0}C. They tend to abrade processing equipment and increase the density of the plastic system. The use of lignocellulosic fibers in thermoplastics has received a lot of interest due to their low densities, low cost, and non-abrasive nature. The inherent polar and hydrophilic nature of the jute and kenaf fibers and the nonpolar characteristics of the polyolefins lead to difficulties in compounding and result in inefficient composites.[6] The high moisture absorption of the lignocellulosic fibers and their low microbial resistance are disadvantages (Table 2.7) that need to be considered, particularly during shipment and long-term storage as well as during processing of the composites.[12] Proper selection of additives is necessary to improve the interaction and adhesion between the fiber and matrix phases. Recent research on the use of jute and kenaf fiber suggests that these fibers have the potential for being used as reinforcing fillers in thermoplastics.[6] The low cost and densities and the nonabrasive nature of the fibers allow high filling levels and thereby result in significant cost savings. The primary advantages of using these fibers as additives in plastics are: low densities, low cost, nonabrasive, high filling levels, low energy consumption, high specific properties, renewability, wide distribution, biodegradability, and improvement of the rural/agricultural-based economy.[6]

Table 2.7: Main advantages and disadvantages of lignocellulosic fibers[12]

Advantages	Disadvantages
Low cost	High moisture adsorption
Renewable	Poor microbial resistance
Low density	Low thermal resistance
Nonabrasive	Local and seasonal quality variations
Low energy consumption	Demand and supply cycles limited
High specific properties	
High strength and elasticity modulus	
No skin irritations	
No residues when incinerated	
Fast water absorption/ desorption	
Good thermal conductivity	
Biodegradability	

Jute and other lignocellulosic materials change dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding.[55] This hydrophilic behavior affects the properties of the fibers themselves as well as the properties of their composites. The hydrophilic character of fibers is usually incompatible with hydrophobic matrix material unless a compatibilizer or coupling agent is used. This leads to poor interfacial adhesion between the fiber and matrix as well as poor fiber dispersion.

In general, cellulosic fillers or fibers have a higher Young's modulus as compared to commodity thermoplastics, thereby contributing to the higher stiffness of the composites. The increase in the Young's modulus with the addition of cellulosic materials depends on many factors such as amount of fibers used, orientation of the fibers, interaction and adhesion between the fiber and matrix.[54] In general, dispersing agents and/or coupling agents, are necessary for the property enhancement, when fibers are incorporated into thermoplastics. Dispersing agent facilitates the fiber dispersion and improves the interfacial adhesion between the fibers and the polymer matrix. Grafting of chemical species on to the fiber surface has also been reported to improve the interaction between the fibers and matrix. Although grafting can improve the properties of the composite to a significant extent, this process increases the material cost of system. The use of dispersing agents and/or coupling agents is a cheaper route to improve properties and makes more practical sense for high volume, low cost composite systems.[54]

In a natural fiber-thermoplastic composite the lignocellulosic phase is present in a wide range of diameters and lengths, some in the form of short filaments and others in the form that seem closer to the individual fiber. The high shearing energy of blending the filaments and the polymer in a mixer results in fiber attrition but can also axially separate the filaments into discrete individual fibers. Cellulosic fillers/fibers can be classified under three categories depending on their performance when incorporated to a plastic matrix. Wood flour and other low cost agricultural based flour can be considered as particulate fillers that enhance the tensile and flexural moduli of the composite with little effect on the composite strength. Wood fibers and recycled newspaper fibers have higher aspect ratios and contribute to an increase in the moduli of composite and can also improve the strength of the composite when suitable additives are used to improve stress transfer between the matrix and the fibers. The improvement in modulus is not significantly different than the cellulosic particulate fillers. The most efficient cellulosic additives are some natural fibers such as kenaf, jute, flax, etc. The specific Young's modulus, specific flexural modulus, the ratio of the composite modulus to the composite specific gravity of composites with natural fibers such as kenaf are significantly higher than those with wood fibers. The specific moduli (the ratio of the compostie modulus to the composite specific gravity) of high fiber volume fraciton of bast fibers-PP composites are high and in the range of glass fibers-PP composites. The most efficient natural fibers are those that have a high cellulose content coupled with a low micro fibril angle resulting in high filament mechanical properties.[54] A list of mechanical properties of PP composites reinforced by different natural fiber and inorganic substances is given Table no. 2.8.[6,56-57]

Table 2.8: Comparison of filled PP composites[6,56-57]

Filled/Reinforcement of PP	ASTM Standard	None	Kenaf	Jute	Talc	Ca_2CO_3	Glass	Mica
% filler by weight		0	50	50	40	40	40	40
% filler by volume (estimated)		0	39	39	18	18	19	18
Tensile modulus, GPA	D 638	1.7	8.3	7.8	4	3.5	9	7.6
Specific tensile modulus, GPa		1.9	7.8	7.2	3.1	2.8	7.3	6.0
Tensile strength, MPA	D 638	33	68	72	35	25	110	39
Specific tensile strength, MPa		37	58	67	28	20	89	31
Elongation at break, %	D 638	10	2.2	2.3	—	—	2.5	2.3
Flexural strength, MPa	D 790	41	91	99	63	48	131	62
Specific Flexural strength, MPa		46	85	92	50	38	107	49
Flexural modulus, GPa	D 790	1.4	7.8	7.7	4.3	3.1	6.2	6.9
Specific flexural modulus, GPa		1.6	7.3	7.1	3.4	2.5	5.0	5.5
Notched Izod impact-J/m	D 256A	24	32	31	32	32	107	27
Specific gravity		0.9	1.07	1.08	1.27	1.25	1.23	1.26
Water absorption %-24 hr	D 570	0.02	1.05	—	0.02	0.02	0.06	0.03
Mold (linear) shrinkage cm/cm		0.028	0.003	—	0.01	0.01	0.004	—

2.3.3 Effect of coupling agents on the composite properties

Coupling agents improve the adhesion between filler and polymer, preferably via chemical bonds; their use confers reinforcing properties on inexpensive extenders, improves the performance of reinforcements, and allows the filler content to be increased. The reinforcing effect of fillers depends on their chemistry, shape (fibers, flakes, spheres), and size (fiber length, particle size). The most important reinforcement effects are[48]

1. Increased strength, ultimate elongation, rigidity (modulus of elasticity), and in some cases impact strength.
2. Improved heat distortion temperature and dimensional stability, reduced shrinkage, and improved stability of mechanical values at high temperatures and over extended times (fatigue)
3. Modification of density (usually increased)
4. Improved chemical resistance and lower water absorption
5. Better surface quality and surface hardness

Special fillers are used to obtain compounds with the following properties:

1. Low flammability
2. Electrical conductivity and electromagnetic shielding
3. Radiation and UV shielding
4. Biodegradability
5. Noise suppression

2.3.4 Some chemical modification for property enhancement of lignocellulosic fiber reinforced thermoplastic composites

The properties of lignocellulosic materials result from the chemistry of the cell wall components. The basic properties of a fiber can be changed by modifying the basic chemistry of the cell wall polymers. Many chemical reaction systems have been reported for the modification of agro-fiber. These chemicals include anhydrides (such as phthalic, succinic, maleic, propionic and butyric anhydride etc.), acid chlorides, ketene carboxylic acids, different types of isocyanates, formaldehyde, acetaldehyde, difunctional aldehydes, chloral, phthaldehydic acid, dimethyl sulfate, alkyl chlorides, beta-propiolactone, acrylonitrile, epoxides (such as, ethylene, propylene, butylene) and some difunctional epoxides.[53] By far, the most research has been done on the reaction of acetic anhydride with cell wall polymer hydroxyl groups to give an acetylated fiber. Many different types of lignocellulosic fibers including wood[21-22], bamboo, bagasse, jute[20], kenaf etc. have been acetylated using a variety of procedures. Although acetylation is not the only chemical modification procedure that has been shown to improve properties of lignocellulosic materials even then it has been the most studied and are used in many cases.[53] Some researchers[58-61] have reported that acetylation of the lignocellulosic fibers have reduced the hydrophilicity and water absorption behavior of lignocellulosic fibers. The scheme of the reaction of lignocellulosic fiber with acetic anhydride is given below:

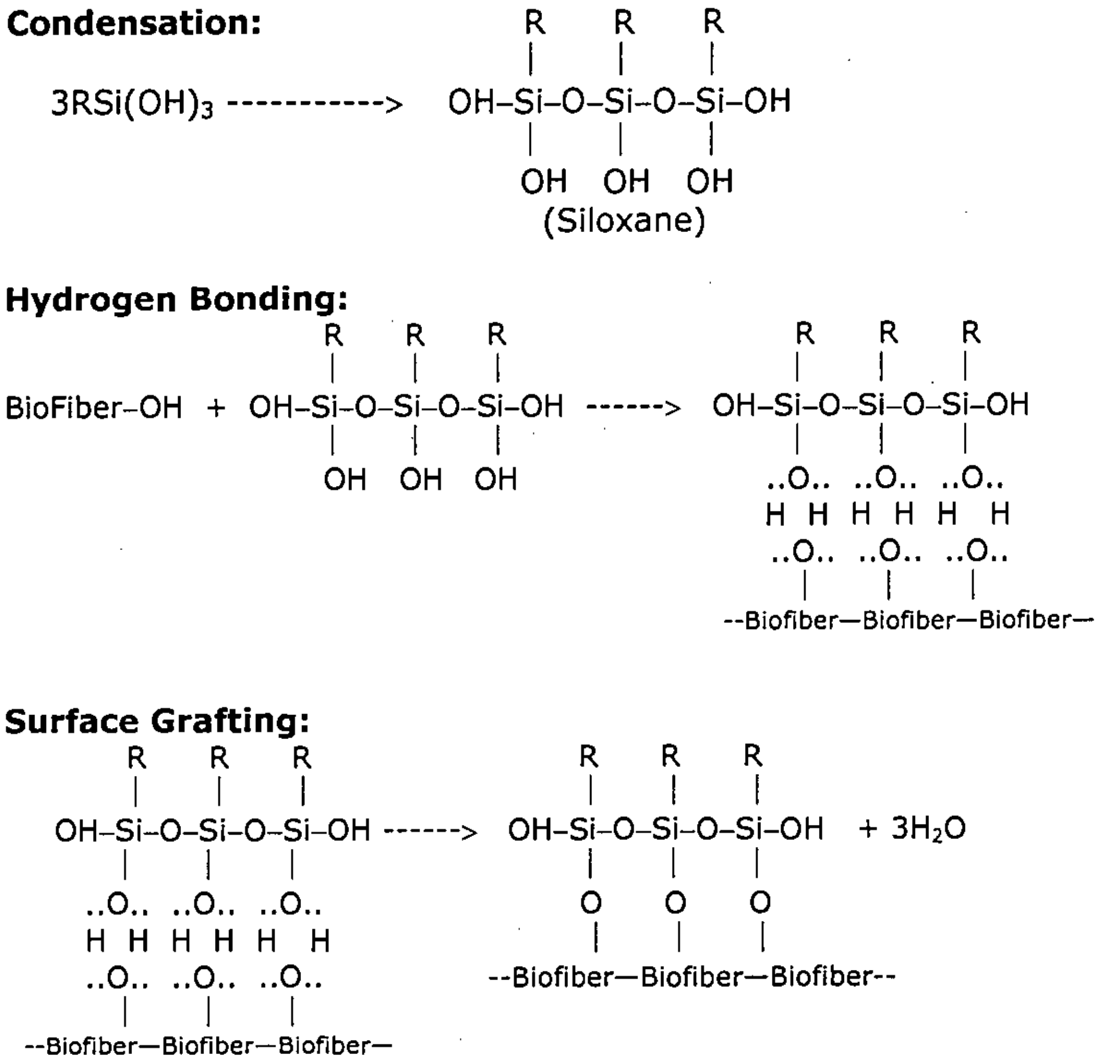
$$\text{Fiber–OH}+CH_3\text{–CO–O–CO–}CH_3\text{------->Fiber–O–CO–}CH_3 + CH_3\text{–CO–OH}$$

Scheme2.1: Reaction of acetic anhydride with natural fiber[61]

Modification of fiber surface by reacting with silane were investigated and reported by some researchers.[40,62] Silane treatment of fibers led to increase mechanical properties of the composites. The reaction steps in the silane grafting of biofibers are shown below:

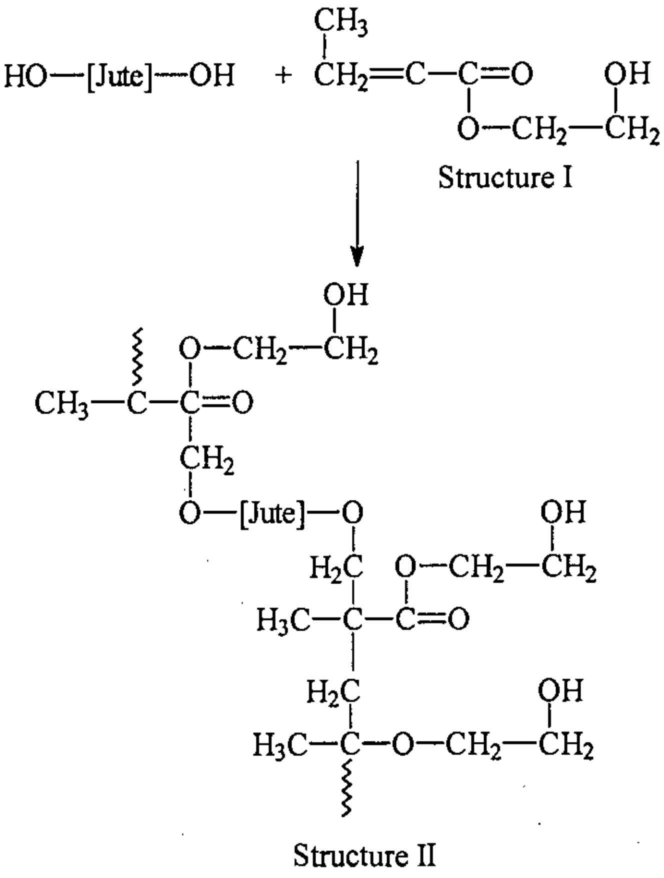
Hydrolysis:

$$RSi(OR)_3 + 3H_2O \text{ ----------> } \underset{\text{(Silanol)}}{RSi(OH)_3} + 3\,ROH$$



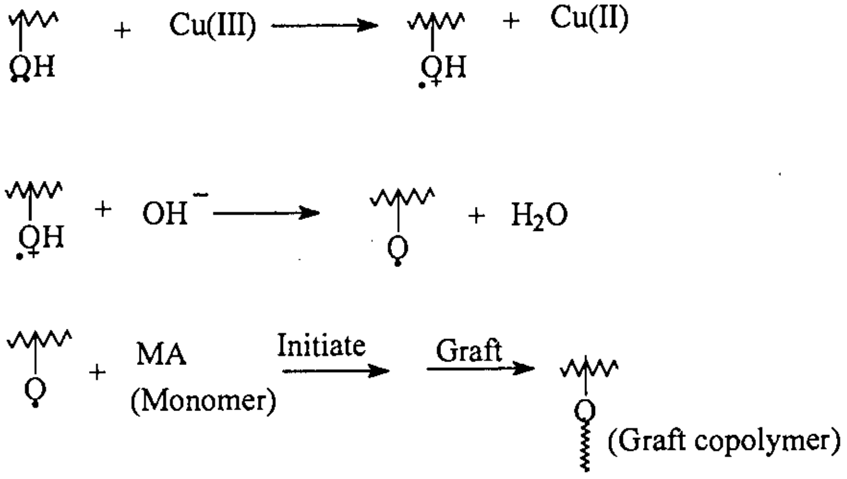
Scheme 2.2: Reaction steps in the silane grafting of biofibers[40]

Modification of jute fiber with HEMA and the effect of HEMA on the mechanical and thermal properties of jute-polycarbonate composite were investigated and repoted.[63] It has been reported that HEMA deposited on hessian cloth might have quite extensively reacted with the cellulosic backbone of cellulose through graft-copolymerization reaction (scheme 2.3).



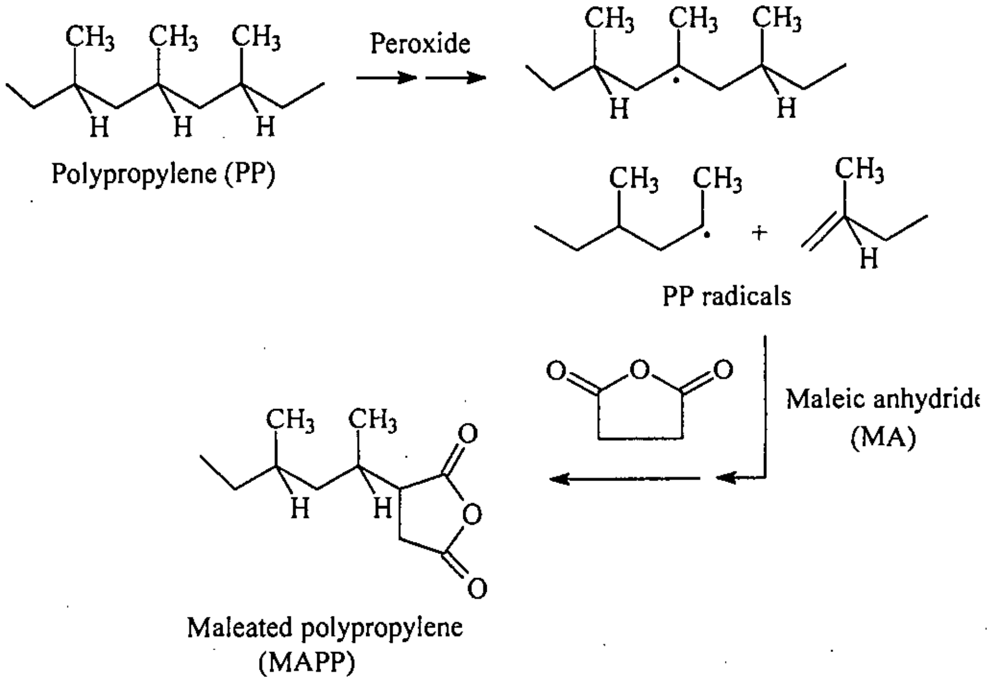
Scheme 2.3: Proposed graft-copolymerization reaction of jute fiber with HEMA [63]

Grafting of polymethyl acrylate (PA) onto pure cellulose by potassium diperiodatocuprate (III) initiating system was carried out by L. Yinghai et al[64] and reported that the thermal stability of grafted product has been improved greatly. The initiation mechanism of grafting reaction is shown below:



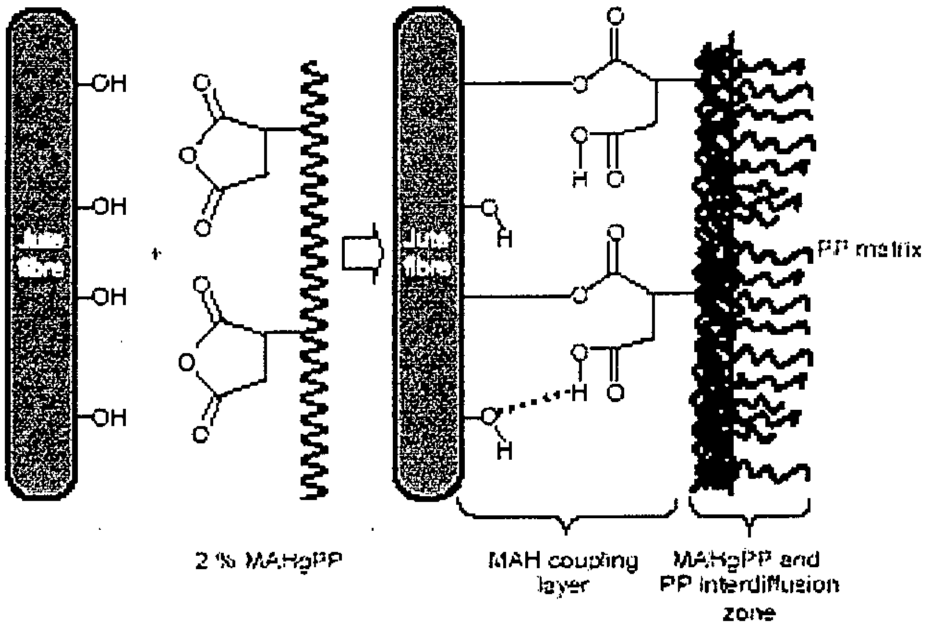
Scheme 2.4: Proposed graft-copolymerization of MA onto cellulose[64]

A considerable amount of research has been done on the use of MA as a coupling agent to improve the compatibility and adhesion between the fibers and matrix using a variety of procedures. A proposed method of grafting MA on PP chain is shown in Scheme 2.5.[40]



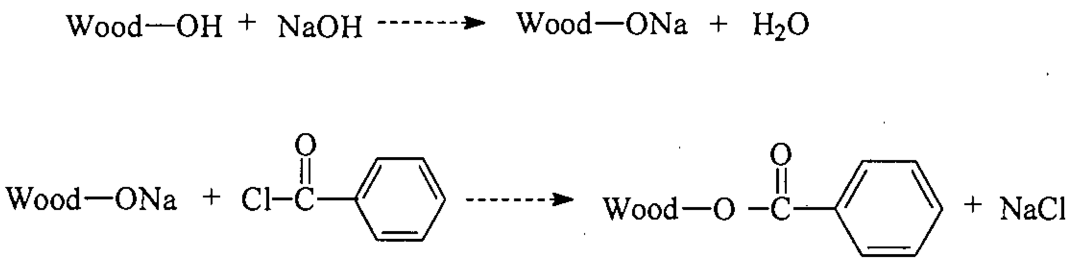
Scheme 2.5: Proposed reaction mechanism of MA on PP chain[40]

It is now evident from the literature that the addition of 0.5-2 wt-% maleic anhydride grafted polypropylene (MAHgPP) to PP matrices significantly improved the adhesion strength of jute fibers and in turn the mechanical properties of composites.[65] A hypothetical structure of coupling of MAHgPP with jute fiber is given below:



Scheme 2.6: Hypothetical structure of MAHgPP coupling with jute fiber at the interface[65]

L. K. Poh et al[66] carried out the esterification of palm oil empty fruit bunch (EFB) fibers using benzoyl chloride and reported that benzoylation treatment has improved the thermal stability and changed the suprastructure of the EFB fibers which may improve the interfacial bonding of the lignocellulosic material and thermoplastic materials. The chamical reactions involved are shown below:



Scheme 2.6: Chemical reactions between EFB fibers and benzoyl chloride[66]

Many other researches on chemical modifications have been reported to modify wood, kenaf, sisal, flax, banana, rice husk powder etc. lignocellulosic fibers using various additives (i.e. alkali, silane, potassium permanganate, sodium chlorite, and acrylic acid treatments) by various procedures.[67-80] Some of these works are briefly presented here.

2.3.5 Some recent work in this field:

Quite a good no. of published article in this field have been reviewed. These have been reported in the previous part of this section. Some other recent works have been presented below in brief:

S. Das et al[55] reported on a new process development to improve the dimensional stability of jute composite. They said that steam pretreatment process can minimize the irreversible swelling of jute fibers without any chemical modification of jute fibers.

C. M. Clemons et al[81] investigated the microstructure of injection-molded polypropylene reinforced with cellulose fiber and reported that there was little fiber orientation at low fiber contents and a layered structure arosed at high fiber contents. They also reported that dynamic fracture toughness (Charpy impact test) increased with cellulose content and with orientation of fibers perpendicular to the crack direction.

K. Takemura[82] reported on the effect of water absorption on static and creep properties for jute fiber reinforced composite (JFRC). He mentioned that the static strength and stiffness for JFRC decreases with increased water absorption. He also mentioned that the effect of water absorption is greater at the secondary creep stage than that of the other creep stages.

B. V. Kokta[83] reported the effect of compounding, molding and fiber length on the properties of wood fiber reinforced thermoplastic composites. He reported that when critical fiber length was achieved the increase of fiber length did not improve composite properties. He also reported that there was practically no difference in resulting properties due to different way of compounding.

X. Li et al[94] reported on biodegradable composites prepared by poly(propylene carbonate) (PPC) reinforced with short *Hildegardia populifolia* natural fibers. They observed the effect of alkali treated fibers comparing with untreated fibers on the composites and reported that better bonding and approximately similar mechanical properties were obtained for both alkali-treated and untreated *Hildegardia populifolia* fiber reinforced PPC composites. They also reported that tensile strength and tensile modulus of the composites increased dramatically with increasing fiber content but elongation at break decreased sharply with increasing fiber content.

M. J. Saad et al[101] reported on the empty fruit bunch (EFB) fiber reinforced polypropylene (PP) composites. They modified the EFB fibers with maleic anhydride (MAH) before preparing the composites. They observed that MAH-treated fiber reinforced PP composites produce higher tensile and better dimensional stability properties.

G. S. Tay et al[102] investigated on the effect of chemical (epichlorohydrin) loading on the epichlorohydrin modified oil palm empty fruit bunch (EFB) fiber reinforced polyurethane composites (PU). The reported that composites made with EFB modified with EPH to 8% weight percent gain (WPG) produced higher tensile properties than the others. They expressed that higher degree of modification could cause disruption of crystalline region to the EFB.

K. Oksman and C. Clemons[104] studied and reported on the mechanical properties and morphology of polypropylene(PP)-wood flour(WF) composites with different impact modifiers and maleated polypropylene (MAPP) as a compatibilizer. They used three types of elastomers as impact modifiers and observed improved impact strength for PP-WF composites. Addition of maleated elastomers gave the greatest improvements in impact strength of the composites. MAPP didn't affect the impact properties of the composites but showed better tensile strength.

H. Ismail et al[105] reported the effect of PPMaH and LICA on properties of paper sludge filled PP/EPDM composites. They observed the improved compatibility between sludge paper and PP/EPDM matrix by the addition of PPMaH as a compatibilizer and LICA as a coupling agent. Consequently, the tensile strength, modulus and water absorption resistance of sludge paper filled PP/EPDM composites with PPMaH and LICA showed better results than untreated composites.

CHAPTER 3: EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene and Jute

A commercial grade polypropylene (PP) was used in this study. It was manufactured by The Polyolefin Company, Pte., Ltd., Singapore; and its commercial name is Cosmoplene. Melting point of this PP was measured and found to be 160^{0}C. Melting point and FT-IR spectroscopic observations indicated that the used PP was an isotactic polypropylene and commercial grade. In the literature it is mentioned that the melting point of commercial grade PP lies in the range 160-170^{0}C but Pure PP melts at 176 ^{0}C.[13]

The jute fibers were collected from Bangladesh Jute research Institute (BJRI), Dhaka, Bangladesh. The supplied jute fibers were mixture grade of Tossa variety (*Corchorus olitorius*). The middle parts of the jute fibers were taken in this study and were chopped into lengths of approximately 3 mm.

3.1.2 Chemicals

The oxidizing agent sodium periodate (reagent grade) was used. The coupling agents used in this study were reagent grade urea, commercial grade urotropine and maleic acid. The list of chemicals used in this study and their suppliers name are given below:

Chemicals/ Reagents used	Name of Suppliers
Sodium Periodate ($NaIO_4$)	Merck, Germany
Urea [$CO(NH_2)_2$]	Merck, Germany
Urotropine [$(CH_2)_6N_4$]	Distillation Products Ind., USA
Maleic Acid [HOOC-CH=CH-COOH]	Techno Pharmachem

Formic acid (HCOOH)	Merck, Germany
Sulfuric Acid (H_2SO_4)	Merck, India
Sodium Hydroxide (NaOH)	Merck, India

3.2 Pre-treatment of jute fibers by oxidation reaction

The raw jute fibers were first cleaned manually and chopped into approximately 3mm length. The fibers were then washed with distilled water and dried in open air. The air-dried fibers were then oven dried at 105^{0}C for 5 hours. Sodium periodate solution (0.06 M) was prepared in distilled water. Dried jute fibers were immersed in 0.06M sodium periodate solution. The fiber to liquor ratio was 1:16 (w/v). The pH of the aqueous solutions was adjusted to 3 by adding sulfuric acid. The oxidation reaction was carried out for 5 hours at 70^{0}C. The reaction mixture was stirred by glass rod occasionally. After completion of the reaction, the mixture was cooled and filtered to isolate the oxidized jute fibers. The oxidized jute fibers were thoroughly washed in tap water and finally washed with distilled water. The pH of the washed fibers was found neutral. The washed oxidized fibers were first air-dried and then dried in oven at 105^{0}C for 6 hours. This oxidized jute fibers were used for composite fabrication followed by post treatment using urea and urotropine.

3.3 Composite fabrication

Jute-polypropylene composites were prepared using raw jute and chemically oxidized jute following the procedure described below:

The raw and oxidized jute fibers were dried in an oven at 105^{0}C for 6 hours. PP polymers were dried in oven for 3 hours at 105^{0}C. Jute fibers were mixed thoroughly with polypropylene to prepare composites. PP matrix and jute fibers were taken in different weight fractions (Table 3.1).

Table 3.1: Relative amounts of reinforcing materials and polymer matrix by weight fraction (%)

Reinforcing material (%)	Polymer Matrix (%)	Composites
None	PP: 100	100 wt % PP
Jute: 20	PP: 80	20:80 (wt %) Jute-PP
Jute: 25	PP: 75	25:75 (wt %) Jute-PP
Jute: 30	PP: 70	30:60 (wt %) Jute-PP
Jute: 35	PP: 65	35:70 (wt %) Jute-PP
Oxidized jute: 20	PP: 80	20:80 (wt %) Oxidized jute-PP
Oxidized jute: 25	PP: 75	25:75 (wt %) Oxidized jute-PP
Oxidized jute: 30	PP: 70	30:65 (wt %) Oxidized jute -PP
Oxidized jute: 35	PP: 65	35:60 (wt %) Oxidized jute -PP

Composites were prepared by passing mixtures through a single screw extruder machine (Fig. 3.1). The processing temperature of extrusion was controlled at 170^0C and pressure was uniform. The jute-PP mixtures were continuously fed into the extruder. The composites were delivered through a die of rod shape at a uniform rate. Then the composites were cutted into small pieces of 15-20 cm length by the Scissor. The small pieces were then crashed into small granules using a grinding mill (Model FFC-23, Speed 5800 rpm, Machinery Co. Ltd., China). The granulated products were dried in an oven at 105^0C for 6 hours and then used in injection moulding.

The extruder used in manufacturing composites was designed and made in our laboratory taking the help of local experts. The photograph of extruder machine is shown below:

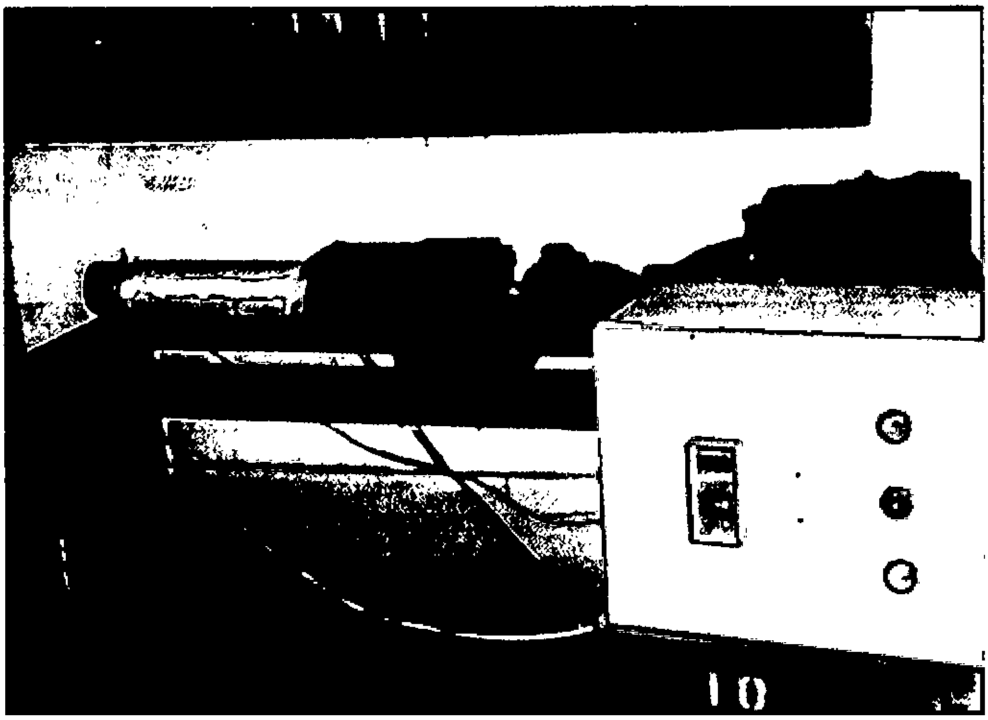
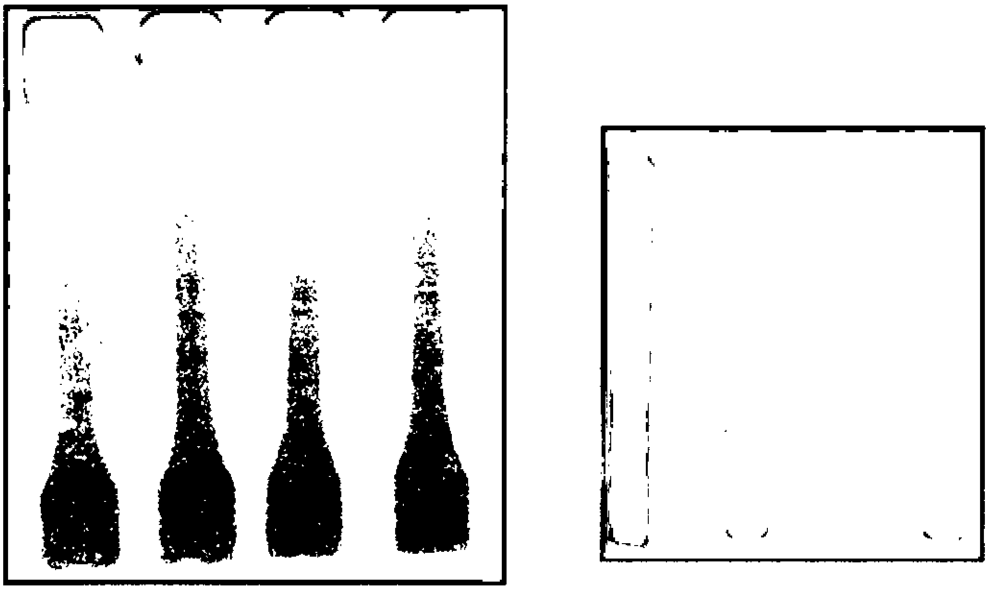


Figure 3.1: Extruder machine

3.4 Preparation of composites by injection moulding

The dried granulated products were moulded as per ASTM standard specimens (tensile and flexural test bars) by an injection-moulding machine (Fig.3.2) at a molding temperature of 175^{0}C. The pressure, temperature and heating time of the samples were controlled at the same rate to prepare all composites. The used injection-moulding machine is vertical and operated manually. The sample was heated to melt in the heating chamber, then pumped into closed mould die applied by the use of a plunger or ram into the heated cylinder. Load (approx. 900 N) was applied for few minutes and then the mould was opened to remove the finished sample. By this way, all the tensile and flexural test specimens were prepared by injection moulding technique. Single moulds were used to prepare tensile and flexural test bars. Injection moulded tensile and flexural test specimens are shown in Figure 3.2. The photograph of injection moulding machine is shown in Figure 3.3 below:



(a) (b)

Figure 3.2:Tensile test specimens (a) and flexural test specimens (b)

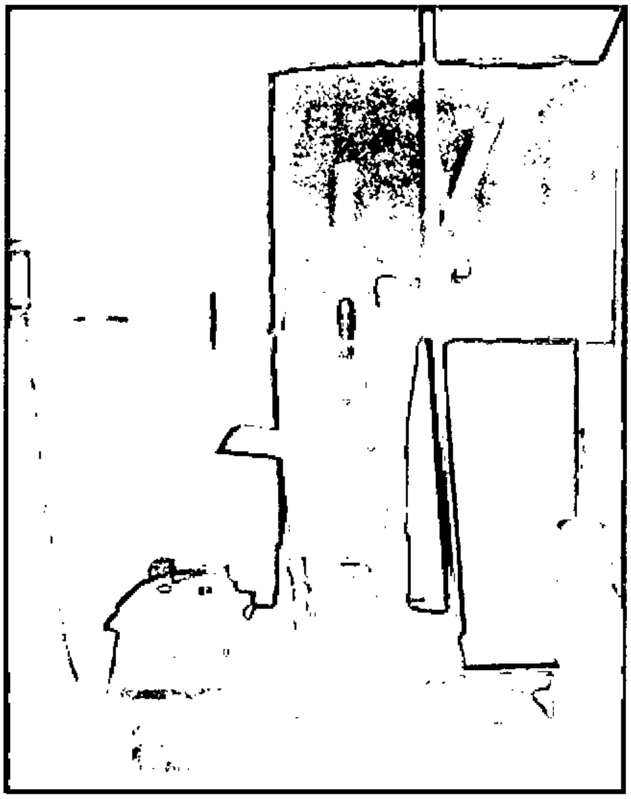


Figure 3.3: Injection-moulding machine

3.5 Post-treatment (chemical) of injection moulded composites

Injection moulded tensile and flexural test specimens were dried in an oven at 105^0 C for 1 hour and recorded the initial weight. The samples were then treated with urea, urotropine and maleic acid (coupling agents) separately. The treatments were performed under different conditions of time, temperature, pH and concentration of coupling agents as described in section 3.5.1.1, 3.5.2.1, and 3.5.3.1 respectively. The reaction progress was monitored by weight gain observation of test specimens. The reaction conditions were carefully observed to find out the suitable conditions for obtaining composites of highest mechanical properties. 25 wt-% fiber reinforced composites were used to find out the reaction conditions to get maximum tensile strength. The reaction parameters such as time, temperature and pH were found out on weight percent gain (WPG) measurement of the composites and the concentration of the coupling agents were found out on increasing the tensile strength property of the composites. Concentration of coupling agent solution was varied from 1 to 25% and it was found that 10%-15% concentrated solution gives the best result.

3.5.1 Urea treatment

The reaction parameters such as, time, temperature and pH for urea treatment were selected from the various reactions results presented in the Table 3.2 and Table 3.3 and these are found to be 2.5 hours, 90^0 C and 3 respectively.

Table 3.2: WPG data of urea treatment by variation of time, temperature and pH of the reactions using 25 wt-% oxidized jute-PP composites.

Reaction No.	Variation of time, temperature & pH of reaction condition at constant urea solution (15%)	Weight Percent Gain (WPG)
1	24 hours at room temperature, pH=3	nil
2	2.5 hours at 60 ^{0}C, pH=3	0.09
3	4 hours at 60 ^{0}C, pH=3	0.11
4	2.5 hours at 80 ^{0}C, pH=3	0.18
5	4 hours at 80 ^{0}C, pH=3	0.20
6	2.5 hours at 90 ^{0}C, pH=6	nil
7	2.5 hours at 90 ^{0}C, pH=10	0.05
8	2.5 hours at 90 ^{0}C, pH=3	0.22
9	2.5 hours at 90 ^{0}C, pH=1.5	0.27
10	4 hours at 90 ^{0}C, pH=3	0.32
11	2.5 hours at 100 ^{0}C, pH=3	0.30

Table 3.3: WPG data of urea treatment by variation of concentrations of urea in impregnating solution using 25 wt-% oxidized jute-PP composites.

Reaction No.	Variation of urea concentration in impregnating solution at constant time, temperature & pH (i.e., 2.5 hours, 90^{0}C and 3 respectively)	Weight Percent Gain (WPG)	Tensile strength, MPa
1	1% urea solution	0.08	26.59
2	5% urea solution	0.14	27.68
3	10% urea solution	0.19	29.73
4	15% urea solution	0.22	29.73
5	20% urea solution	0.24	29.01
6	25% urea solution	0.25	29.01

3.5.1.1 Procedure of post treatment with urea

Urea was dissolved in distilled water in a wide flat bottom conical flask and the pH of the solution was adjusted at 3 by adding formic acid. The injection moulded tensile and flexural test specimens were taken into the 15% urea solution. The samples were floated on the surface of the solution except 35% fiber loading composites. 35% fiber loaded composites were submerged into the solution. The reaction was carried out at 90^{0}C using a magnetic stirrer hotplate by direct heating for 2.5 hours. The samples were stirred occasionally and changed their position into reverse side after every 15-minutes interval period to get reaction properly on the both surfaces of the samples. After the completion of the reaction, the samples were taken out and thoroughly washed with water by using a soft brush. The water from the surface of composites was removed with a soft cloth. The samples were then oven dried to a constant weight and the final weights were taken. The weight gain was calculated by subtracting initial weight from the final weight. The results are reported as weight percent gain (WPG) and presented in the results and discussion chapter.

3.5.2 Urotropine treatment

The reaction parameters such as, time, temperature and pH for urotropine treatment were selected from the various reactions results presented in the Table 3.4 and Table 3.5 and these are found to be 2.5 hours, 80^0 C and 5 respectively.

Table 3.4: WPG data of urotropine treatment by variation of time, temperature and pH of the reactions using 25 wt-% oxidized jute-PP composites.

Reaction No.	Variation of time, temperature & pH of reaction condition at constant urotropine solution (15%)	Weight Percent Gain (WPG)
1	24 hours at room temperature, pH=5	0.07
2	2.5 hours at 60 ^{0}C, pH=5	0.09
3	4 hours at 60 ^{0}C, pH=5	0.15
4	2.5 hours at 80 ^{0}C, pH=5	0.24
5	2.5 hours at 80 ^{0}C, pH=10	0.11
6	2.5 hours at 90 ^{0}C, pH=4	0.20
7	4 hours at 80 ^{0}C, pH=3	0.26
8	2.5 hours at 80 ^{0}C, pH=8	0.05
9	2.5 hours at 95 ^{0}C, pH=5	0.27
10	4 hours at 95 ^{0}C, pH=5	0.30

Table 3.5: WPG data of urotropine treatment by variation of concentrations of urotropine in impregnating solution using 25 wt-% oxidized jute-PP composites.

Reaction No.	Variation of concentration of urotropine in impregnating solution at constant time, temperature & pH (i.e., 2.5 hours, 80 ^{0}C and 5 respectively)	Weight Percent Gain (WPG)	Tensile strength, MPa
1	1% urotropine solution	0.07	27.32
2	5% urotropine solution	0.15	27.80
3	10% urotropine solution	0.19	29.01
4	15% urotropine solution	0.24	29.37
5	20% urotropine solution	0.26	28.77
6	25% urotropine solution	0.28	28.52

3.5.2.1 Procedure of post treatment with urotropine

Urotropine was dissolved in distilled water in a wide flat bottom conical flask and the pH of the solution was adjusted at 5 by adding formic acid. The injection moulded tensile and flexural test specimens were taken into the 15% urotropine solution. The samples were floated on the surface of the solution except 35% fiber loading composites. 35% fiber loaded composites were submerged into the solution. The reaction was carried out at 80^0C using a magnetic stirrer hotplate by direct heating for 2.5 hours. The samples were stirred occasionally and changed their floating position into reverse side after every 15-minutes interval period to get reaction properly on the both surfaces of the samples. After the completion of the reaction the samples were thoroughly washed with water by using a soft brush. The water from the surface of composite samples was removed with a soft cloth. The samples were then oven dried to a constant weight and the final weights were taken. The weight gain was calculated by subtracting initial weight from the final weight. The results are reported as weight percent gain (WPG) and presented in the results and discussion section.

3.5.3 Maleic acid treatment

The reaction parameters such as, time and temperature for maleic acid treatment were selected from the various reactions results presented in the Table 3.6 and Table 3.7 and these are found to be 6 hours and 65^0 C. Concentrated sulfuric acid (2%) was added into the reaction mixture to increase the reaction progress.

Table 3.6: WPG data of maleic acid treatment by variation of time and temperature of the reactions using 25 wt-% raw jute-PP composites.

Reaction No.	Variation of time and temperature at constant maleic acid solution (15%)	Percentage of sulfuric acid	Weight Percent Gain (WPG)
1	24 hours at room temperature	2	0.08
2	3 hours at 65 ^{0}C	nil	nil
3	3 hours at 65 ^{0}C	2	0.17
4	6 hours at 65 ^{0}C	2	0.30
5	3 hours at 75 ^{0}C	2	0.25
6	6 hours at 75 ^{0}C	2	0.39

Table 3.7: WPG data of maleic acid treatment by variation of concentrations of maleic acid in impregnating solution using 25 wt-% raw jute-PPcomposites.

Reaction No.	Variation of temperature and concentration of maleic acid in impregnating solution adding 2% sulfuric acid	Weight Percent Gain (WPG)	Tensile strength, MPa
1	1% maleic acid solution at 65 ^{0}C for 6 hours	0.08	25.50
2	5% maleic acid solution at 65 ^{0}C for 6 hours	0.11	25.99
3	10% maleic acid solution at 65 ^{0}C for 6 hours	0.21	26.11
4	15% maleic acid solution at 65 ^{0}C for 6 hours	0.30	26.35
5	15% maleic acid solution at 75 ^{0}C for 6 hours	0.41	25.04
6	15% maleic acid solution at 75 ^{0}C for 3 hours	0.26	25.99
7	20% maleic acid solution at 65 ^{0}C for 6 hours	0.39	25.24

3.5.3.1 Procedure of post treatment with maleic acid

Maleic acid was dissolved in distilled water in a wide flat bottom conical flask. Concentrated sulfuric acid (2%) was added into the solution. The injection moulded tensile and flexural test specimens were taken into the 15% maleic acid solution. The samples were floated on the surface of the solution except 35% fiber loading composites. 35% fiber loaded composites were submerged into the solution. The reaction was carried out at 65^{0}C using a magnetic stirrer hotplate by direct heating for 6 hours. The samples were stirred occasionally and changed their floating position into reverse side after every 15-minutes interval period to get reaction properly on the both surfaces of the samples. After the completion of the reaction the samples were thoroughly washed with water by using a soft brush. The water from the surface was removed with a soft cloth. The samples were then oven dried to a constant weight and the final weights were taken. The weight gain was calculated by subtracting initial weight from the final weight. The results are reported as weight percent gain (WPG) and presented in the results and discussion chapter.

3.6 Characterization of composites

The composite materials were characterized by FT-IR Spectroscopy and Scanning Electron Microscopy as stated below:

3.6.1 FT-IR Spectroscopy

The infrared spectra of the PP polymer, raw jute fiber, oxidized jute fiber and 30 wt-% fiber reinforced composites were recorded on a Shimadzu FTIR-8101 spectrophotometer. The samples pellets for FT-IR spectroscopy were prepared as follows:

Approximately 0.5 mg of powdered samples was mixed thoroughly with approximately 100 mg of dried powdered potassium bromide in a small agate morter pestle. The mixture was taken in a die of specific dimensions. Pellets were made by applying vacuum pressure. IR spectra with all information about absorbance were obtained in the printed form. IR spectra obtained this study are presented in the result and discussion section.

3.6.2 Scanning electron microscopy (SEM)

The fractured surfaces of the tensile test specimens were used to examine by a scanning electron microscopy (JSM-5510, JEOL Co. Ltd., Japan). The SEM analysis was carried out the Institute for Molecular Science, 444-8585 Myodaiji, Japan. The photographs are presented in the result and discussion section.

3.7 Mechanical properties of the composites

In order to investigate the mechanical properties of the prepared composites the following tests were carried out; (a) tensile (b) three point flexural (c)charpy impact and (d) hardness. For these tests the appropriate ASTM methods were followed. Specification and picture of the used machines, set-up of the tests, operating conditions and dimension of the test specimens are described below.

3.7.1 Tensile test

The static tensile test of the composites were carried out in an universal tensile testing machine, model: MSC-5/ 500, capacity: 5KN, Ogawa Seiki C. Ltd., Japan (Fig. 3.5) at a cross head speed of 10mm/min. Tensile tests were conducted following ASTM D 638-01[86] and each test was performed until tensile failure occurred except 100% PP composite. Dumbbell-shaped injection moulded composites were used as test specimen without having any kind of machining. Dimension of tensile test specimen is shown in Fig. 3.4

and its length, width, thickness were 148 mm, 10mm and 4mm respectively. Eight to ten specimens of each composition were tested and the average values were reported by calculating of maximum five values. The load vs elongation curves were obtained by the electronic chart recorder of the instrument. The maximum (peak) load values were also recorded by the instrument, which can be recalled after the completion of the test. The highest load in the tensile test gives the tensile, or ultimate strength. The tensile strength (σ_{UT}) is calculated from the following equation[86]:

Tensile strength, $\sigma_{UT} = W / A_T$

Where W is breaking load and A_T is the cross sectional area.

Tensile stress and strain values were calculated from the load vs elongation curves. Then the tensile stress vs strain curves were drawn and tensile modulus were determined from the initial slope of the stress-strain curve.

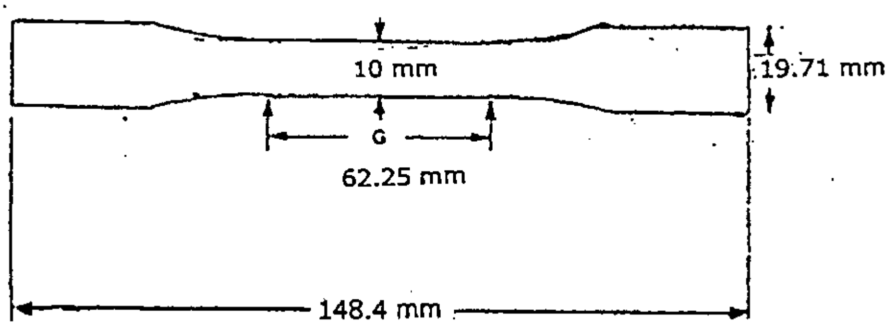


Figure 3.4: Dimension of tensile test specimen

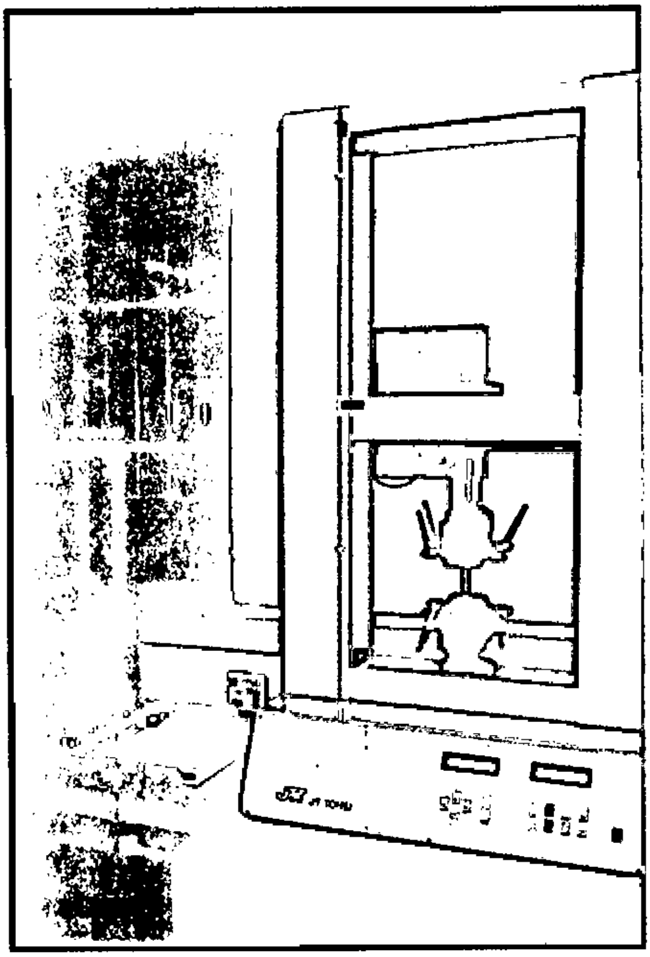


Figure 3.5: Tensile test machine

3.7.2 Three point flexural test

The static flexural tests of the composites were carried out by same machine that was used for tensile test only by changing the attachment. Set-up of the three point flexural test and dimension of the specimen are shown in Fig.3.6. Dimension of flexural test specimen is 79 mm length, 10 mm width and 4.1mm thickness. Flexural tests were conducted following ASTM D 790-00[87] at a cross head speed of 10 mm/min. Injection moulded test specimens (Fig. 3.6) were used directly to perform the flexural testing operation and the operating conditions were similar to that of the tensile test. Five specimens of each composition were tested and the average values were reported. The load displacement curves were obtained from the electronic chart recorder and the maximum (peak) load values were also recorded by the instrument, which can be recalled after the completion of the test. The flexural strength (σ_{fM}) and modulus of elasticity (E_B) were calculated by the following equations[87]:

Flexural strength, $\sigma_{fM} = 3PL / 2bd^2$

where,

P= Maximum load on the load-deflection curve, N

L= Support span, 63.7 mm

b= width of beam tested, 10 mm and

d = Thickness of beam tested, 4.1 mm

Modulus of elasticity, $E_B = L^3 m / 4bd^3$

where,

L= Support span, 63.7 mm

b= width of beam tested, 10 mm and

d = Thickness of beam tested, 4.1 mm

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm of deflection.

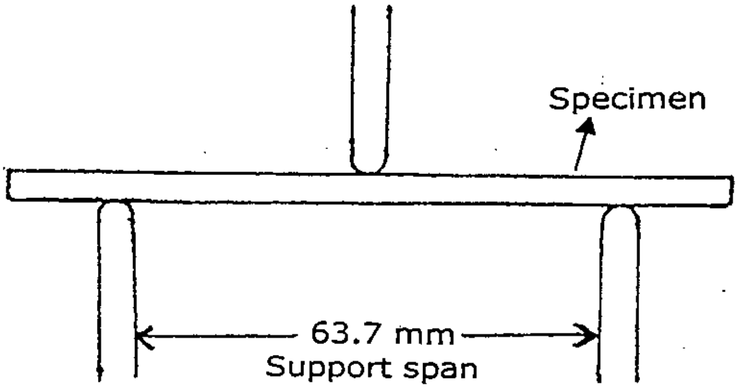


Figure 3.6: Set-up of three point flexural test and dimension of specimen.

3.7.3 Charpy Impact test

The dynamic charpy impact tests of the composites were done according to ASTM D 6110-97[88]. Figure 3.8 shows the photograph of Universal Impact Testing Machine, Type: TIT-30, Tokyo Testing Machine MFG. Co. Ltd., Japan. This machine was used to perform charpy impact tests of all the samples. Weight of the hammer of this machine was 3.72 kg and span between the supports was 40 mm. The charpy impact test specimens were injection-moulded without having any kind of machining on them. The width, thickness and length of the specimen are 10mm, 4.1 mm and 79 mm respectively. Test method of ASTM D 6110-97 was followed to conduct this experiment. Notched specimens were used. The dimension of the test specimen and the design of notch cut on it is shown below (Fig. 3.7).

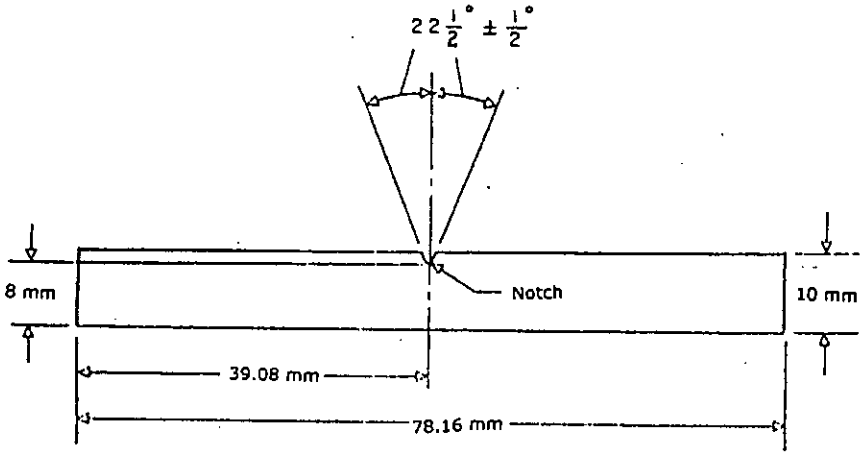


Figure 3.7: Dimensions of simple beam, charpy type, impact test specimen

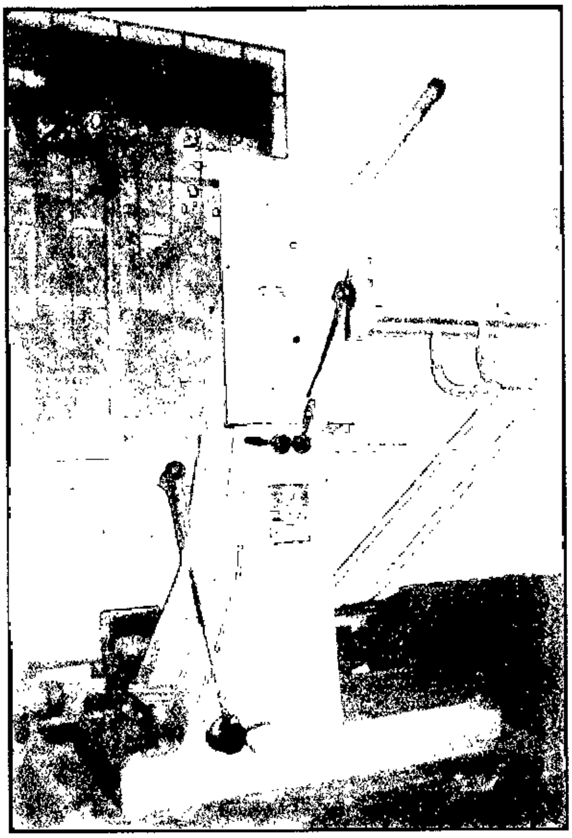


Figure 3.8: Pendulum type impact strength tester

Notching of the test specimens was done on a milling machine and the contour and depth of notch cut are shown in figure 3.8. In this experiment, as the width and thickness are 10 mm and 4.1 mm so notch cut were made on the 4.1 mm shorter side. So the width of this test specimen will be 4.1 mm and depth will be 10 mm. ASTM D 6110-97 test methods specified the notch depth should be 2.54 mm on the 12.7 mm depth test specimen. So, we made 2 mm depth notch cut on the 10 mm depth test specimen and the radius of curvature at the apex of notch cut was 2.5 mm. The impact tests were performed after 30 hours of notching. To conduct this experiment, according to test method, the specimen was supported on a horizontal simple beam and was broken by a single swing of the pendulum with the impact line midway between the supports and directly opposite to the notch. Free rotational angle of the hammer was 140^0 and the radius of the pendulum movement was 0.495 m. The results were calculated in terms of energy absorbed per unit of specimen width from the following equation:

$$\text{Impact Strength} = WH_1 - WH_2 / t$$
$$= W (H_1 - H_2) / t$$

Where,

t = Width of specimen or width of notch

W= Weight of pendulum

$(H_1 - H_2)$ = Height difference before and after striking

3.7.4 Hardness test

Rockwell hardness of composites were carried out following ASTM D 785-98.[89] A Rockwell hardness number is a number derived from the net increase in depth impression as the load on an indenter increased from a fixed minor load to a major load and then returned to a minor load. [89] Specimen samples used in flexural test were used to conduct this experiment. Procedure A was followed using L scale with a 6.35 mm diameter indenter and 490 N major load. Rockwell hardness testing instrument is shown in Figure 3.9. Five measurements were taken for each type specimen and the results were averaged. The results are presented in the results and discussion chapter.

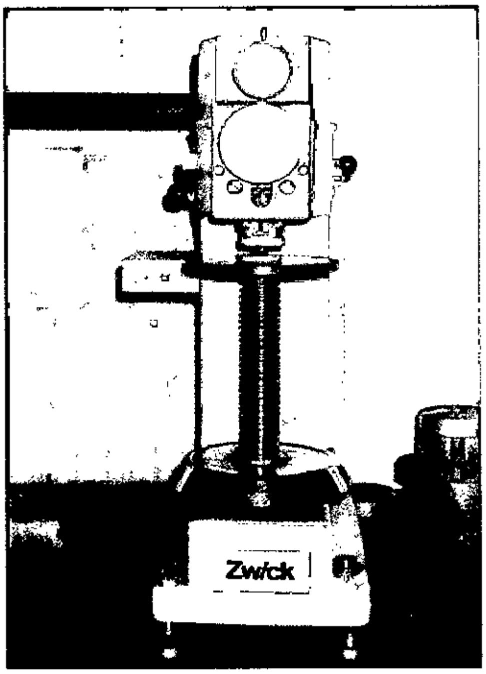


Figure 3.9: Rockwell hardness testing instrument

3.8 Water absorption test of composites

In order to measure the water absorption of the composites flexural tested rectangular specimens were cut from each sample having dimensions of 39 mm x 10mmx 4.1mm . The samples were dried in an oven at 105^{0}C for 2 h, cooled in a desiccator using silica gel and immediately weighed to the variation of 0.0001 g. Denver Instron balance was used for this test. The dried and weighed samples were immersed in distilled water for about 24 h at room temperature and in boiling water for 2 hours as described in ASTM procedure D570-99 (ASTM 2002).[90] Excess water on the surface of the samples was removed by using a soft cloth. Then the weights of the samples were taken. Three replicate specimens were tested and the results were presented as average of the tested specimens. The percentage increase in weight during immersion was calculated as follows[90]:

$$\text{Increase in weight, \%} = \frac{(\text{wet wt - conditioned wt})}{(\text{conditioned wt})} \times 100$$

CHAPTER 4: RESULTS AND DISCUSSION

In this work, physico-mechanical properties of jute reinforced polypropylene composites have been studied. Different types composites have been prepared, vize raw jute-PP composites, oxidized jute-PP composites, urea treated oxidized jute-PP composites, urotropine treated oxidized jute-PP composites and maleic acid treated raw jute-PP composites. Before preparing the composites jute fibers have been chemically modified (oxidized) with an aim to have better coupling reactions with urea and urotropine. As the oxidizing agent sodium periodate is used. The structural changes of jute fiber due to oxidation are confirmed by IR-spectra (shown in Figure 4.3). Raw and oxidized jute fibers were used separately to prepare jute fiber polypropylene composites by using a single screw extruder. To study the mechanical properties, sample specimens of specific size and shape have been prepared by using an injection moulding machine. Tensile strength, telsile modulus, elongation at break, flexural strength, flexural modulus and charpy impact strength of the prepared composites were measured by using Universal testing machine. The prepared composites were treated with different coupling agents. The treated composite samples were studied following the same procedures mentioned above. The results are presented in the following sections.

4.1 FT-IR spectroscopic analysis of raw jute fiber and polypropylene (PP) polymer

FT-IR spectra of raw jute, chemically oxidized jute were taken in the Infra-red Spectrophotometer (Shimadzu FTIR-8101). The spectra and their brief description are presented below:

4.1.1 FT-IR spectroscopic analysis of raw jute fiber

The FT-IR spectrum of raw jute fiber is shown in Fig.4.1. The peak assignments of the absorption bands corresponding to various groups are summarized in Table 4.1. which are quite similar to the literature value.[91-94]

Table 4.1: FT-IR spectral data of untreated raw jute fiber

Position/ cm^-	Assignment
~ 3600-3200	v(OH) broad, strong band from the cellulose, hemicellulose and lignin of jute
~ 3000-2900	v(C-H) in aromatic ring and alkanes
~ 1750-1710	v(C=O) most probably from the lignin and hemicellulose
~1650-1630	possibly aromatic ring
~ 1635	adsorbed water
~ 1608	v(C=C) aromatic in-plane
~ 1508.2	v(C=C) aromatic skeletal ring vibration due to lignin
~ 1455	δ(C-H); δ(C-OH) 1° & 2° alcohol
~ 1419.5	δ(C-H)
~ 1365	δ(C-H)
~ 1315	δ(C-H)
~ 1280	δ(CH_2) twisting
~ 1255.6	δ(C-OH) out-of-plane
~ 1200	δ(C-OH); δ (C-CH)
~ 1155	v(C-C) ring breathing, asymmetric
~ 1105	v(C-O-C) glycosidic
~ 1050	v(C-OH) 2° alcohol
~ 1033.8	v(C-OH) 1° alcohol
~ 1005	p(-CH-)
~ 985	ρ(-CH-)
~ 895	v(C-O-C) in plane, symmetric

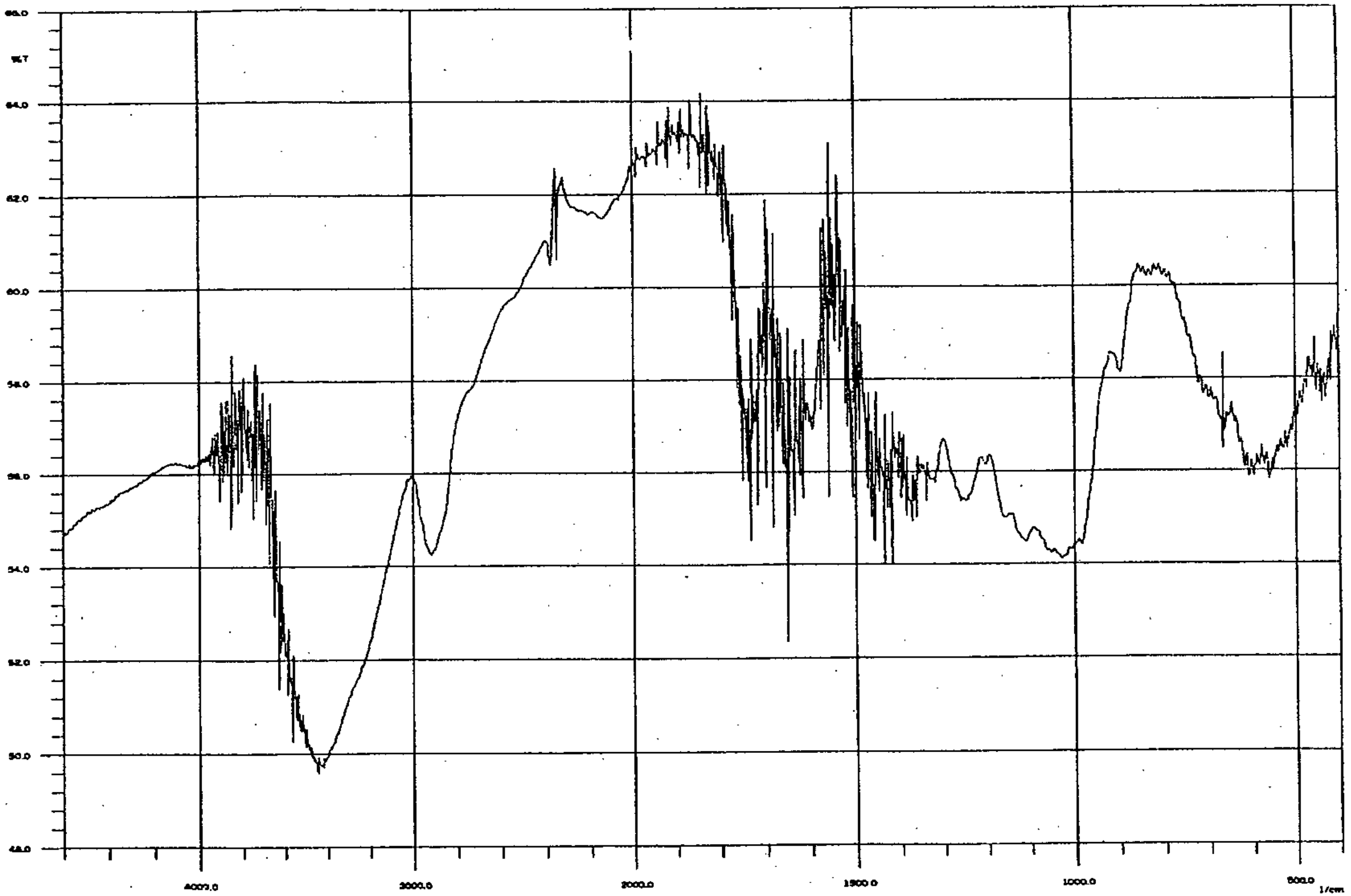


Figure 4.1: Infrared spectrum of raw jute

4.1.2 FT-IR spectroscopic analysis of polypropylene (PP)

Polypropylene is a semicrystalline polymer. For a semicrystalline polymer its crystallinity depends on the content of the ordered phase, which is defined as the molar fraction of chain atoms which possess a specified steric configuration related to their immediate neighbors along the chain. To investigate the structure of PP, an IR spectrum was taken which has been presented in Figure 4.2. FT-IR spectroscopic observation was used to identify the crystalline and amorphous domains in the PP structure. Absorptions at 1167.1, 997.3, 898.9, 842 and 808.3 cm^{-1}positions are due to the crystalline phase of PP and absorptions at 974.2 cm^{-1}positions is due to the amorphous or irregular phase of PP. The peak assignments of the absorption bands of PP are summarized in Table 4.2 which are quite similar to the literature value.[48, (95-97)] The main peaks, their associated vibrational modes, associated microstructures, and dipole moment orientation angles with respect to the main chain are listed below:

Table4.2: FTIR spectral data of polypropylene (PP)

Wave Number (cm^{-1})	Possible Assignment
~ 2900—2880	Doublet due to C—H vibration of —(CH_3) group
~ 1458.4	Methyl asymmetric deformation vibration
~ 1377.3	Methyl symmetric deformation vibration
~ 1167.1	C—C stretching, CH_3 wagging
~ 997.3	C—C stretching, CH_2 rocking, CH_3 rocking Absorptions are due to the crystalline phase of PP
~ 974.2	C—C stretching, CH_2 rocking, CH_3 rocking Absorption due to the amorphous or irregular phase of PP
~ 898.9	C—C stretching, Coupled C—H deformation
~ 841.1	C—C stretching, CH_2 rocking
~ 808.3	C—C stretching, Coupled C—H deformation

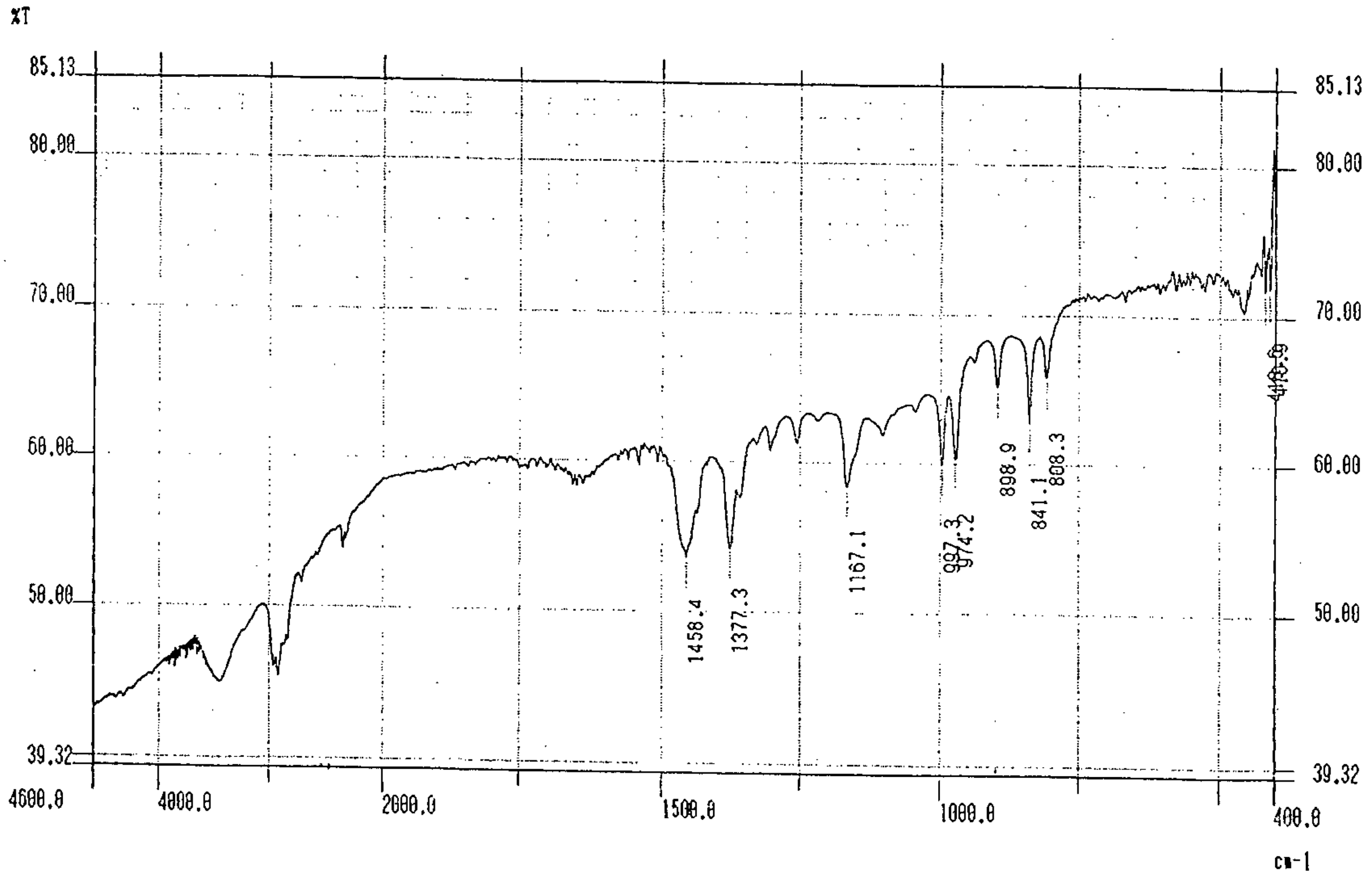


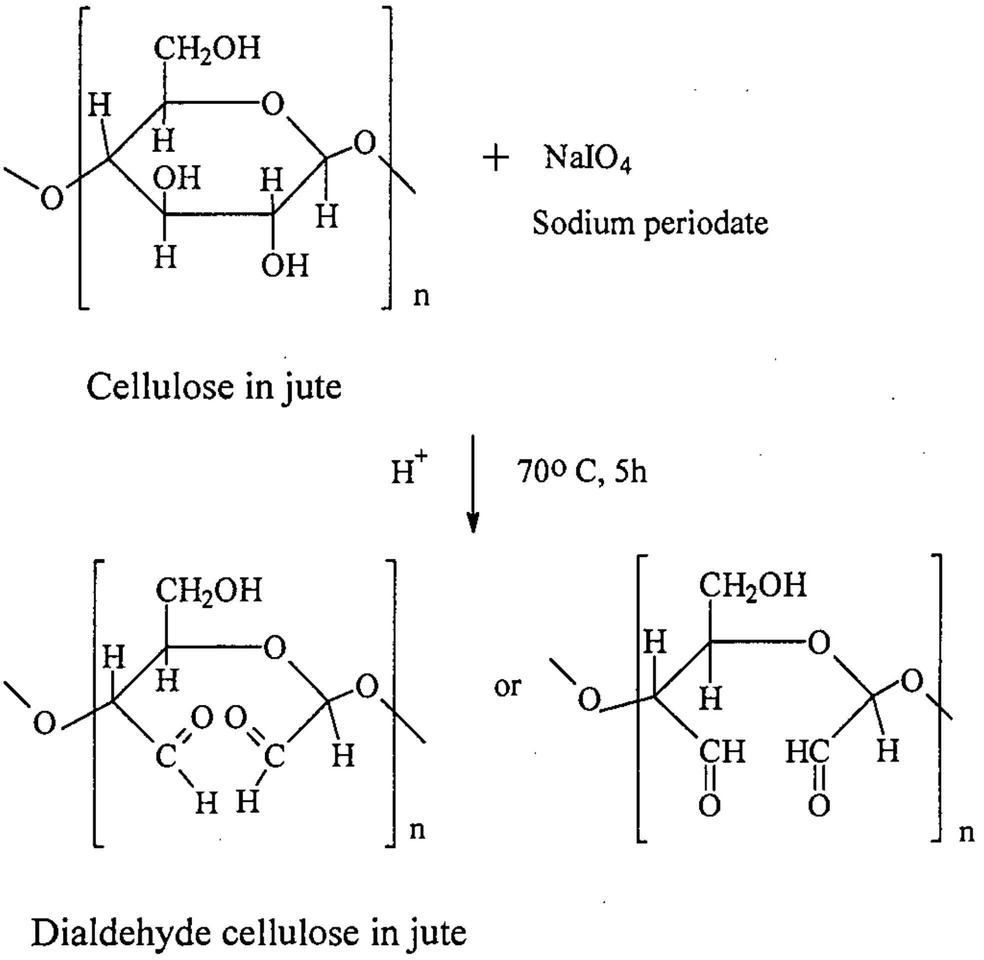
Figure 4.2: Infrared spectrum of polypropylene (PP)

4.2 Surface modification of jute fibers by oxidation reaction

Unbleached raw jute fibers were taken to modify its surface by sodium periodate oxidation process to make it more active to the coupling agent.

4.2.1 Reaction of cellulose in raw jute fiber with sodium periodate

The reaction of sodium periodate with cellulose in raw jute fibers at 70^{0}C yielded the oxidized product 2,3-dialdehyde cellulose (jute), as illustrated in Scheme 1. Depending on the type of oxidizing agent and the pH of the reaction medium cellulose (90%) of cotton is oxidized in two products^6. One is the reducing oxycellulose in which hydroxyl groups have been converted to carbonyl groups or aldehydes and the other is the acidic oxycellulose in which the hydroxyl groups have been converted to carboxyl groups or acids. The oxidation product is dependent on the class of oxidizing agent and the pH of the reaction medium. Three hydroxyl groups are there on cellulose anhydroglucose unit, one is a primary hydroxyl group (at C_6) and other two are secondary hydroxyl groups (at C_2 and C_3). Though primary alcohols are more reactive than secondary alcohol but periodic acid and periodate salts break the anhydroglucose ring between carbon atoms 2 and 3 and convert the two secondary hydroxyl groups to aldehyde groups^6. On the basis of this fact we have selected the sodium periodate as oxidizing agent to oxidize cellulose (69%) of raw jute to dialdehyde cellulose. The detail of the reaction was described in the experimental section.



Scheme 4.1: Oxidation reaction of cellulose in jute with sodium periodate

4.2.2 FT-IR spectroscopic characterization of oxidized jute fibers

The oxidized product 2,3-dialdehyde cellulose has been characterized by infrared spectroscopic analysis. The IR spectrum of raw jute fibers has been described in the Table 4.1. The IR spectrum of oxidized jute fiber is presented in Fig.4.3. The IR spectrum shows characteristic bands of aldehyde group at the region of 2850 cm^{-1} and 2750 cm^{-1} due to C-H stretching and at the region of near 1716 cm^{-1} due to carbonyl stretching. Untreated jute fibers show the absorption band near 1716 cm^{-1} due to the carbonyl group of acetyl ester in hemicellulose and carbonyl aldehyde in lignin[2]. But in the oxidized jute fibers, there is an increased absorption band near 1716 cm^{-1} as compared to the untreated jute fibers which is due to the carbonyl aldehyde of dialdehyde cellulose.

4.3 Raw and oxidized jute fiber reinforced polypropylene (PP) composites

As mentioned earlier jute reinforced polypropylene composites were prepared both by using raw and oxidized jute fiber. The composites were characterized by IR-spectroscopic method. The results are presented below.

4.3.1 FT-IR spectroscopic characterization of raw and oxidized jute fiber reinforced polypropylene (PP) composites

The FT-IR spectra of 30% (w/w) raw jute fiber polypropylene composites is shown in Figure 4.4. The peak assignments of the absorption bands corresponding to various groups of jute and PP are summarized in Table 4.3.

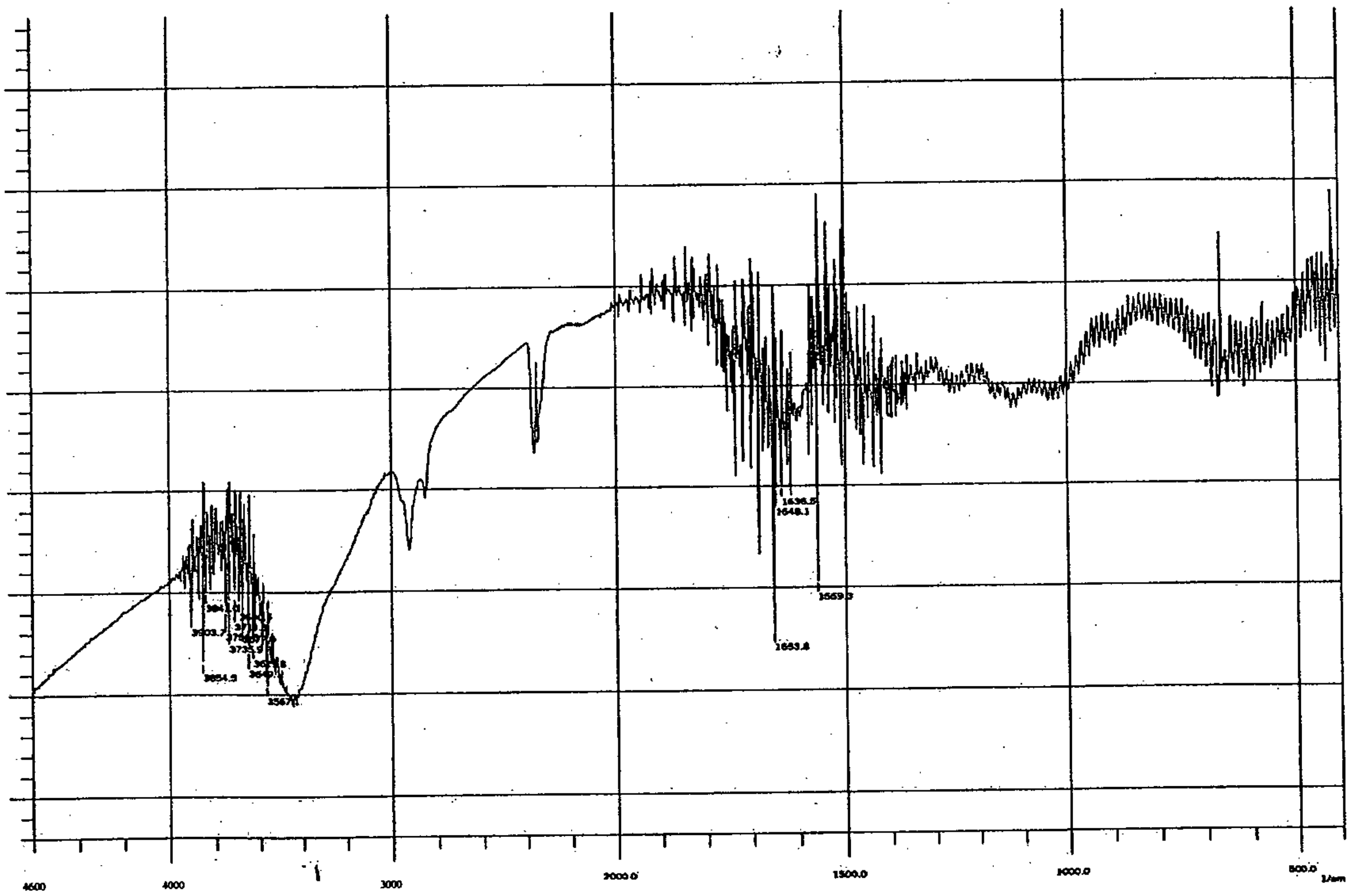


Figure 4.3: Infrared spectrum of sodium periodate oxidized jute

Table4.3: FTIR spectral data of 30 % (w/w) raw jute fiber reinforced polypropylene (PP) composite

Position/ cm^{-}	Assignment
~ 3600-3200	v(OH) broad, strong band from the cellulose, hemicellulose and lignin of jute
~ 3000-2800	v(C-H) due to C—H vibration of —(CH$_3$) group of PP and jute
~ 1750-1710	v(C=O) most probably from the lignin and hemicellulose of jute
~1650-1630	possibly aromatic ring of jute
~ 1635	adsorbed water of jute
~ 1608	v(C=C) aromatic in-plane of jute
~ 1508.2	v(C=C) aromatic skeletal ring vibration due to lignin of jute
~ 1458.4	Methyl asymmetric deformation vibration of PP
~ 1455	δ(C-H); δ(C-OH) 1° & 2° alcohol of jute
~ 1419.5	δ(C-H) of jute
~ 1377.3	Methyl symmetric deformation vibration
~ 1365	δ(C-H) of jute
~ 1315	δ(C-H) of jute
~ 1280	δ(CH$_2$) twisting of jute
~ 1255.6	δ(C-OH) out-of-plane
~ 1167.1	C—C stretching, CH$_3$ wagging of PP
~ 1105	v(C-O-C) glycosidic of jute
~ 1050	v(C-OH) 2° alcohol of jute
~ 1033.8	v(C-OH) 1° alcohol of jute
~ 997.3	C—C stretching, CH$_2$ rocking, CH$_3$ rocking absorptions are due to the crystalline phase of PP
~ 974.2	C—C stretching, CH$_2$ rocking, CH$_3$ rocking absorption due to the amorphous or irregular phase of PP
~ 898.9	C—C stretching, Coupled C—H deformation of PP
~ 841.1	C—C stretching, CH$_2$ rocking of PP
~ 808.3	C—C stretching, Coupled C—H deformation of PP

FT-IR spectra of 30 % (w/w) oxidized jute reinforced PP composites are shown in Figure 4.5. The characteristic aldehyde band of oxidized jute fibers (Fig. 4.3) and C–H vibration of methyl group for PP (Fig. 4.2) are merged at the same region. The presence of 70 % (w/w) PP in the FT-IR spectrum shows the absorption bands intensity more in PP than the absorption bands intensity in jute fibers. Injection moulded fractured tensile test specimens were used to take FT-IR spectrum of the composites. It is observed that peak or absorption band numbers of jute (both untreated and oxidized) in jute-PP composites show less number than the FT-IR spectra of pure untreated jute and oxidized jute. It may be due to the degradation of some ingredients of untreated and oxidized jute through injection moulding process at a high temperature of about 175^{0}C.

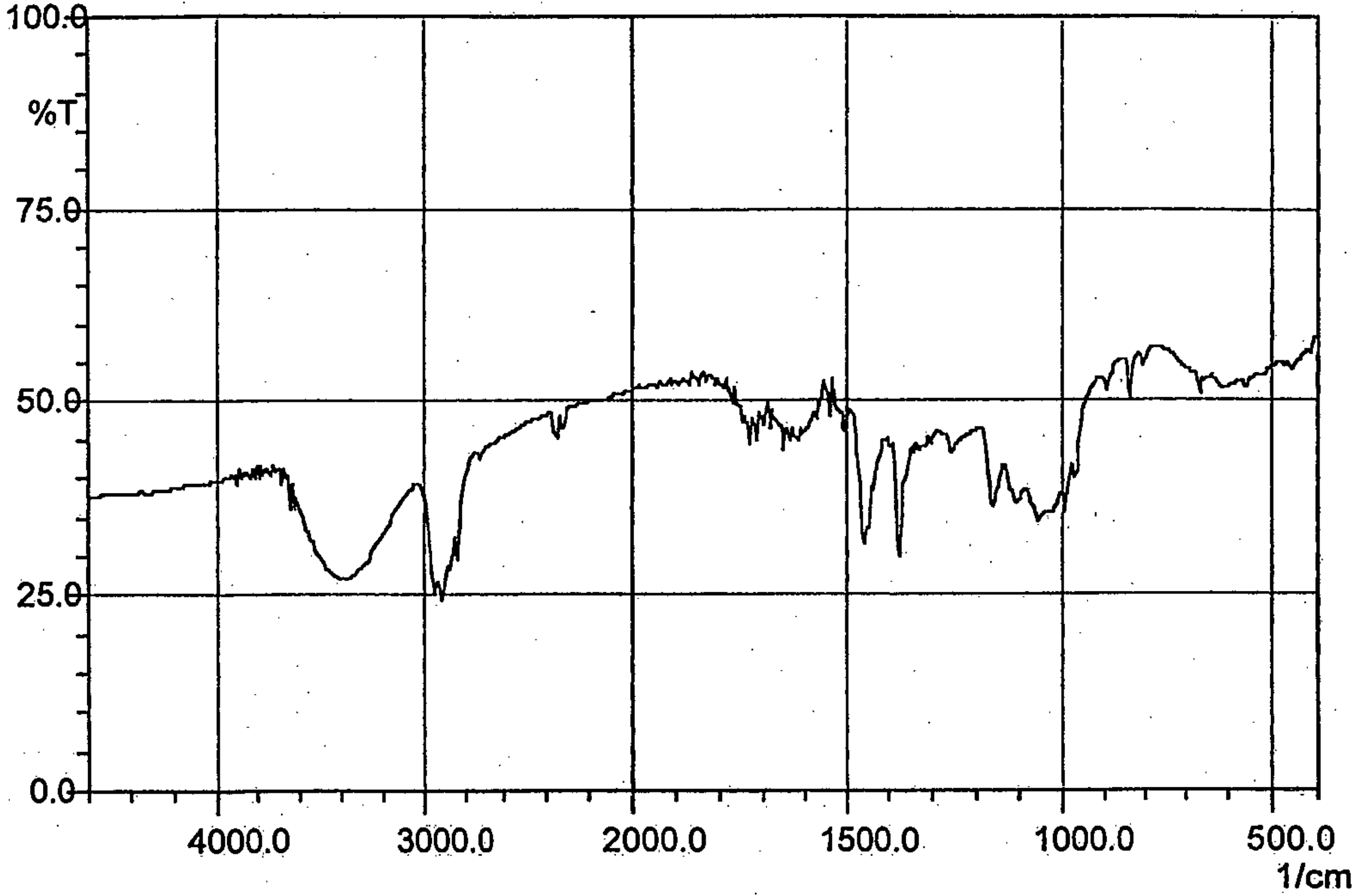


Figure 4.4: Infrared spectrum of 30 % (w/w) raw jute fiber reinforced polypropylene composites

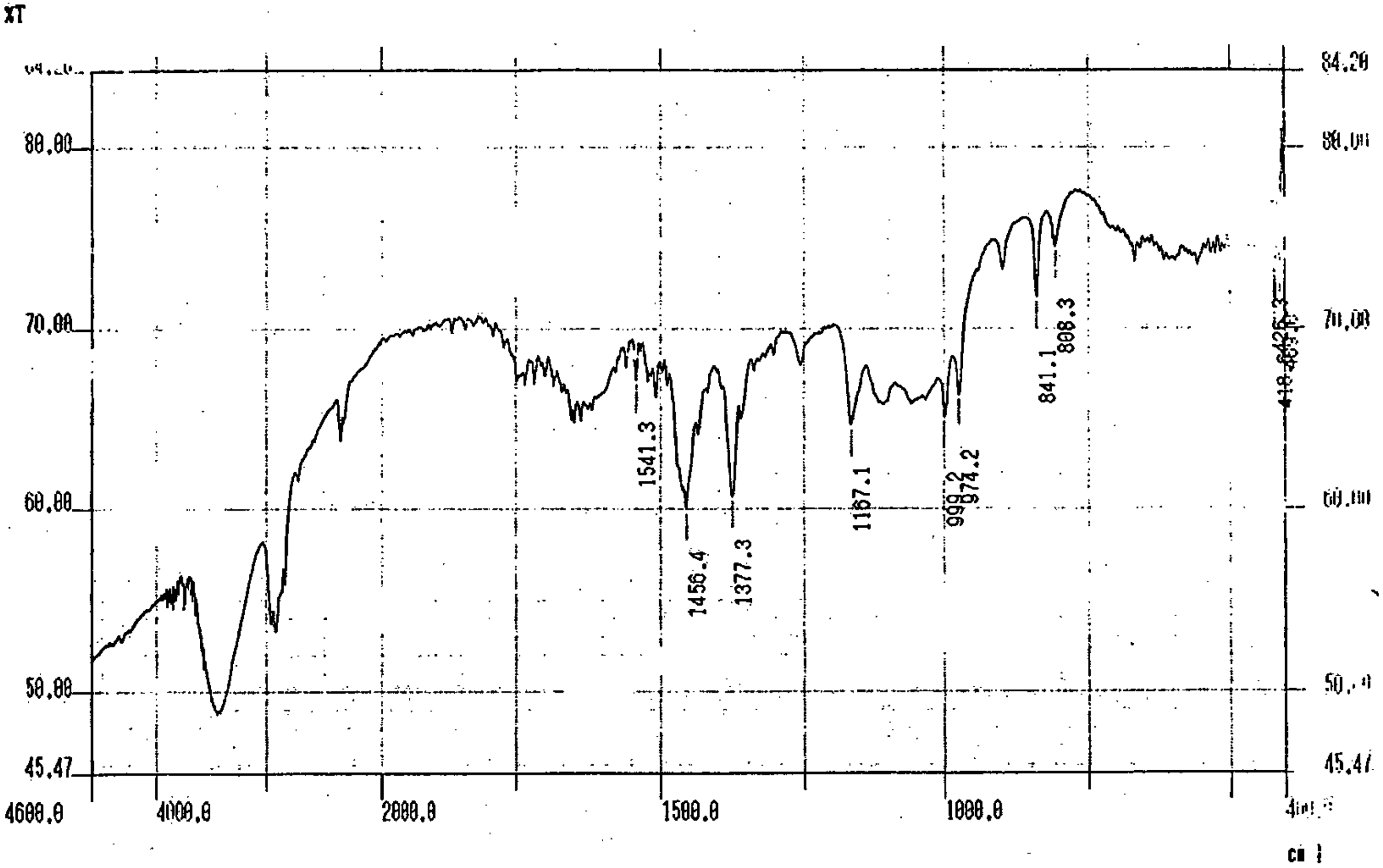


Figure 4.5: Infrared spectrum of 30 % (w/w) oxidized jute fiber reinforced polypropylene composites

4.3.2 Mechanical properties of raw and oxidized jute fiber reinforced polypropylene composites

Tesile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, charpy impact strength and hardness of the raw and oxidized jute fiber reinforced polypropylene composites have determined following the ASTM method described in the experimental sections. The results obtained in this study are presented below.

4.3.2.1 Tensile strength, modulus and elongation at break

The tensile strengths of the raw jute fiber reinforced PP composites decrease with increasing fiber loading by weight fraction from 20% (w/w) to 30% (w/w) (Fig.4.6). This may be due to the lack of stress transfer from the PP matrix to fibers. However, the tensile strength of composites starts to increase at 35% (w/w) jute fibers loading. Approximately similar results were found for kenaf-PP composites[40] and empty fruit bunch (EFB) fibers-PP composites[101] in the literature. The Tensile modulus increases with increasing fiber loading (Fig. 4.7) as compared to 100 wt-% PP. Elongation at break decreases with increasing fiber loading (Fig. 4.8). Stress versus strain curves of the raw jute-PP composites are shown in Figure 4.9, where a decrease in failure strain was observed with an increase in fiber content.

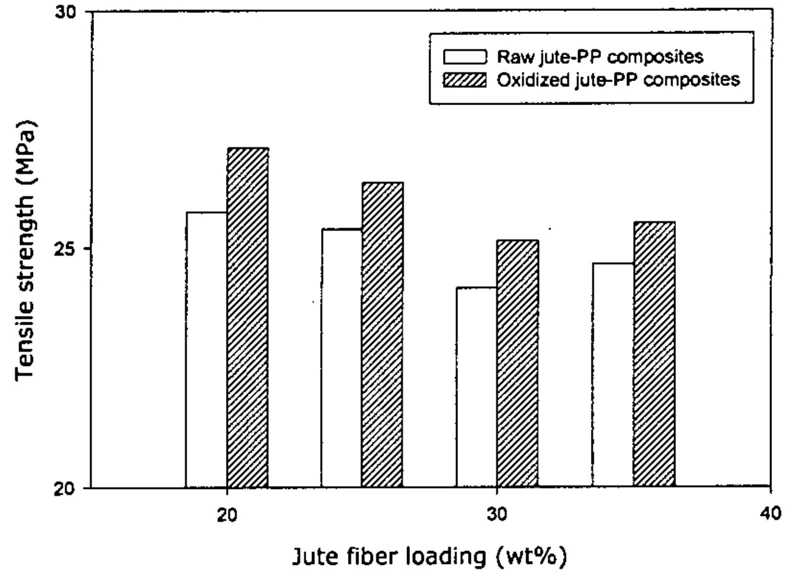


Figure 4.6: Tensile strength vs fiber content (wt%) curves for raw and oxidized jute-PP composites

From the Figure 4.6 it is observed that the tensile strengths of the oxidized jute fiber reinforced PP composites are 3 to 5% more than that of raw jute-PP composites. But tensile strength of the oxidized jute-PP composites decreases with increasing fiber loading by weight fraction from 20 wt-% to 30 wt-% like raw jute-PP composites. It is also observed from the figure the tensile strength starts to increase at 35 wt-% fiber loading. Figure 4.7 and 4.9 shows that with the increase of fiber loading to the polymer composites the tensile modulus increases and elongation at break decreases. It is also found that elongation at break of oxidized jute-PP composites is slightly higher than that of untreated jute-PP composites. Increasing of the elongation at break of the composites increases the toughness or ductility of the composites. Stress versus strain curves of 20 wt-% untreated and oxidized jute-PP composites are shown in Figure 4.10 with comparing to 100 wt-% matrix polymer PP. It is observed that the initial tensile modulus or stiffness of the composites significantly increases with increasing fiber loading as compared to 100 wt-% PP matrix.

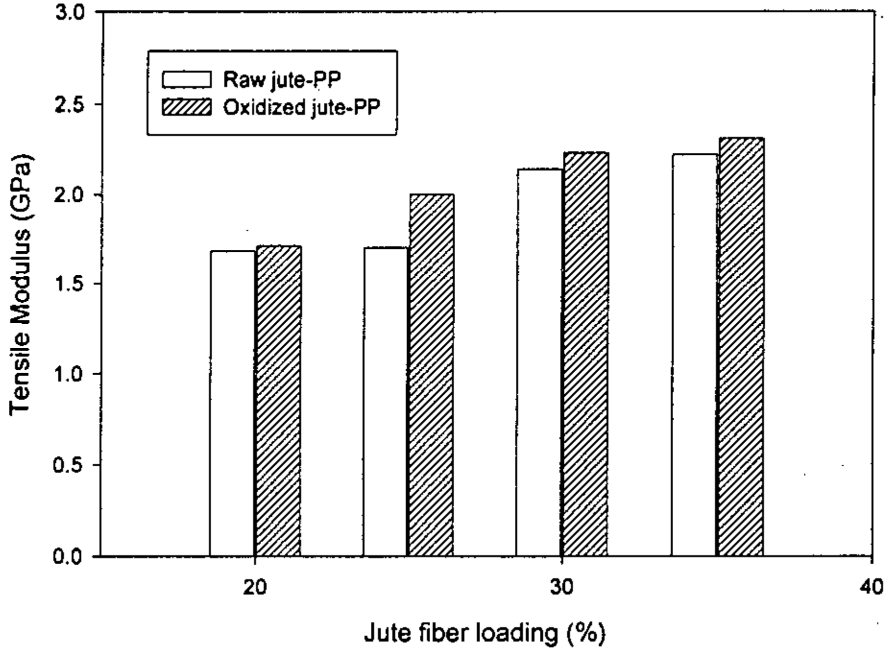


Figure 4.7: Tensile modulus vs fiber loading (wt.%) curves for raw and oxidized jute-PP composites

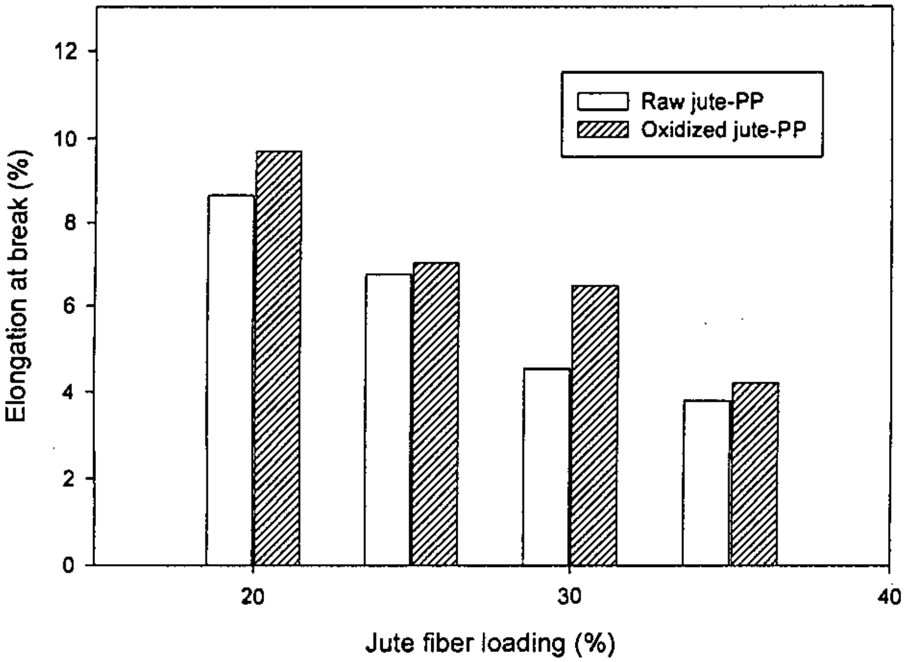


Figure 4.8: Elongation at break vs fiber loading (wt.%) curves for raw and oxidized jute-PP composites

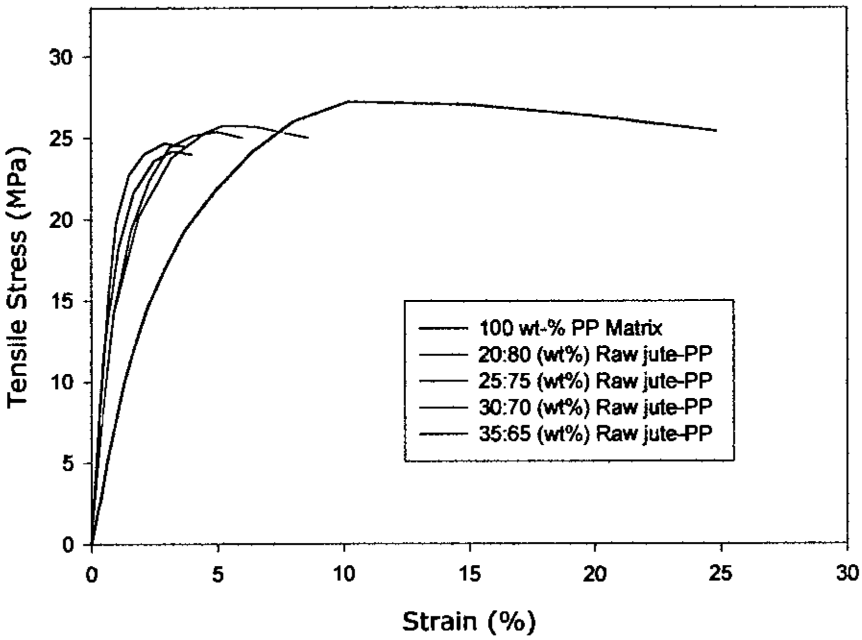


Figure 4.9: Tensile stress vs strain (%) curves for raw jute-PP composites

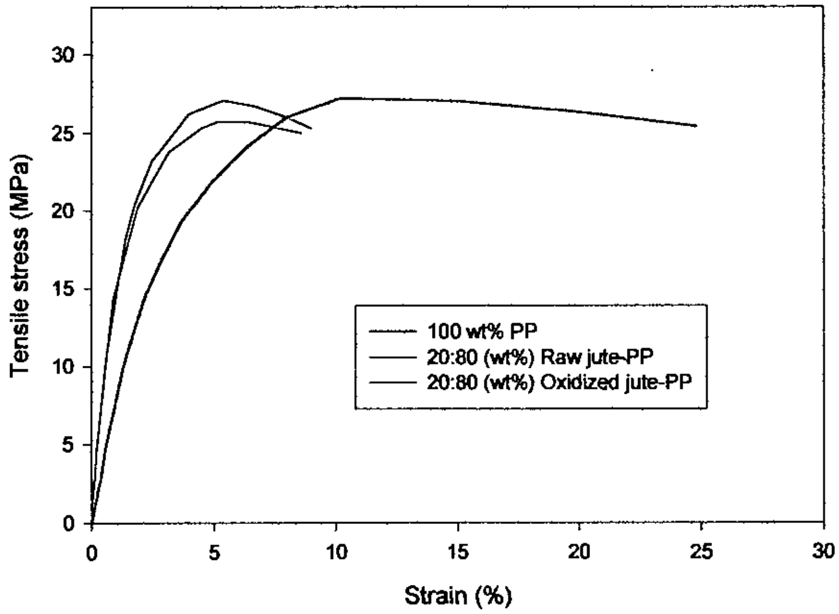


Figure 4.10: Tensile stress vs strain (%) curves for PP matrix, 20 wt% raw and oxidized jute reinforced jute-PP composite

4.3.2.2 Flexural strength and modulus

Results on flexural strength of the raw and oxidized jute-PP composites have been presented in Figure 4.11 against the percentage (wt) of fiber loading. It is observed from the figure that the values of flexural strength for both the composites increase with increasing fiber loading up to 30 wt-%, then it starts to decrease at 35 wt-% fiber loading as compared to 100 wt-% PP matrix. The experimental values of flexural modulus at different fiber loading have been presented in Figure 4.12. It is observed from the figure that flexural modulus for both raw and oxidized jute-PP composites increases significantly with increasing fiber loading. It is also seen from the figure that the flexural strength and modulus of oxidized jute-PP composites have similar fiber content effects like raw jute-PP composites. However, higher values of flexural strength and flexural modulus observed in the case of oxidized jute-PP composites than that of raw jute-PP composites. This may be due to the better compatibility of oxidized jute fiber for the formation of jute-PP composites than that of raw fiber. The better compatibility may arise from the opening of glucoside ring of cellulose molecules (Scheme 4.1). It is quite logical to expect that better entanglement is possible from the open chain large molecule than the cyclic molecule.

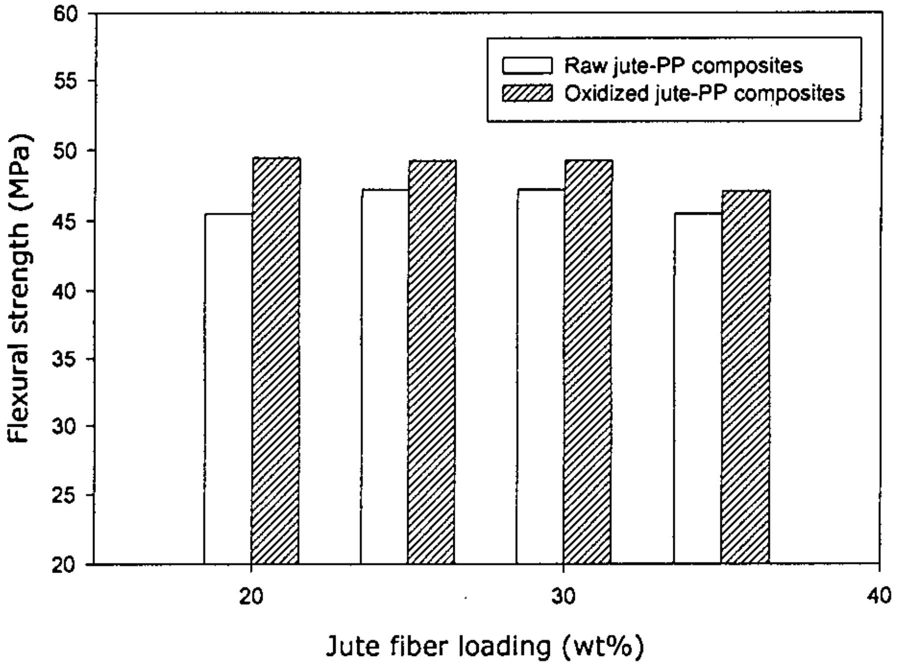


Figure 4.11: Flexural strength vs fiber content (wt%) curves for raw and oxidized jute-PP composites

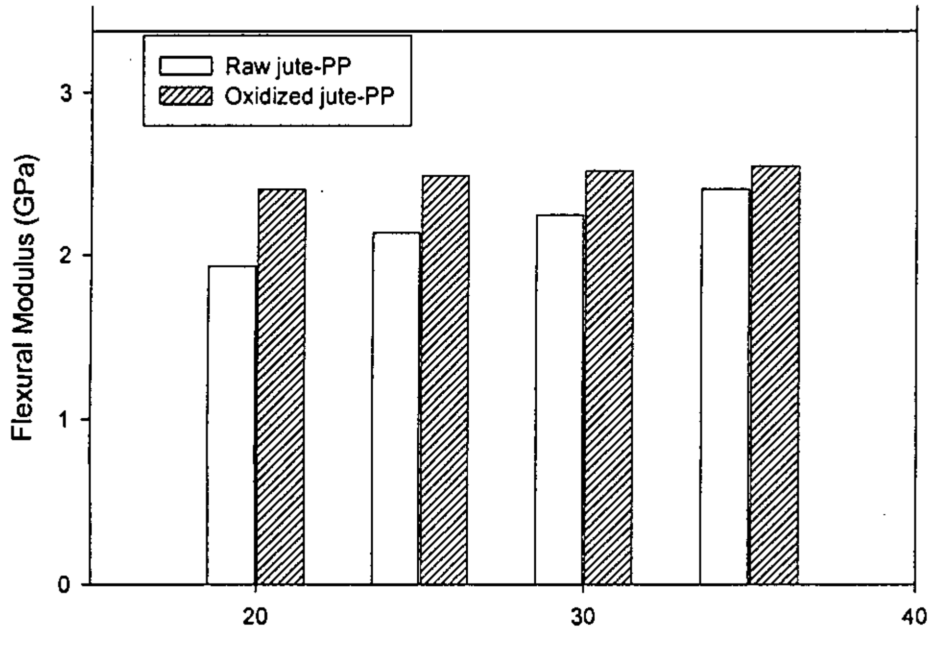


Figure 4.12: Flexural modulus vs fiber loading (wt%) curves for raw and oxidized jute-PP composites

4.3.2.3 Charpy impact strength

The charpy impact strength of the raw and oxidized jute-PP composites are shown in Figure 4.13 and Table 4.4. It is apparent from the result presented in these figure and table that values of charpy impact strength of jute- PP composites are significantly more than that of unfilled PP polymer. Charpy impact strength decreases with increasing fiber loading. Oxidized jute-PP composites show better result than raw jute-PP composites.

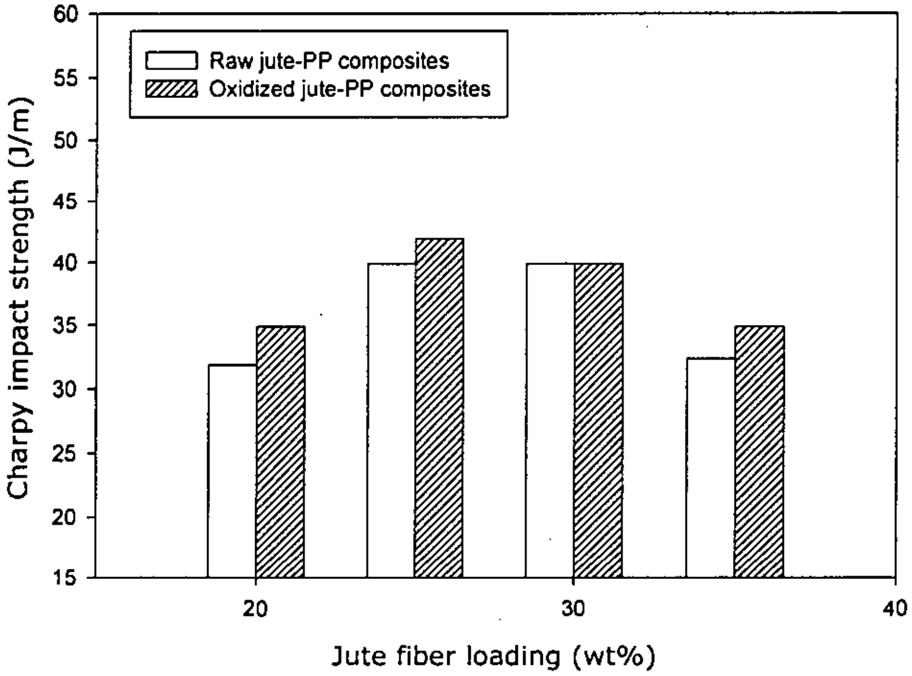


Figure 4.13: Charpy impact strength vs fiber content (wt%) curves for raw and oxidized jute-PP composites

4.3.2.4 Hardness

A Rockwell hardness number is directly related to the indentation hardness of a plastic material, with the higher the reading the harder the material.[89] Rockwell hardness of the composites are shown in Table 4.4. It is found that Rockwell hardness of the oxidized jute-PP composites is higher than raw jute-PP composites. It is also found that Rockwell hardness of the composites is higher than PP polymer matrix and it increases with increasing fiber loading.

4.3.3 Effect of surface modification of fibers on the mechanical properties of oxidized jute reinforced PP composites

All the mechanical properties according to series of formulation based on the raw jute-PP and oxidized jute-PP composites are summarized in the Table 4.4. All of the results are significantly more for oxidized jute-PP composites than raw jute-PP composites. The reasons of these enhancement results may be explained on the basis of hydrophilic nature of jute and hydrophobic nature of PP matrix. There is very poor wettability and adhesion between hydrophilic jute fiber and hydrophobic PP matrix. Oxidation of jute fibers decreases its hydrophilic nature as compared to raw jute fibers. Cellulosic hydroxyl group of jute forms intermolecular hydrogen bonding and so weakly dispersed in the raw jute-PP composite. But oxidized jute fibers contains dialdehyde cellulose and aldehyde groups are not capable of forming intermolecular hydrogen bonds since aldehyde groups contain hydrogen bonded only to carbon[99]. Polarity of aldehyde group is less than hydroxyl group and there is no intermolecular hydrogen bonding in the dialdehyde cellulose. So it increases the wettability and adhesion of oxidized jute fibers to PP matrix. The improved interfacial bonding between oxidized jute fibers and PP matrix in the oxidized jute-PP composites increases their mechanical properties as compared to raw jute-PP composites. M. Kazayawoko et al[39] also investigated and reported that presence of strong intermolecular hydrogen bonding in the hydrophilic bleached kraft pulp (BKP) fibers decreases the tensile strength properties of BKP reinforced PP composites.

Table 4.4: Results of mechanical tests of raw and oxidized jute reinforced PP composites.

Material	Tensile			Flexural		Charpy Impact Strength, J/m	Rockwell Hardness (L Scale)
	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)		
PP only	27.20	0.79	More than 150	42.63	1.28	22.34	66.4
PP-Raw jute 20 % (wt)	25.74	1.68	8.65	45.47	1.93	31.84	77.2
PP-Raw jute 25 % (wt)	25.38	1.70	6.75	47.17	2.14	39.87	80.2
PP-Raw jute 30 % (wt)	24.17	2.14	4.53	47.17	2.25	39.87	82.4
PP-Raw jute 35 % (wt)	24.66	2.22	3.79	45.47	2.41	32.34	85.4
PP-Oxidized jute 20% (wt)	27.07	1.71	9.68	49.45	2.41	34.85	77.6
PP-Oxidized jute 25 % (wt)	26.35	2.00	7.02	49.22	2.49	41.88	80.4
PP-Oxidized jute 30 % (wt)	25.14	2.23	6.48	49.22	2.52	39.87	83.6
PP-Oxidized jute 35 % (wt)	25.50	2.31	4.2	47.06	2.55	34.85	87.4

4.3.4 Morphological (SEM) characterization of raw and oxidized jute fiber reinforced polypropylene composites

To study the surface morphology of the prepared composites scaning electron micrograph (SEM) were taken using 30 wt-% raw and oxidized jute fiber loading PP composites. Scratched pieces from fracture surfaces of tensile test specimens were used to take SEM and are shown in Figures 4.14 and 4.15. SEM of raw jute-PP composite indicates that there is a lack of interfacial interaction that gives the insufficient adhesion between the raw jute and PP matrix. Due to intermolecular hydrogen bond formation between jute fibers and hydrophobic nature of PP matrix, hydrophilic jute fibers tend to agglomerate into bundles and become unevenly distributed throughout the matrix.

SEM observation of the oxidized jute-PP composite (Fig. 4.15) indicates the better interfacial adhesion between oxidized jute fiber and PP matrix in the oxidized jute-PP composite as compared to raw jute-PP composite (Fig. 4.14). Raw jute weakly dispersed in the raw jute-PP composite due to intermolecular hydrogen bonding and agglomeration. But oxidized jute fibers contains aldehyde group which are not capable of forming intermolecular hydrogen bonds since aldehyde groups contain hydrogen bonded only to carbon[99]. So, oxidized jute fibers dispersed uniformly in the oxidized jute-PP composites. The improved interfacial bonding of oxidized jute-PP composite is clearly seen in the Figure 4.15 than that of raw jute-PP composite (Fig. 4.14).

Figure 4.14: SEM micrograph of 30 wt-% raw jute-PP composite

Figure 4.15: SEM micrograph of 30 wt-% oxidized jute- PP composite

4.3.5 Water absorption

Water absorption and specific gravity of lignocellulosic fiber composties are important characteristics that determine end use applications of these materials[54]. Water absorption could lead to a decrease in some of the properties and needs to be considered when selected for applications. It is difficult to eliminate entirely the absorption of moisture from the composites without using expensive surface barriers on the composite surface. Water absorption in lignocellulosic based composites can lead to build up of moisture in the fiber cell wall and also in the fiber-matrix interphase region. Moisture build up in the cell wall could result in fiber swelling and concerns on the dimension stability cannot be ignored[54]. So chemical modification is needed to reduce the moisture absorption of the fibers.

Results of water absorption obtained in our study are shown in Figure 4.16. It is observed from the figure that water absorption of the composites increases with increasing fiber loading. But water absorption of the oxidized jute-PP composites are less than that of raw jute-PP composites. Cellulose, hemicellulose and lignin of jute contains hydroxyl group. Hydroxyl group forms hydrogen bond with water molecule. Aldehyde group of oxidized jute also forms hydrogen bond with water molecule. But the aldehyde group is less polar than hydroxyl group. So, hydroxyl group absorbs more water than aldehyde group. As a result, water absorption of oxidized jute-PP composites are less than that of untreated jute-PP composites. Chemical modification of hydroxyl group of cellulose in jute to aldehyde group of dialdehyde cellulose in jute influence to get these improved results.

Table 4.5: Water absorption of the raw and oxidized jute-PP composites

Material	2 h in boiling water (%)	24 h in cold water (%)
PP only	0.09	0.02
PP-Raw jute (20 wt-%)	0.78	0.39
PP-Raw jute (25 wt-%)	0.89	0.44
PP-Raw jute (30 wt-%)	1.02	0.51
PP-Raw jute (35 wt-%)	1.26	0.71
PP-Oxidized jute (20 wt-%)	0.73	0.32
PP-Oxidized jute (25 wt-%)	0.77	0.38
PP-Oxidized jute (30 wt-%)	0.84	0.40
PP-Oxidized jute (35 wt-%)	0.95	0.50

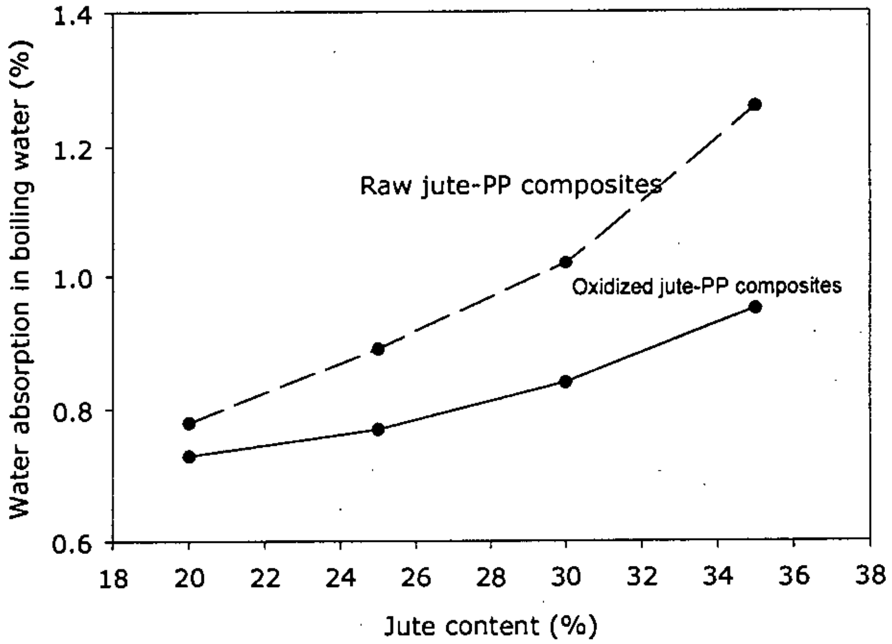


Figure 4.16: Water absorption vs fiber content (wt%) curves for raw and oxidized jute-PP composites

4.4 Urea treated oxidized jute fiber reinforced polypropylene (PP) composites

In this work oxidized jute reinforced polypropylene composites of different composition have been treated with urea to increase the mechanical strength of prepared composite materials. It was expected that coupling reaction between aldehydic groups of jute fiber with coupling agent would take place which might improve the physicomechanical properties of jute reinforced-PP composites. The results obtained in this study are presented below.

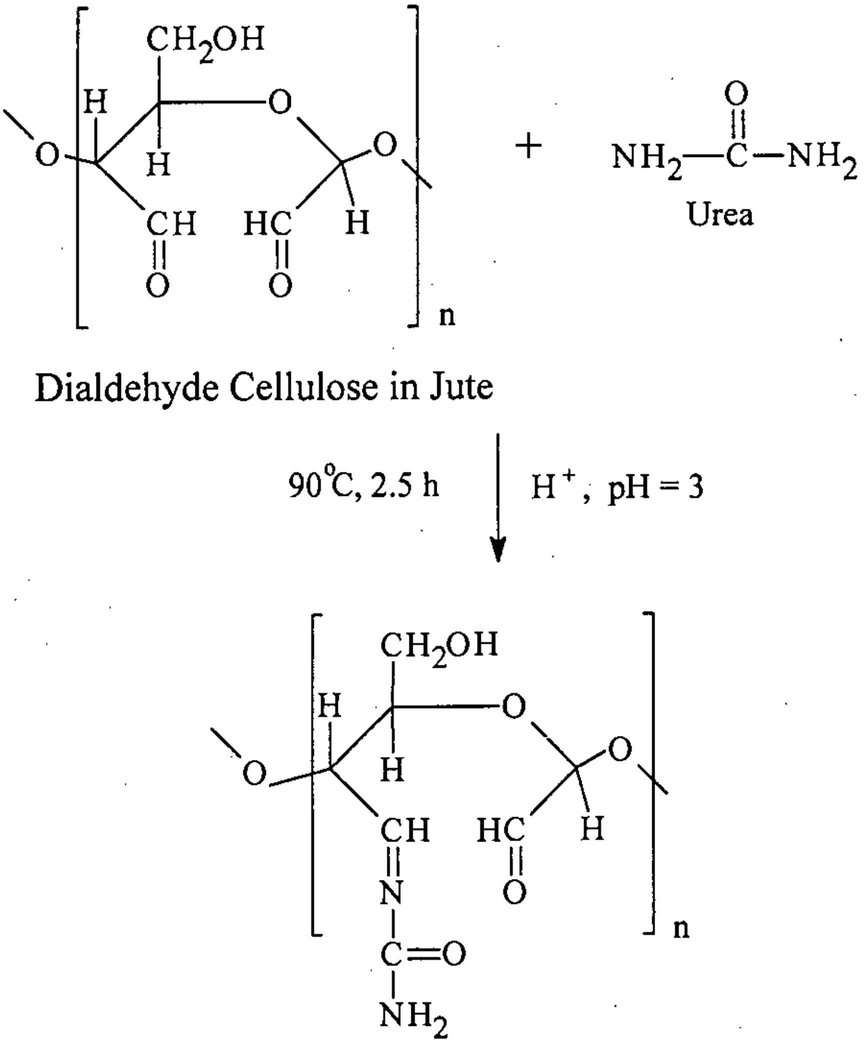
4.4.1 Coupling reaction of urea with oxidized jute fiber reinforced polypropylene (PP) composites

The reaction procedure of urea with oxidized jute-PP composites has been described in the experimental section. Reaction parameters such as time, temperature, pH and concentration of urea were investigated to get the proper reaction condition. 25 wt-% fiber reinforced composites were used to find out the reaction condition to get maximum tensile strength. The reaction parameters time, temperature and pH were investigated on weight percent gain (WPG) measurement of the composites and these were found to be 2.5 hours, 90^0C and 3 respectively. The concentration of urea in impregnating solution was measured on increasing of tensile strength property and was found to be 10-15% (wt). It was found that the WPG increases with increasing time, temperature, pH and concentration of the urea solution. It was also found that the tensile strength didn't increase with increasing WPG after a certain level. This may be due to the fact that at higher WPG than 15% (wt) the crystalline region of jute-PP composites might be disrupted. G.S. Tay et al[102] reported approximately similar observation about the effect of WPG on tensile strength of composites made with EFB fibers modified with epichlorohydrin. The concentration of urea in impregnating solution after 10-15% (wt) didn't affect the WPG and tensile strength property considerably. M. Andersson et al[20] reported the similar observation on acetylation of jute fiber.The WPG data for all composites at 15% urea treatment solution are given in Table 4.6 below:

Table 4.6: WPG data of urea treated oxidized jute-PP composites

Urea treated composites	WPG of the composites	WPG according to jute content of the composites
20:80 (wt %) Oxidized jute-PP	0.13	8.44
25:75 (wt %) Oxidized jute-PP	0.22	11.24
30:70 (wt %) Oxidized jute -PP	0.34	14.04
35:65 (wt %) Oxidized jute -PP	0.52	18.31

It is observed from the table that the percentage of weight gain increases with the increase of proportion of jute fiber in the composites. From this observation it may be suggested that coupling between urea and aldehyde group of jute took place during post treatment of jute-PP composites. The proposed reaction of urea with oxidized jute in the oxidized jute-PP composites is as follows:



Scheme 4.2: Proposed reaction mechanism of urea with oxidized jute in the oxidized jute-PP composite

Schiff base product may be formed by covalent linking of dialdehyde cellulose in jute with amino group of urea. This type of covalent coupling bonding was also investigated and reported by the C. L. Tien et al.[111] and they reported that schiff's-base linkages were formed between aldehyde groups of alginate with amino groups of enzyme. The FT-IR spectroscopic characterization of proposed reaction's schiff-base product is given below.

4.4.2 FT-IR spectroscopic characterization of urea treated oxidized jute fiber reinforced polypropylene composites

The FT-IR spectrum of urea treated 30 wt-% oxidized jute-PP composites is shown in Figure 4.17. The change in the absorption bands was compared with the absorption bands of 30 wt-% oxidized jute-PP composite (Fig. 4.5). The expected additional absorption bands for the group of C=O and $-NH_2$ of new schiff base product may be merged or overlapped with other absorption bands of jute in the same region as jute shows complex FT-IR spectra for the presence of its various polymeric ingredients. But the expected absorption band for the azomethine group (C=N) of new schiff base product was detected as a separate new absorption band at 1590 cm^{-1} region which is the main evidence of this reaction. Urea treated oxidized jute-PP composite shows some difference of absorption bands at some other region comparing with the spectrum of oxidized jute-PP composite. The absorption bands in the region 1710-1750 cm^{-1} may be arose from the carbonyl stretching due to the acetyl and carboxyl groups of hemicelluloses, aldehyde or aliphatic ketone and esters in lignin and extractives of the natural fibers. From the spectroscopic observation of urea treated oxidized jute-PP composite compared with oxidized jute-PP composite, it is assumed that one aldehyde group of dialdehyde cellulose might be participated in the reaction and the other aldehyde group was free due to short time reaction period. So, there is no significant change of decrease in the carbonyl region at 1716 cm^{-1}. This might be due to the overlapping of this free aldehyde group with the other various carbonyl groups in the jute fibers. The C=O stretching vibration and $-NH_2$ bending vibration of new schiff-base product might be merged at the region of 1660cm^{-1} and 1650 cm^{-1} respectively. The absorption band at 1290 cm^{-1} might be due to C-N stretching of schiff-base product. The strong and broad absorption bands at 3400-3600 cm^{-1} region might be due to the overlapping of large amount -OH groups of various ingredients of jute and small amount of $-NH_2$ group stretching vibrations of schiff-base product.

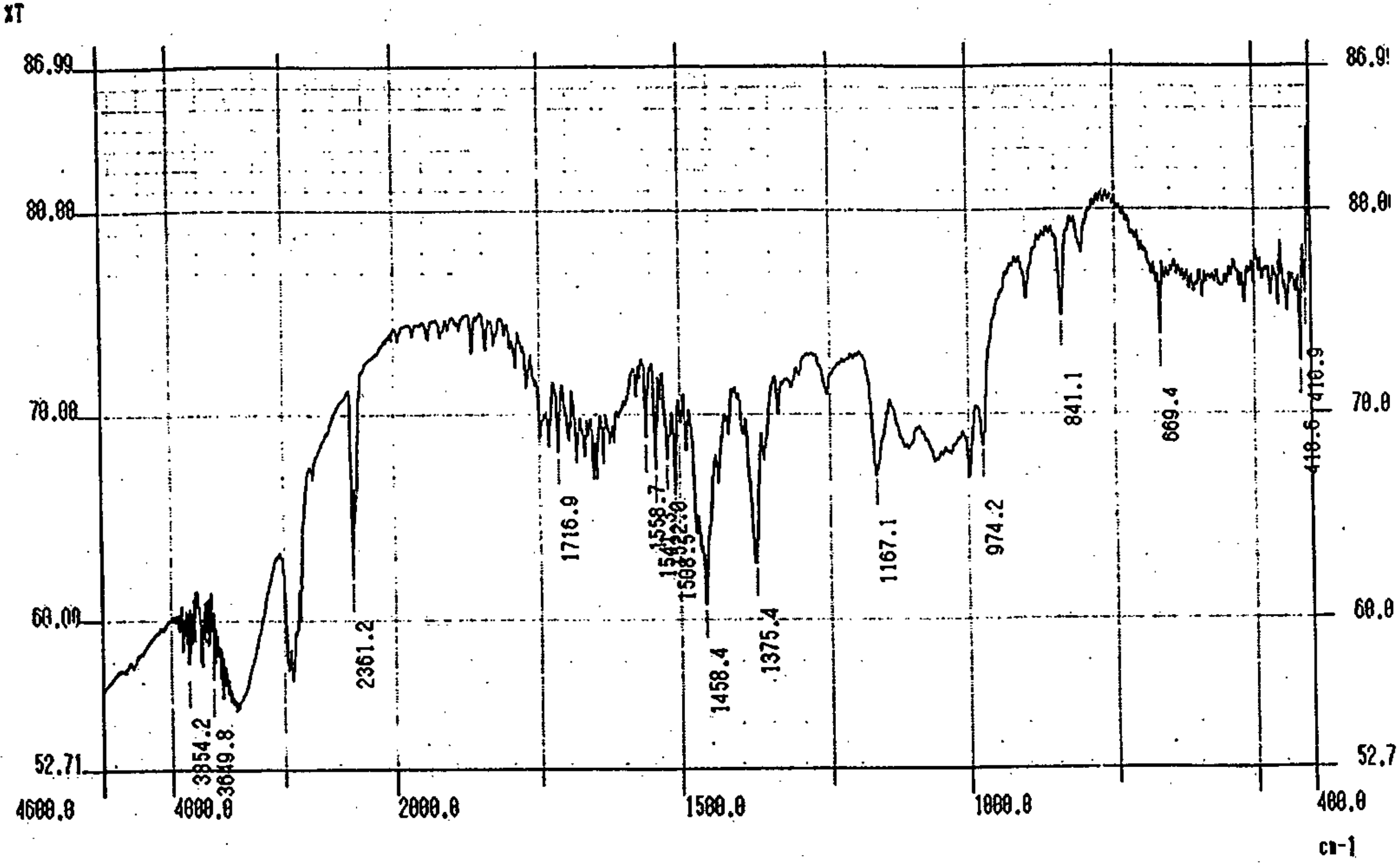


Figure 4.17: Infrared spectrum of urea treated 30% wt oxidized jute fiber reinforced polypropylene composites

4.4.3 Mechanical properties of urea treated oxidized jute fiber reinforced polypropylene composites

Tesile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, charpy impact strength and hardness of urea treated oxidized jute fiber reinforced polypropylene composites have determined following the ASTM method described in the experimental sections. The results obtained in this study are presented below.

4.4.3.1 Tensile strength, modulus and elongation at break

The tensile strengths of the urea treated oxidized jute-PP composites are significantly greater than those of PP matrix and untreated jute-PP composites. Therefore it can be said that the stress transferred from the PP matrix to the fiber. At 35 wt-% fibers loading, the tensile strength is approximately similar to the PP matrix. It is found that tensile strength increases approximately 10% to 20% over the raw jute-PP composites but it increases by 6% to 14% more than that of oxidized jute-PP composites. The tensile strength of the composites decreases with increasing fiber loading (Fig. 4.18). Tensile modulus of the composites increases with increasing fiber loading (Fig. 4.19). It is also found that elongation at break of the composites increases comparing with the untreated and oxidized jute-PP composites (Fig.4.20). This means that ductility of the composites increases. Tensile stress vs strain graph for urea treated 20 wt-% oxidized jute-PP composites comparing with PP matrix, 20 wt-% raw and oxidized jute-PP composites are shown in Figure 4.21.

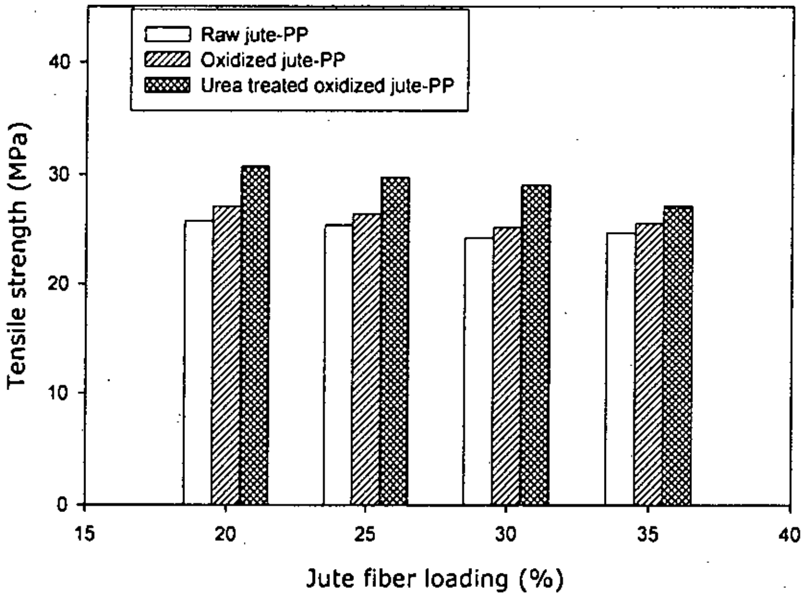


Figure 4.18: Tensile strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urea treated oxidized jute-PP composites

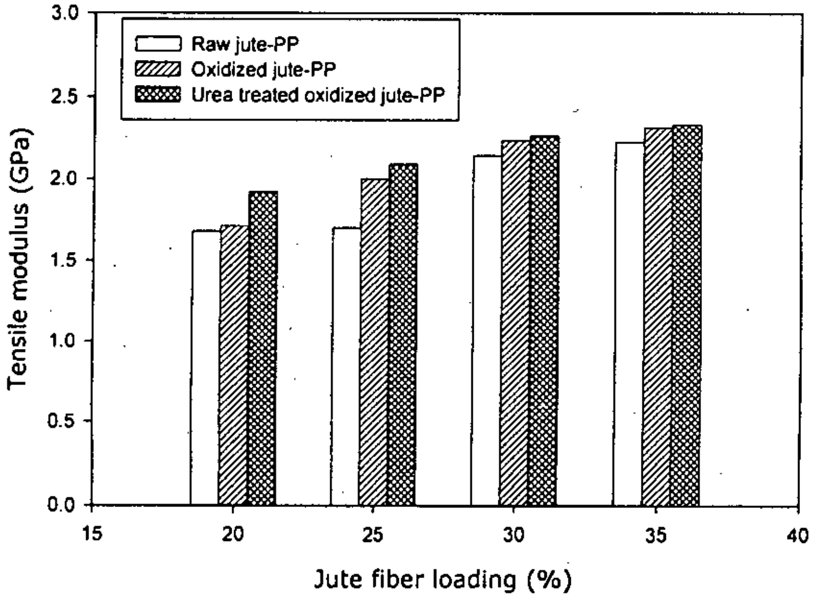


Figure 4.19: Tensile modulus vs fiber loading (wt%) curves for raw, oxidized jute-PP compoaites and urea treated oxidized jute-PP composites

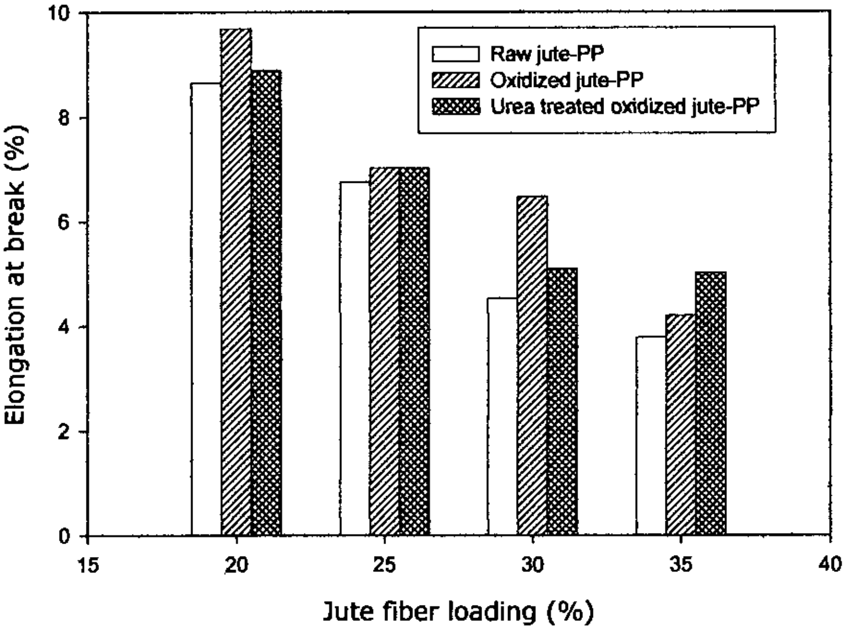


Figure 4.20: Elongation at break vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urea treated oxidized jute-PP composites

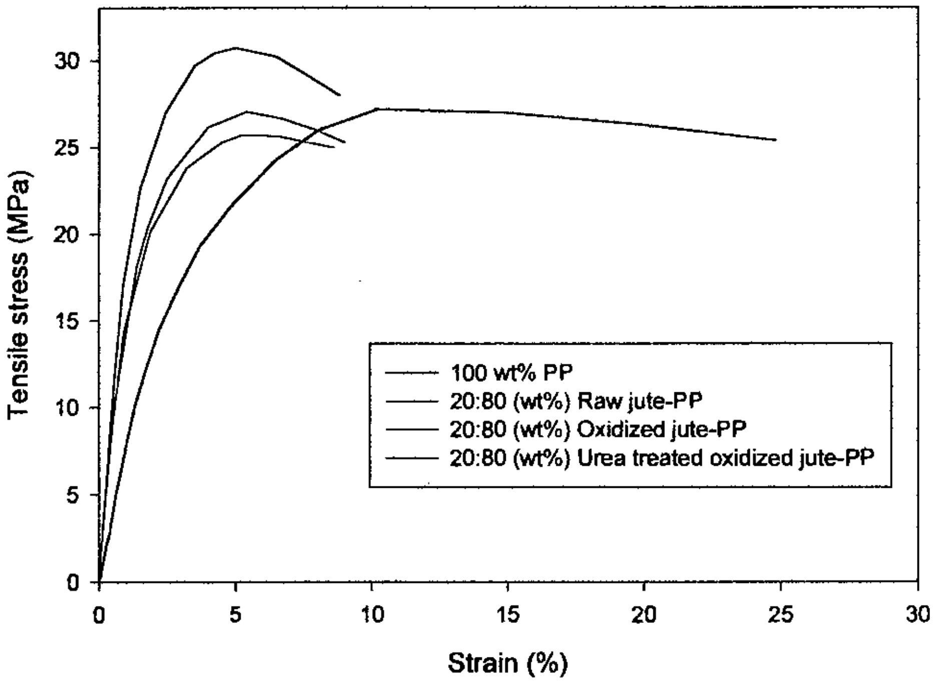


Figure 4.21: Tensile stress vs strain (%) curves for PP matrix, 20 wt% raw and oxidized jute-PP composites and urea treated oxidized jute-PP composite

4.4.3.2 Flexural strength and modulus

The flexural strength and modulus of urea treated composites were carried out in a similar manner that have been done for untreated and oxidized jute-PP composites. The experimental results found for flexural strength and modulus of the urea treated oxidized jute-PP composites are presented in Figure 4.22 and 4.23 respectively. It is observed from the figure 4.22 that flexural strength increases with increasing fiber loading up to 30 wt-% and then decreases. However, it is found from figure 4.23 that flexural modulus increases with increasing fiber loading. But all the values of flexural strength and flexural modulus are lager than those of 100 wt-% PP matrix and untreated and oxidized jute-PP composites. It is also found that flexural strength of the urea treated jute-PP composites increases from 6% to 22% approximately comparing with raw jute-PP composites but it is approximately 3% to 11% higher comparing with oxidized jute-PP composites.

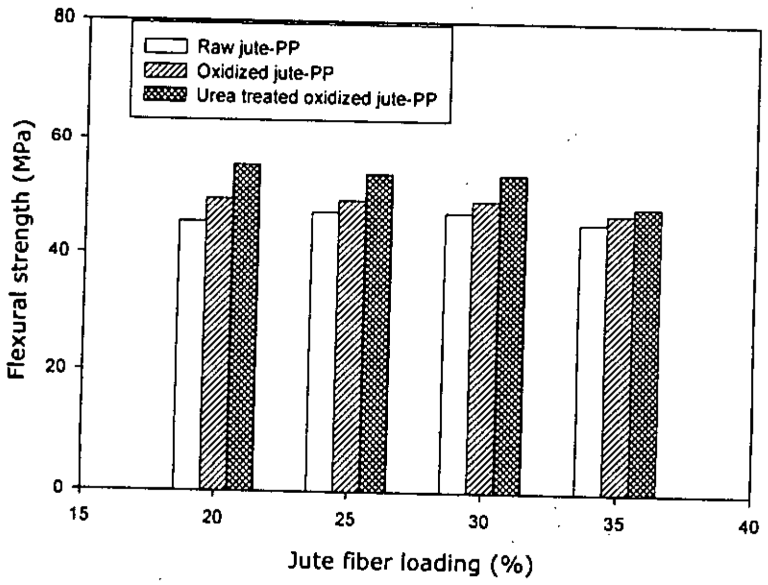


Figure 4.22: Flexural strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urea treated oxidized jute-PP composites

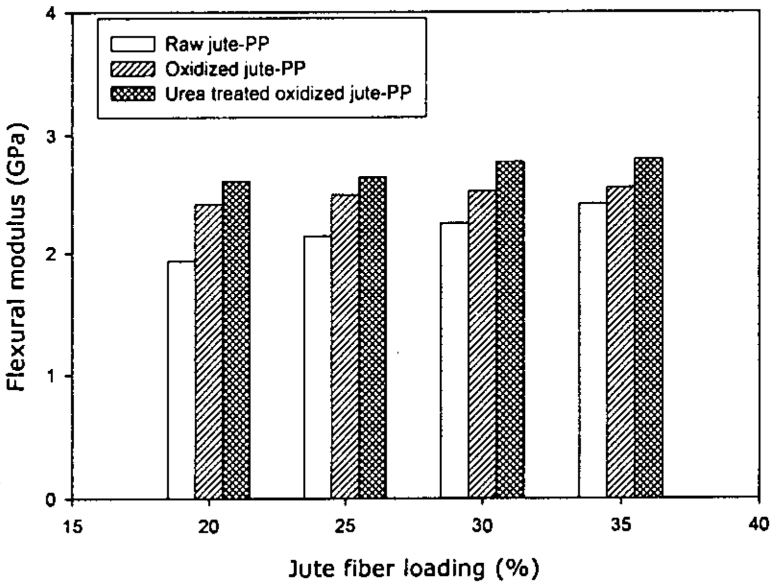


Figure 4.23: Flexural modulus vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urea treated oxidized jute-PP composites

4.4.3.3 Charpy impact strength

The charpy impact test of urea treated oxidized jute-PP composites were carried out in a similar way as that of untreated and oxidized jute-PP composites. The charpy impact strength of the urea treated oxidized jute-PP composites are shown in Figure 4.24. and Table 4.6. It is observed from the figure that charpy impact strength of urea treated oxidized jute-PP composites increases significantly than the untreated jute-PP and oxidized jute-PP composites. These may be first due to mechanical entanglement between the jute fiber and polymer matrix (for raw jute-PP composites), secondly better mechanical entanglement between open structure of oxidized jute and PP matrix and finally coupling reactions between aldehyde group of oxidized jute with urea molecule in the composite material.

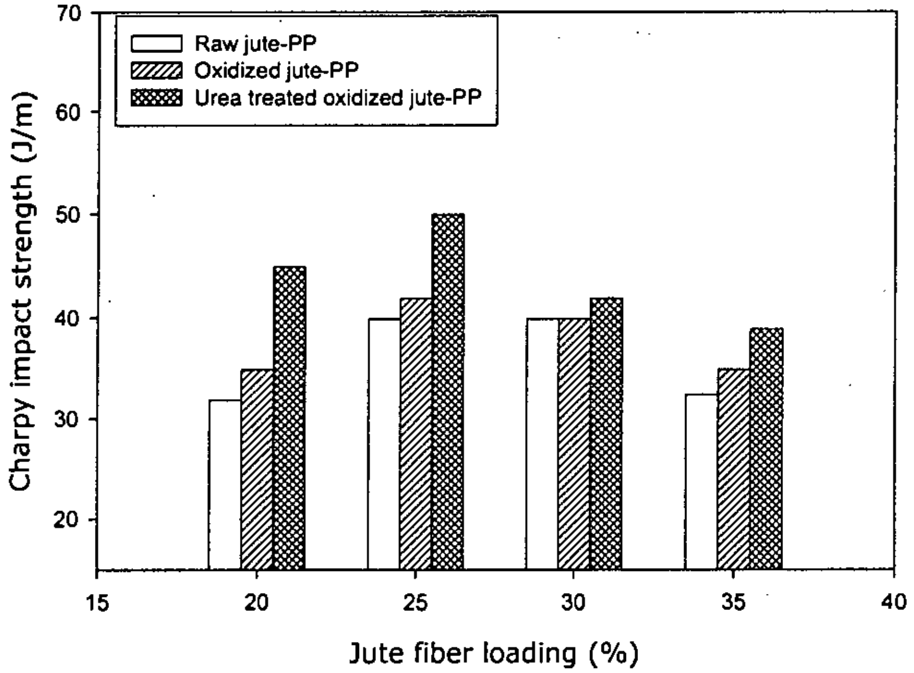


Figure 4.24: Charpy impact strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urea treated oxidized jute-PP composites

4.4.3.4 Hardness

Rockwell hardness results of the composites are presented in Table 4.7. It is observed from the table that urea coupling increases the Rockwell hardness of the urea treated oxidized jute-PP composites than the raw jute-PP composites and oxidized jute-PP composites. It is also found that Rockwell hardness increases with increasing fiber loading of the composites. Rockwell hardness of the composites is significantly higher than the PP polymer matrix.

4.4.4 Effect of urea on the mechanical properties of composites

In this work the mechanical properties of 20 wt% to 35 wt% fiber loaded urea treated composites have been investigated. All the mechanical properties according to series of formulations of the composites are given in the Table 4.6. The observed mechanical properties of urea treated jute-PP composites are in general higher than the raw and oxidized jute-PP composites. Coupling of urea in the oxidized jute-PP composites enhances the mechanical properties of the composites by improving the interfacial adhesion between urea reacted jute and PP matrix. The hydrophilic nature of urea treated oxidized jute may not be less than the hydrophilic nature of untreated jute as carbamide group is more polar than hydroxyl group. So it can be said that coupling of urea to the oxidized jute enhances the mechanical properties of urea reacted oxidized jute-PP composites but not the hydrophilic nature. Tensile strength of the composites increases significantly. Elongation at break of the composites also increases which indicates that urea coupling reaction increases the ductility of the composites. It is also found that tensile strength of all different types of composites decreases with the increase of polymer loading. R. Karanani et al[40] reported the improved mechanical properties of silane modified kenaf fiber reinforced maleic anhydride modified PP composites. They obtained the increased tensile and bending property with increasing fiber loading and this was happened by forming a new covalent bond of the modified fiber surface with modified PP matrix. In our observation, hydrophobic nature of PP was unaffected in the urea treatment procedure and thus it may be assumed that there is no chemical bond formation between PP matrix with fiber. This might be cause of not improving the tensile strength with increasing fiber loading. Though urea reacted with oxidized jute but there is no direct chemical bond between PP matrix and urea reacted jute or between PP matrix and urea. So the mechanical properties of urea reacted oxidized jute-PP composites were increased up to 30 wt-% fiber loading and then decreased after this limit. This may be attributed to the fact that the presence of large amount of fibers in the composite increases the intermolecular type of attraction between urea reacted fiber to urea reacted fiber than the urea reacted fiber to PP matrix. Intermolecular or intramolecular attraction between urea treated fibers or within urea treated fiber decreases the adhesion and wettability of urea treated jute to the PP matrix. So, from this observation, it may be said that the bonding between PP matrix and urea reacted jute fiber is needed to keep the increased mechanical properties at large amount fiber loading in the composites, which might be possible by the chemical modification of PP matrix there by changing its hydrophobic nature to hydrophilic nature.

Table 4.7: Results of mechanical tests of urea treated oxidized jute reinforced PP composites comparing with the raw jute-PP and oxidized jute-PP composites.

Material	Tensile			Flexural		Charpy Impact Strength, J/m	Rockwell Hardness (L Scale)
	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)		
PP only	27.20	0.79	More than 150	42.63	1.28	22.34	66.4
PP-Raw jute 20% (wt)	25.74	1.68	8.65	45.47	1.93	31.84	77.2
PP-Raw jute 25% (wt)	25.38	1.70	6.75	47.17	2.14	39.87	80.2
PP-Raw jute 30% (wt)	24.17	2.14	4.53	47.17	2.25	39.87	82.4
PP-Raw jute 35% (wt)	24.66	2.22	3.79	45.47	2.41	32.34	85.4
PP-Oxidized jute 20% (wt)	27.07	1.71	9.68	49.45	2.41	34.85	77.6
PP-Oxidized jute 25% (wt)	26.35	2.00	7.02	49.22	2.49	41.88	80.4
PP-Oxidized jute 30% (wt)	25.14	2.23	6.48	49.22	2.52	39.87	83.6
PP-Oxidized jute 35% (wt)	25.50	2.31	4.2	47.06	2.55	34.85	87.4
Urea treated PP-Oxidized jute 20% (wt)	30.70	1.92	8.88	55.42	2.61	44.90	89.4
Urea treated PP-Oxidized jute 25% (wt)	29.73	2.09	7.02	53.99	2.64	49.93	91.2
Urea treated PP-Oxidized jute 30% (wt)	29.01	2.26	5.10	53.99	2.77	41.88	91.6
Urea treated PP-Oxidized jute 35% (wt)	27.07	2.33	5.02	48.31	2.79	38.86	92.2

4.4.5 Morphological (SEM) characterization of urea treated oxidized jute fiber reinforced polypropylene composites

To study the surface morphology of the prepared composites scaning electron micrograph (SEM) were taken using urea treated 30% wt oxidized jute-PP composite. Scratched pieces from fracture surfaces of tensile test specimens were used to take SEM. It is shown in the Figure 4.25.

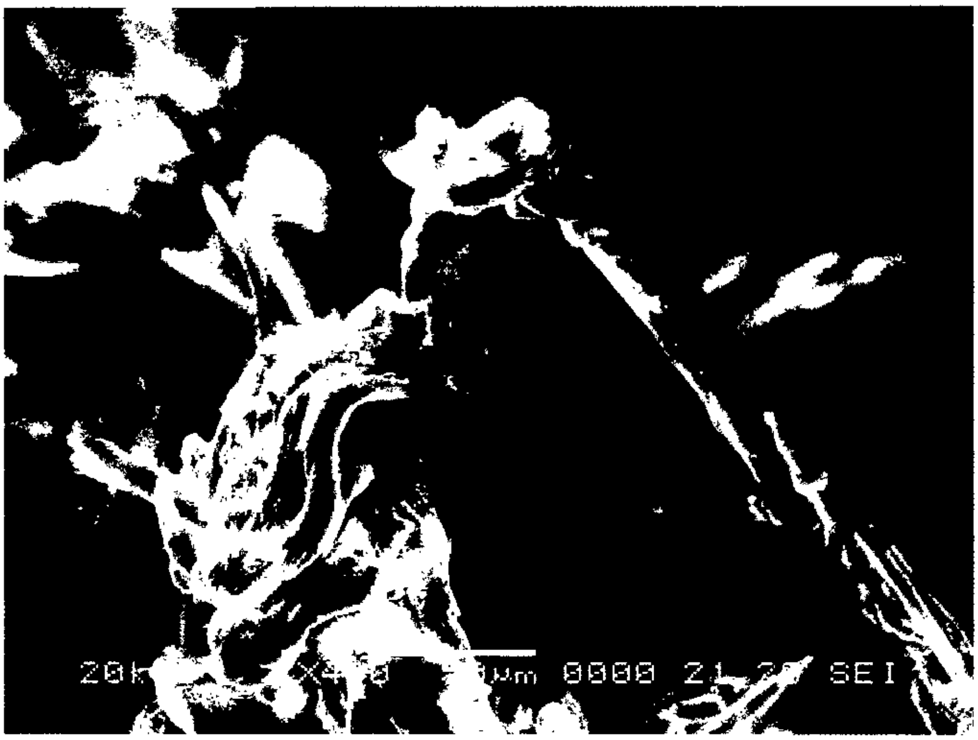


Figure 4.25: SEM micrograph of urea treated 30 wt-% oxidized jute- PP composite

It is found that PP matrixes are attached on the fiber surfaces due to the adhesion and wettability between urea reacted fiber and PP matrix. Interfacial interaction between fiber and matrix is more in the urea treated oxidized jute-PP composite than raw jute-PP composite. Coupling of urea with oxidized jute might be increases this interfacial adhesion and bonding of fiber and PP matrix in the urea treated oxidized jute-PP composites.

4.4.6 Water absorption

Water absorption of urea treated oxidized jute-PP composites are found to more than those of raw and oxidized jute-PP composites. So the water absorption results are not good for urea treated oxidized jute-PP composites. This may be due to the effect of polarity of functional group. Organic amide group is more polar than aldehyde and hydroxyl group. Urea is a carbamide and has amide group. So, treatment with of urea though increases the mechanical properties of the composites but didn't decrease the water absorption of the composites. Results of water absorption of the urea treated jute-PP composites are shown in the Figure 4.26 and Table 4.8.

Table 4.8: Water absorption of the urea treated oxidized jute-PP composites

Material	2 h in boiling water (%)	24 h in cold water (%)
PP only	0.099	0.03
urea treated PP-Oxidized jute (20 wt-%)	0.81	0.48
urea treated PP-Oxidized jute (25 wt-%)	0.97	0.56
urea treated PP-Oxidized jute (30 wt-%)	1.15	0.67
urea treated PP-Oxidized jute (35 wt-%)	1.32	0.76

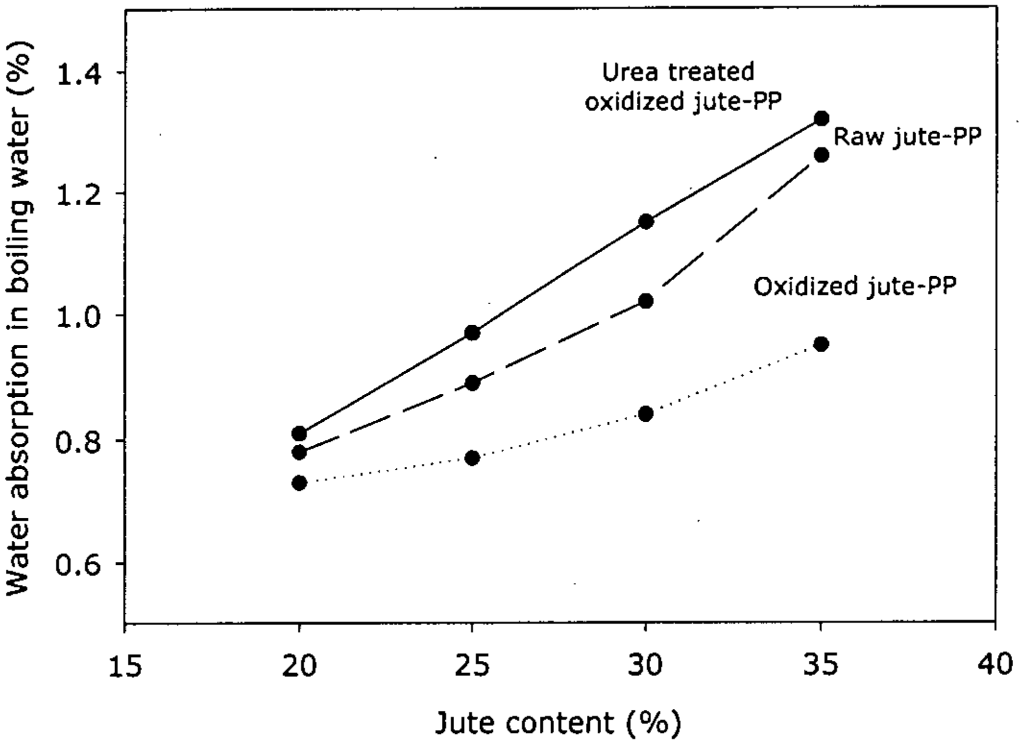


Figure 4.26: Water absorption vs fiber content (wt%) curves for raw, oxidized jute-PP composites and urea treated jute-PP composites

4.5 Urotropine treated oxidized jute fiber reinforced polypropylene (PP) composites

To improve the physico-mechanical properties of jute reinforced composites we have treated our prepared composites with urotropine. urotropine is a very cheap and easily available organic substances which contains interlinked four rings. Each ring contains nitrogen atoms with loan pair of electrons. The loan pair of electron may help to occur coupling reaction with jute fiber. As a result there is a possibility of improving the mechanical properties of the composites.

4.5.1 Coupling reaction of urotropine with oxidized jute fiber reinforced polypropylene (PP) composites

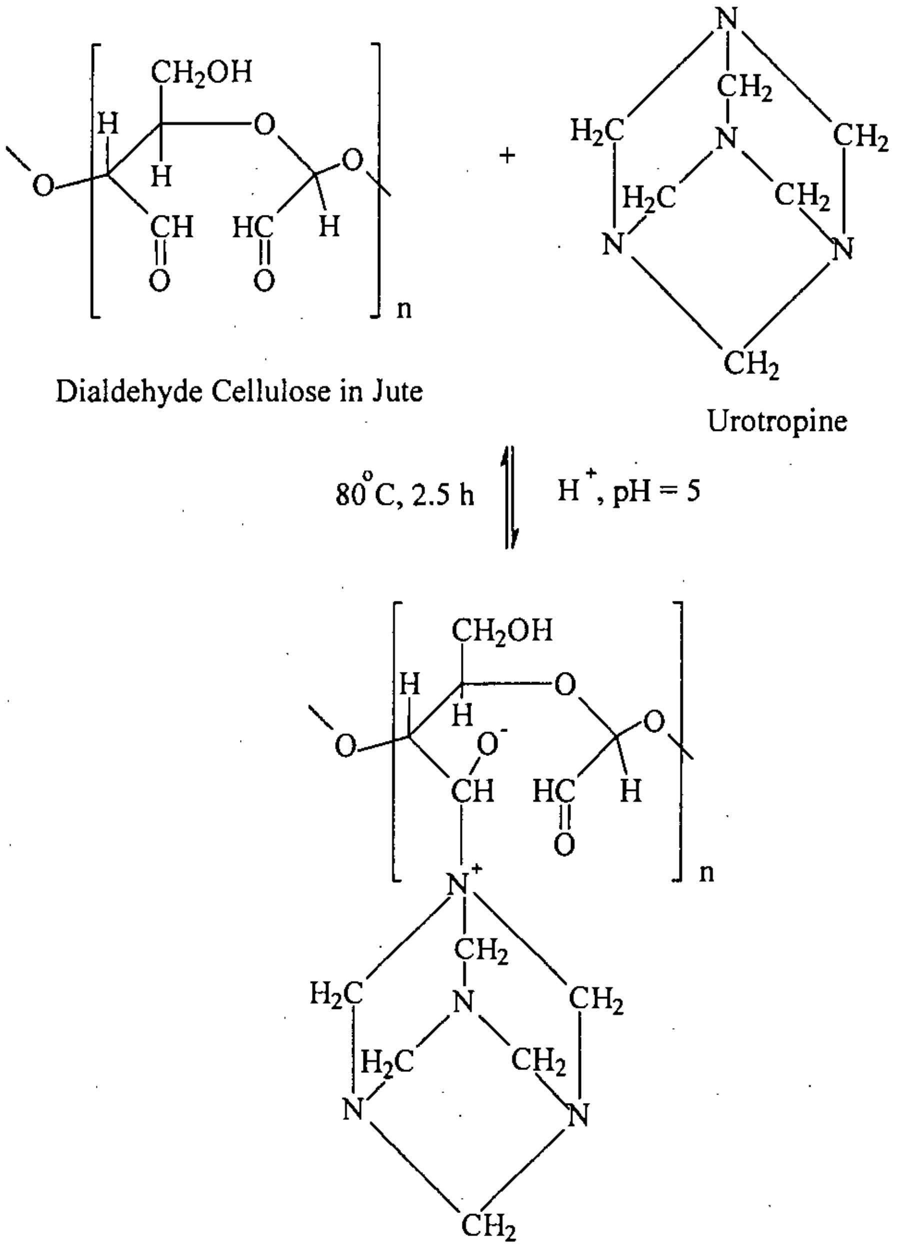
Urotropine is a tertiary amine which is used in the preservation of hides and in medicine as an antibacterial agent. It is a non-hygroscopic and stable reagent of low toxicity. The reaction procedure of urotropine with oxidized jute-PP composites has been described in the experimental section. Reaction parameters such as time, temperature, pH and concentration of urotropine were investigated to get the proper reaction condition. 25 wt-% fiber reinforced composites were used to find out the reaction condition to get maximum tensile strength. The reaction parameters time, temperature and pH were investigated on weight percent gain (WPG) measurement of the composites and these were found to be 2.5 hours, 80^0C and 5 respectively. The concentration of urotropine in impregnating solution was measured on increasing of tensile strength property and was found to be 15% (wt). It was found that the WPG increases with increasing time, temperature, pH and concentration of the urotropine solution. It was also found that the tensile strength didn't increase with increasing WPG after a certain level. This may be due to the fact that at higher WPG than 15%

(wt) the crystalline region of jute-PP composites might be disrupted. G.S. Tay et al[102] reported approximately similar observation about the effect of WPG on tensile strength of composites made with EFB fibers modified with epichlorohydrin. The concentration of urotropine in impregnating solution after 10-15% (wt) didn't affect the WPG and tensile strength property considerably. M. Andersson et al[20] reported the similar observation on acetylation of jute fiber. The WPG data for all composites at 15% urotropine treatment solution are given in the Table below:

Table 4.9: WPG data of urotropine treated oxidized jute-PP composites

Urotropine treated composites	WPG of the composites	WPG according to jute content of the composites
20:80 (wt %) Oxidized jute-PP	0.19	12.32
25:75 (wt %) Oxidized jute-PP	0.24	12.16
30:70 (wt %) Oxidized jute -PP	0.35	14.45
35:65 (wt %) Oxidized jute -PP	0.51	17.96

Similar to the treatment with urea it is also observed from the table that the percentage of weight gain increases with increase of percentage of jute fiber in the composites. From this result it may be suggested that coupling reaction between urotropine and oxidized jute-PP composites takes place during the post treatment of jute composite. The proposed reaction scheme of urotropine with oxidized jute in the oxidized jute-PP composites is as follows:



Scheme 4.3: Proposed reaction mechanism of urotropine with oxidized jute in the oxidized jute-PP composite

During oxidation of jute fiber the alcohol group of cellulose molecules has been converted into aldehyde group. Aldehyde group of oxidized cellulose might be linked with urotropine by quaternization of its tertiary amine group during the post treatment of composites. A zwitterionic type product might be formed by azomethinium ion linkage. Such type zwitterionic amine-aldehyde adduct was shown to form and reported by A. J. Kirby et al.[112] Such type bonding was also reported by E. M. Hawes[113]. He reported that a quaternary ammonium-linked glucuronide metabolite (*i.e.* N^+-glucuronide) was formed by Glucuronidation of either an aliphatic or aromatic tertiary amine group in a molecule. Here, azomethinium ion formed between carboxyl group and tertiary amine group. From results of our study this type of azomethinium linkage between aldehyde group and tertiary amine group is also expected. The FT-IR spectroscopic characterization of proposed reaction's product is given below.

4.5.2 FT-IR spectroscopic characterization of urotropine treated oxidized jute fiber reinforced polypropylene composites

The FT-IR spectrum of urotropine treated 30 wt-% oxidized jute-PP composites is shown in Figure 4.27. The change in the absorption bands was compared with the absorption bands of 30 wt-% oxidized jute-PP composite (Fig. 4.5). Approximately similar type spectroscopic observations were found both for urea and urotropine treated oxidized jute-PP composites at the region 1500-1750 cm^{-1}. But different spectrum region were found at 3000-4000 $cm^{-1}$and 1250-1500 cm^{-1}. A comparison of IR spectra of oxidized jute-PP composites with urotropine treated oxidized jute-PP composites indicates that the peak intensity of hydroxyl group at the region

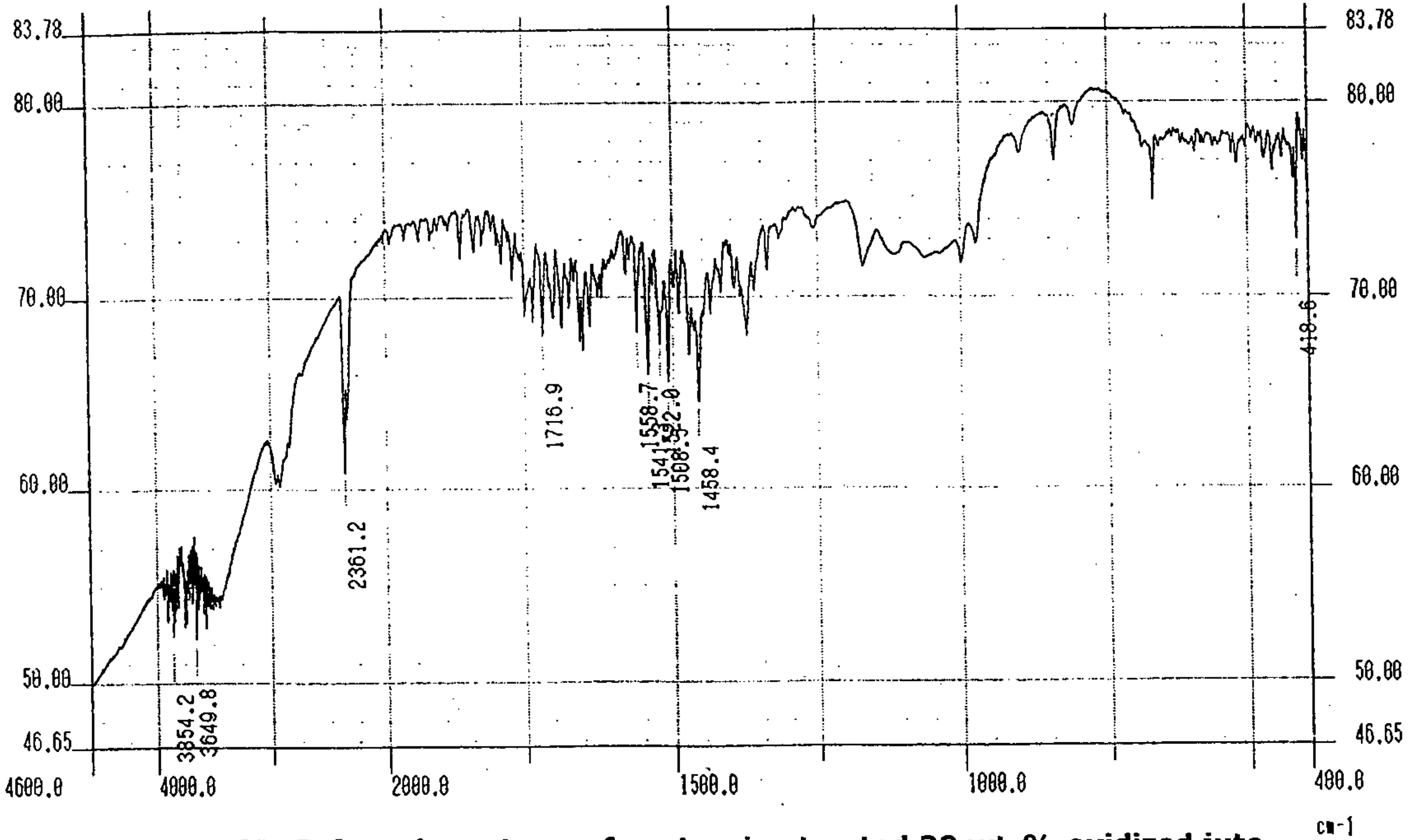


Figure 4.27: Infrared spectrum of urotropine treated 30 wt-% oxidized jute fiber reinforced polypropylene composites

3200-3600 cm^{-1} of urotropine treated oxidized jute-PP composite decreases significantly. This observation indicates that the tertiary amine ring of urotropine didn't break in the reaction. Since tertiary amines do not absorb in this region of the spectrum[91] so the peak intensity didn't increase at this region by overlapping. But the reduced peak intensity at this region of urotropine treated oxidized jute-PP composites comparing with oxidized jute-PP composite indicate that there might be some bond formation between hydroxyl group and urotropine which reduces the peak intensity of hydroxyl group. E. M. Hawes[113] reported that there is no sharp absorption band in an IR spectrum characteristic of the cationic center. But in our study we have observed approximately the similar spectrum at the region 1500-1750 cm^{-1} of urotropine treated oxidized jute-PP composite comparing with urea treated oxidized jute-PP composite. The new additional absorption band was found at the region 1590cm^{-1} like urea treated oxidized jute-PP composite and from this observation we assumed that azomethinium ion of urotropine treated oxidized jute-PP composite might be given the same absorption band like azomethine group of urea treated oxidized jute-PP composite.The absorption bands in the region 1710-1750cm^{-1} may be arised from the carbonyl stretching due to the acetyl and carboxyl groups of hemicelluloses, aldehyde or aliphatic ketone and esters in lignin and extractives of natural fibers. From the spectroscopic observation of urotropine treated oxidized jute-PP composite comparing with oxidized jute-PP composite, it is assumed that one aldehyde group of dialdehyde cellulose might be participated in the reaction and the other aldehyde group was free due to short time reaction period. So, there is no significant change in the crabonyl region at 1716 cm^{-1}. This might be due to the overlapping of this free aldehyde group with other various carbonyl groups present (above said) in the jute fibers. Absorption band at

1320 cm^{-1} might be due to C-N stretching of urotropine. So, though the FT-IR spectrum of this sample is quite complex but the above said evidences of different peak assignments support this reaction.

4.5.3 Mechanical properties of urotropine treated oxidized jute fiber reinforced polypropylene composites

Tesile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, charpy impact strength and hardness of urotropine treated oxidized jute fiber reinforced polypropylene composites have determined following the ASTM method described in the experimental sections. The results obtained in this study are presented below.

4.5.3.1 Tensile strength, modulus and elongation at break

The tensile strengths of the urotropine treated oxidized jute-PP composites are significantly higher than those of raw jute fiber reinforced-PP and oxidized jute fiber reinforced-PP composites up to 30% (wt) fiber loading. At 35 wt-% fibers loading, the tensile strength is similar to the PP matrix. In our experimental results it is found that tensile strength of urotropine treated oxidized jute fiber reinforced PP composites increases approximately 10% to 21% over the raw jute-PP composites but it is increased by approx. 7% to 17% than that of oxidized jute-PP composites. It is also found that elongation at break of the composites also increases in comparison to raw jute-PP composites. This indicates that the ductility of the composites increases by the urotropine treatment of jute fiber. The tensile strength of the composites decreases with increasing fiber loading (Fig. 4.28). However, the tensile modulus of the composites increases with increasing fiber loading (Fig. 4.29). Tensile stress vs strain graph for urotropine treated 20 wt-% oxidized jute-PP composites are shown in Figure 4.31 along with those of 100 wt-% PP matrix, raw and oxidized jute-PP composites.

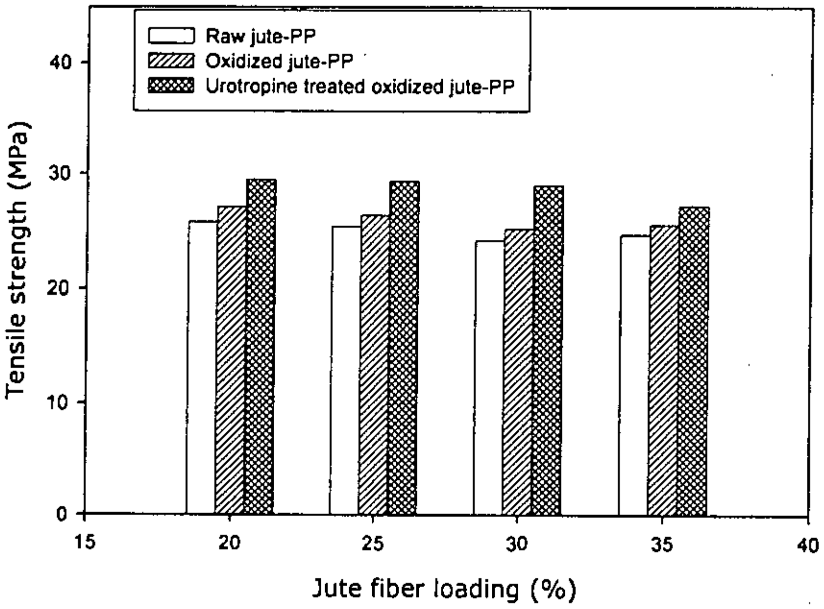


Figure 4.28: Tensile strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

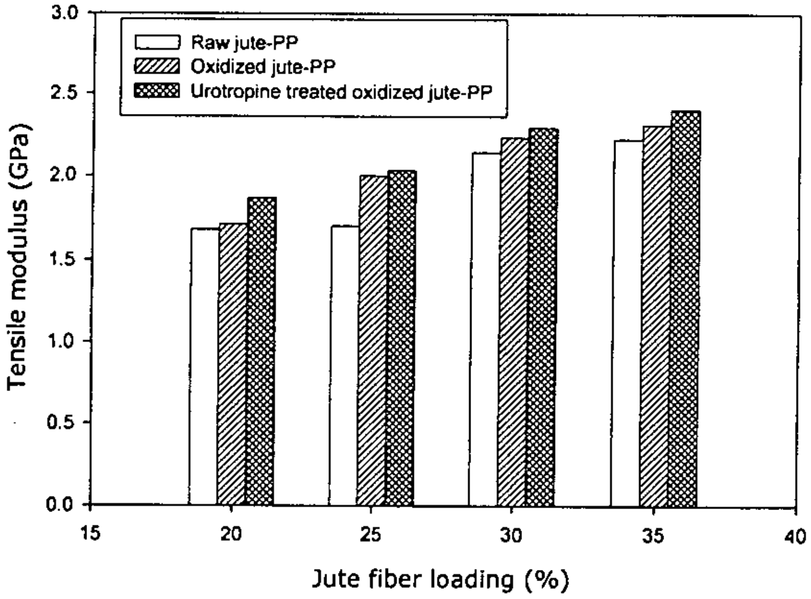


Figure 4.29: Tensile modulus vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

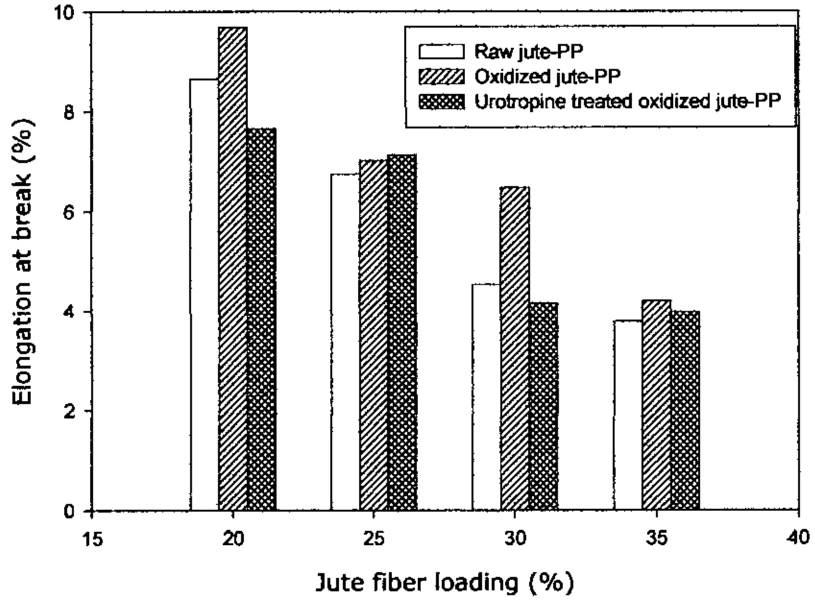


Figure 4.30: Elongation at break vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

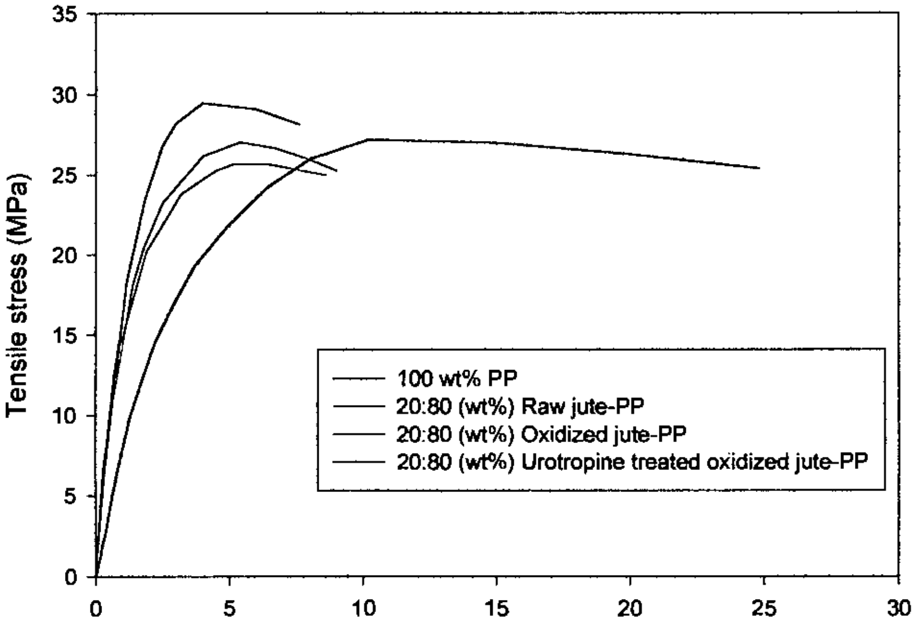


Figure 4.31: Tensile stress vs strain (%) curves for PP matrix, 20 wt% raw and oxidized jute-PP composite and urotropine treated oxidized jute-PP composite

4.5.3.2 Flexural strength and modulus

Flexural strength and modulus of the prepared composites are determined following methods described earlier in experimental section. The results on flexural strength and flexural modulus are presented in figure 4.32 and 4.33 respectively. It is observed from the results that the flexural strength of urotropine treated oxidized jute-PP composites increases with increasing fiber loading up to 30 wt-% and then decreases (Fig. 4.32). However, the flexural modulus increases with increasing fiber loading (Fig. 4.33) without any decrease. The values of flexural strength and flexural modulus of all oxidized jute fiber-PP and urotropine treated jute fiber PP-composites are found to be more than that of raw jute fiber-PP composites. It is also found that flexural strength of the urotropine treated jute-PP composites increases 7% to 19% approximately compare to the raw jute-PP composites but it is approximately 4% to 8% higher compare to oxidized jute-PP composites.

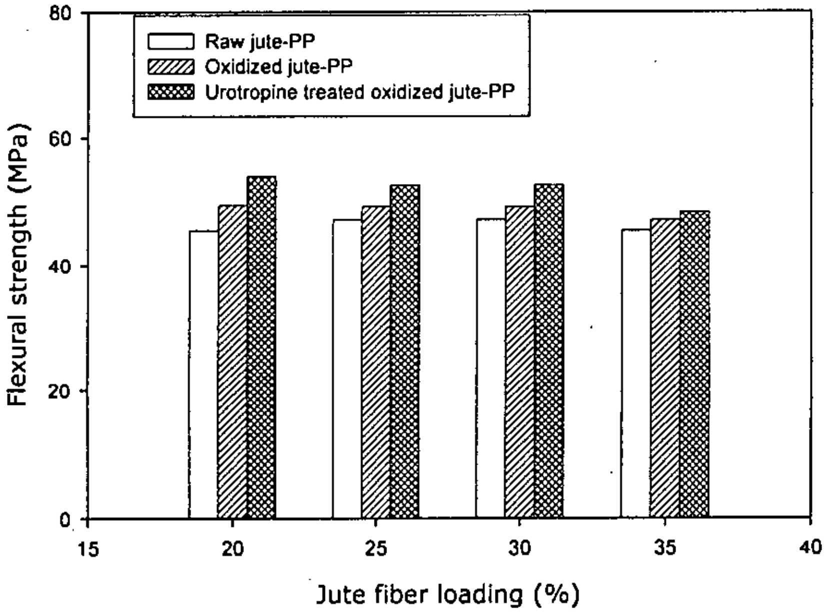


Figure 4.32: Flexural strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

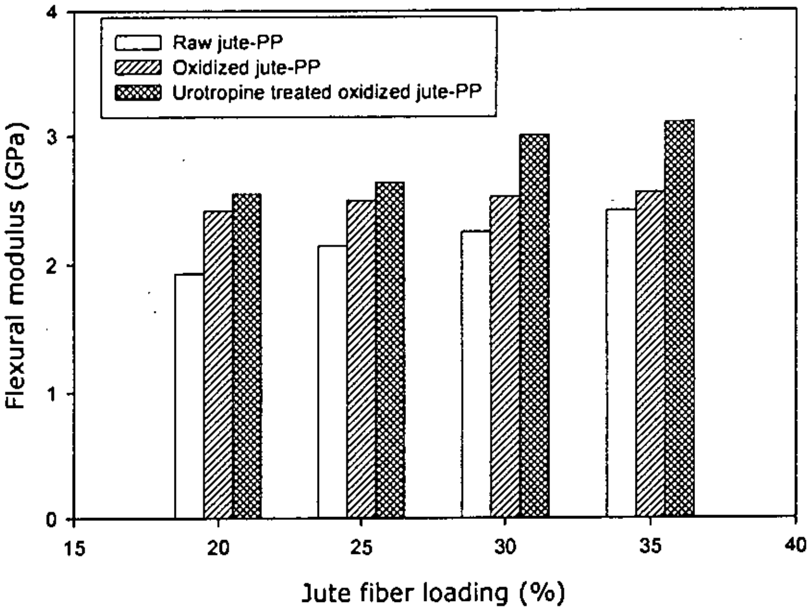


Figure 4.33: Flexural modulus vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

4.5.3.3 Charpy impact strength

The charpy impact strength of the urotropine treated oxidized jute-PP composites are shown in Figure 4.34. and Table 4.10. It is apparent from the figure that charpy impact strength of all composites is significantly higher than PP polymer matrix. Charpy impact strength of the composites decreases with increasing fiber loading. Improved results were obtained for urotropine treated oxidized jute-PP composites than raw and oxidized jute-PP composites.

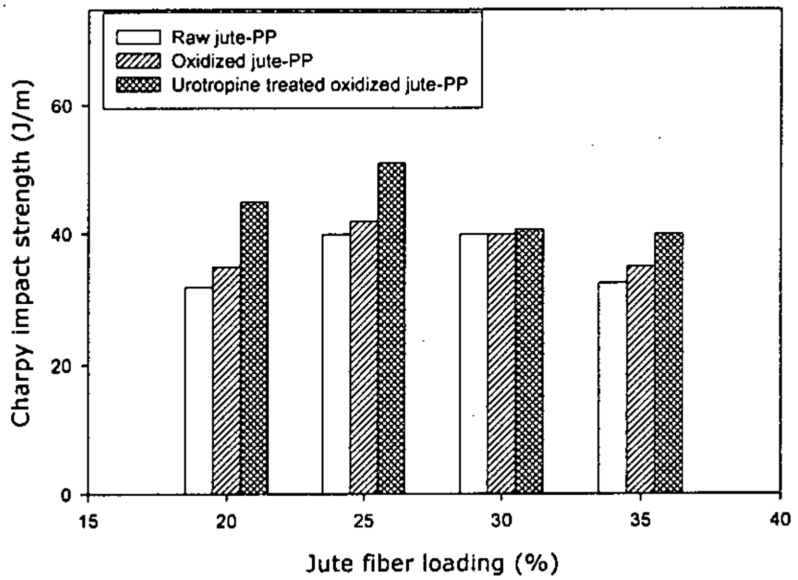


Figure 4.34: Charpy impact strength vs fiber loading (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

4.5.3.4 Hardness

Rockwell hardness results of the composites are presented in Table 4.10. It is found that Rockwell hardness of the urotropine treated oxidized jute-PP composites is higher than raw jute-PP composites and oxidized jute-PP composites. It is also found that Rockwell hardness of the composites is higher than PP polymer matrix and it increases with increasing fiber loading of the composites.

4.5.4 Effect of urotropine on the mechanical properties of composites

In this work we have investigated the mechanical properties of 20 wt% to 35 wt% fiber loaded urotropine treated composites. All the mechanical properties according to series of formulations of the composites are given in the Table 4.10. The mechanical properties of urotropine treated jute-PP composites are found to be more than the raw and oxidized jute-PP composites. Coupling of urotropine in the oxidized jute fiber reduces the hydrophilic nature of the oxidized jute, which might increase the mechanical properties of the urotropine treated oxidized jute-PP composites. Urotropine coupling increases the interfacial adhesion between urotropine treated oxidized jute and PP matrix. From experimental values it is found that mechanical properties didn't increase significantly at 35 wt-% fiber loaded jute-PP composite. R. Karanani et al[40] reported the improved mechanical properties of silane modified kenaf fiber reinforced maleic anhydride modified PP composites. They obtained the increased tensile and bending strength with increasing fiber loading and this was happened by forming a new covalent bond of the modified fiber surface with modified PP matrix. In this work it is observed that the tensile strength of jute-PP composite decreases with the increase of jute fiber loading. This may be due to the fact that the hydrophobic polypropylene may remain unaffected information of composite between raw, oxidized and urotropine treated jute fiber. No chemical bond formation takes place between the treated or untreated jute fiber with the PP matrix. As a result although urotropine reacted with oxidized jute fiber but there is no direct chemical bond formation between PP matrix and urotropine reacted jute or between PP matrix and urotropine. So the mechanical properties of urotropine reacted oxidized jute-PP composites increased up to 30 wt-% fiber loading and then decreased after this limit. This may be attributed that presence of large amount fibers in the composite increases the intermolecular type attraction between urotropine reacted fiber to urotropine reacted fiber than urotropine treated fiber to PP matrix. As a result tensile strength of composite containing large amount fiber decreases. So, it may be said that the bonding between PP matrix and urotropine reacted jute fiber is needed to keep the increased mechanical properties at large amount fiber content. From these observations, it might be expected that tensile property of the urotropine treated jute-PP composites will increase with increasing large amount fiber loading by the chemical modification of PP matrix by changing its hydrophobic nature to hydrophilic nature.

Table 4.10: Results of mechanical tests of urotropine treated oxidized jute reinforced PP composites comparing with the raw jute-PP and oxidized jute-PP composites.

Material	Tensile			Flexural		Charpy Impact Strength, J/m	Rockwell Hardness (L Scale)
	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)		
PP only	27.20	0.79	More than 150	42.63	1.28	22.34	66.4
PP-Untreated jute (20 wt-%)	25.74	1.68	8.65	45.47	1.93	31.84	77.2
PP-Untreated jute (25 wt-%)	25.38	1.70	6.75	47.17	2.14	39.87	80.2
PP-Untreated jute (30 wt-%)	24.17	2.14	4.53	47.17	2.25	39.87	82.4
PP-Untreated jute (35 wt-%)	24.66	2.22	3.79	45.47	2.41	32.34	85.4
PP-Oxidized jute (20 wt-%)	27.07	1.71	9.68	49.45	2.41	34.85	77.6
PP-Oxidized jute (25 wt-%)	26.35	2.00	7.02	49.22	2.49	41.88	80.4
PP-Oxidized jute (30 wt-%)	25.14	2.23	6.48	49.22	2.52	39.87	83.6
PP-Oxidized jute (35 wt-%)	25.50	2.31	4.2	47.06	2.55	34.85	87.4
Urotropine treated PP-Oxidized jute (20 wt-%)	29.49	1.87	7.66	53.99	2.54	44.90	90.4
Urotropine treated PP-Oxidized jute (25 wt-%)	29.37	2.03	7.13	52.57	2.63	50.94	91.4
Urotropine treated PP-Oxidized jute (30 wt-%)	29.01	2.29	4.16	52.57	3.00	40.62	92.2
Urotropine treated PP-Oxidized jute (35 wt-%)	27.20	2.40	3.98	48.31	3.10	39.87	92.4

4.5.5 Morphological (SEM) characterization of urotropine treated oxidized jute fiber reinforced polypropylene composites

Scanning electron microscopy is concerned with surface structure (morphology) of polymer. It reflects the physical chemical interaction between adjacent particles. The morphology of polymer composites mainly depends upon the physical or chemical interaction between components of the composites. In this study scanning electron micrograph of composites were taken and an attempt has been made to correlate the observed mechanical properties with the morphology of the composite.

SEM observation of urotropine treated 30 wt-% oxidized jute-PP composite was taken using scratched pieces of fractured tensile test specimen. It is shown in the Figure 4.35. Strong interfacial bonding is found between the PP matrix and fiber in the composite interphase. Coupling of the urotropine to oxidized jute in the composite increases the interfacial adhesion and wettability between urotropine treated fiber and PP matrix. So, interfacial interaction and bonding between fiber and matrix increases and it is more in the urotropine treated oxidized jute-PP composite comparing with SEM of the raw jute-PP composite (Fig. 4.14).

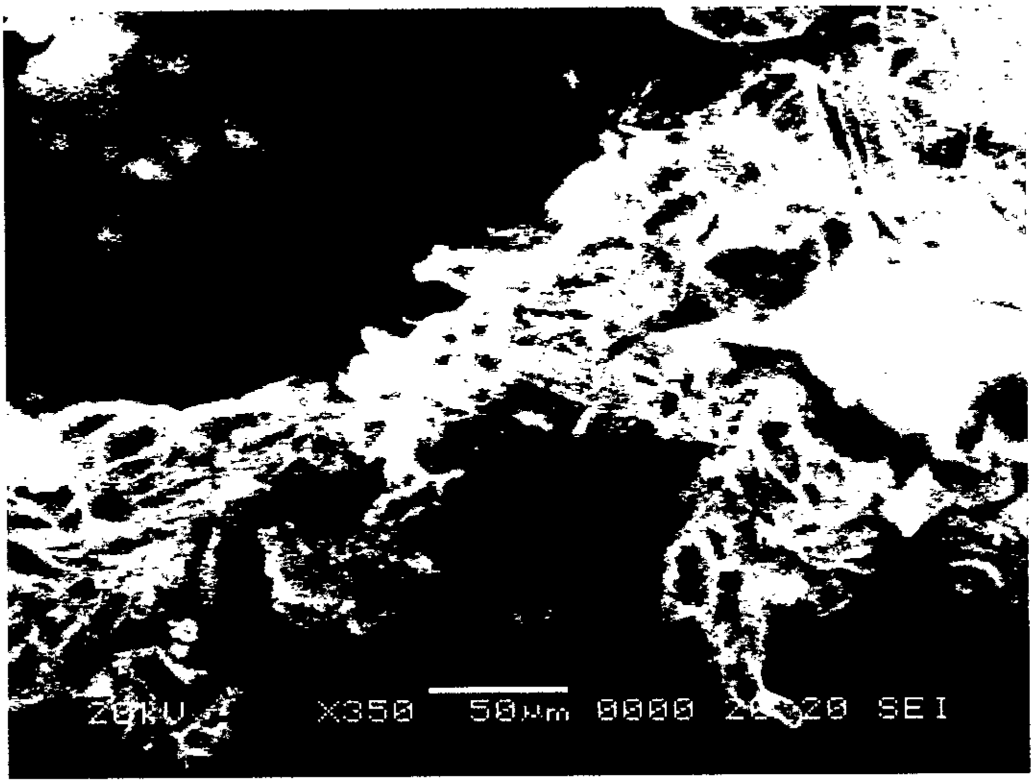


Figure 4.35: SEM micrograph of urotropine treated 30 wt-% oxidized jute- PP composite

4.5.6 Water absorption

Water absorption test is an important tool to investigate quality of jute reinforced composite and their application. Cellulose molecules of jute fiber contain hydroxyl groups which are polar in nature and attract moisture from the atmosphere which is not desirable for a good quality of composites. Water absorption tests of composites in this study were carried out by using the standard method. The results obtained in this study are discussed below:

Results of water absorption of the urotropine treated jute-PP composites are shown in the Table 4.11 and Figure 4.36. It is observed from the results presented in table 4.11 that water absorption of urotropine treated oxidized jute-PP composites are less than that of raw jute-PP composites. But it is approximately similar with the oxidized jute-PP composites. The decrease water absorption of chemically (urotropine) treated oxidized jute-PP composites may be due to tertiary amino group of urotropine is less polar than aldehyde and hydroxyl group. So, the coupling of urotropine decreases the water absorption property of the composites which will improve the dimensional stability of the composites.

Table 4.11: Water absorption of the urotropine treated oxidized jute-PP composites

Material	2 h in boiling water (%)	24 h in cold water (%)
PP only	0.099	0.03
Urotropine treated PP-Oxidized jute (20 wt-%)	0.70	0.30
Urotropine treated PP-Oxidized jute (25 wt-%)	0.77	0.39
Urotropine treated PP-Oxidized jute (30 wt-%)	0.83	0.44
Urotropine treated PP-Oxidized jute (35 wt-%)	0.94	0.50

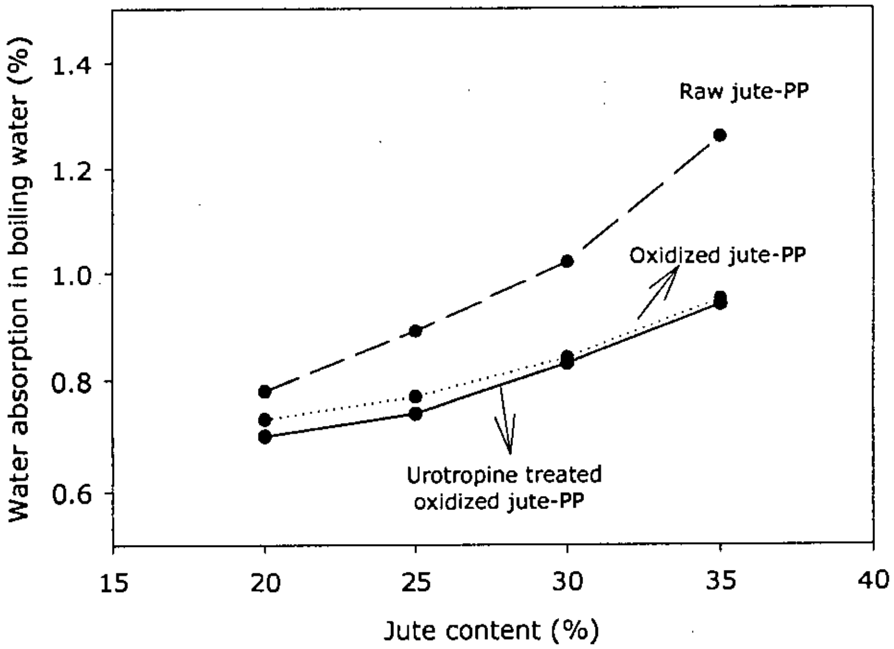


Figure 4.36: Water absorption vs fiber content (wt%) curves for raw, oxidized jute-PP composites and urotropine treated oxidized jute-PP composites

4.6 Maleic acid treated raw jute fiber reinforced polypropylene (PP) composites

In the previous two section the effects of post-treatment of oxidized jute reinforced PP composites using urea and urotropine have been discussed. In this section effect of maleic acid treatment of raw jute reinforced PP composites on their physico-mechanical properties has been discussed.

4.6.1 Coupling reaction of maleic acid with raw jute fiber reinforced polypropylene (PP) composites

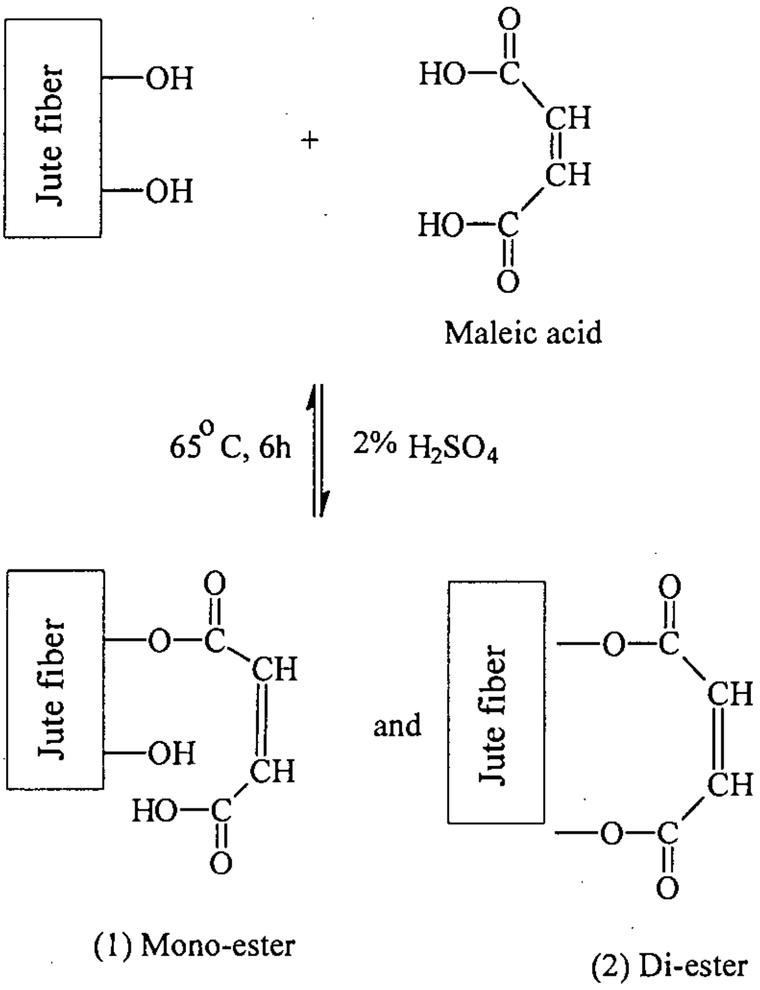
The reaction procedure of maleic acid with raw jute-PP composites has been described in the experimental section. Reaction parameters such as time, temperature and concentration of maleic acid were investigated to get the proper reaction condition. 25 wt% fiber reinforced composites were used to find out the reaction condition to get maximum tensile strength. The reaction parameters time and temperature were investigated on weight percent gain (WPG) measurement of the composites and these were found to be 6 hours and 65^{0}C. The concentration of maleic acid in impregnating solution was measured on increasing of tensile strength property and was found to be 15% (wt). It was found that the WPG increases with increasing time, temperature and concentration of the maleic acid solution. It was also found that the tensile strength didn't increase with increasing WPG after a certain level. This may be due to the fact that at higher WPG than 15% (wt) the crystalline region of jute-PP composites might be disrupted. G.S. Tay et al[102] reported approximately similar observation about the effect of WPG on tensile strength of composites made with EFB fibers modified with epichlorohydrin. The concentration of maleic acid in impregnating solution after 10-15% (wt) didn't affect the WPG and tensile strength property considerably. M. Andersson et al[20] reported the similar observation on acetylation of jute fiber. The WPG data for all composites at 15% maleic acid treatment solution are given in the Table below:

Table 4.12: WPG data of maleic acid treated raw jute-PP composites

Maleic acid treated composites	WPG of the composites	WPG according to fiber content of the composites
20:80 (wt %) Oxidized jute-PP	0.22	14.26
25:75 (wt %) Oxidized jute-PP	0.30	15.32
30:70 (wt %) Oxidized jute -PP	0.39	16.10
35:65 (wt %) Oxidized jute -PP	0.47	16.55

It is observed from the results presented in table 4.11 that WPG increases with the increase of percentage of fiber loading. This may be due to larger amount of maleic acid takes part in the coupling reaction with higher percentage of jute fiber. The proposed reaction of maleic acid with raw jute in the raw jute-PP composites is shown in Scheme 4.4.

According to reaction conditions the produced product might be only the monoester. This is the expected product of our investigation. M. A. Hassan et al[103] reported on the esterification of bagasse fibers by succinic anhydride. They reported that the production of diester contents increased with increasing time and temperature of esterification but the production of monoester contents decreased. They observed, WPG also increased with increasing time, temperature and concentration of succinic acid. M. A. Hassan et al[41] also investigated the effect of esterification on some mechanical properties of bagasse composite. They have reported that diester



Scheme 4.4: Proposed reaction mechanism of maleic acid with raw jute in the raw jute-PP composite

content didn't increase the mechanical properties of the esterified bagasse composites. So, in our study we tried to avoid the production of diester content by controlling the reaction condition. By FT-IR spectroscopic observation it is found that our product seems to be a monoester. The presence of bulky groups near the site of reaction, whether it is alcohol or acid, slows down esterification, as well as it reverses hydrolysis[100]. Steric hindrance, short time reaction period and the presence of large excess maleic acid comparing with the cellulosic fibers present in the composites might slow down the reverse reaction and formation of diester content though the reaction medium was aqueous. The FT-IR spectroscopic characterization of proposed reaction's product is given below.

4.6.2 FT-IR spectroscopic characterization of maleic acid treated raw jute fiber reinforced polypropylene composites

The FT-IR spectrum of maleic acid treated 30 wt-% raw jute-PP composites is shown in Figure 4.37. The change of the absorption bands was compared with the absorption bands of 30 wt-% raw jute-PP composite (Fig. 4.4). The proposed reaction of maleic acid with cellulose in jute was shown in the Scheme 4.4. Comparison with IR spectra of raw jute-PP and maleic acid treated raw jute-PP composites it is clearly observed that the absorption band significantly increased at the region 1735 cm^{-1} which might be due the C=O stretching band of ester linkages. Similar type spectroscopic observation for esterification of fibers were reported by M. Kazayawoko et al[39], L. M. Matuana et al[2] and M. L. Hassan et al[103]. New absorption band is found at the region 1620 cm^{-1} which might be due to C=C of ester. M.J. Saad et al[101] reported the approximately similar spectroscopic evidence of C=C and C=O bond for the maleic anhydride treated empty fruit bunch fibers. The magnified spectra of the region from 1000-2000 cm^{-1} of the raw jute-PP and maleic acid treated raw jute-PP composites are shown in the Figure 4.38 and 4.39 to see the additional absorption bands clearly at 1735 cm^{-1} and 1620 cm^{-1}. These are due to the C=O and C=C stretching. Two absorption bands for C-O-C stretching vibration of ester might be the 1170 cm^{-1} and 1050 cm^{-1} absorption bands of the spectrum. The C=O absorption band of carboxyl group of monoester might be merged at the region 1716 cm^{-1} . And –OH stretching of carboxyl group also might be merged in the region 3200-3600 cm^{-1} so peak intensity didn't reduce at this region. In the spectrum some spectral changes were observed at the absorption bands of PP matrix that might be due to some chemical change or some degradation of PP matrix with maleic acid.

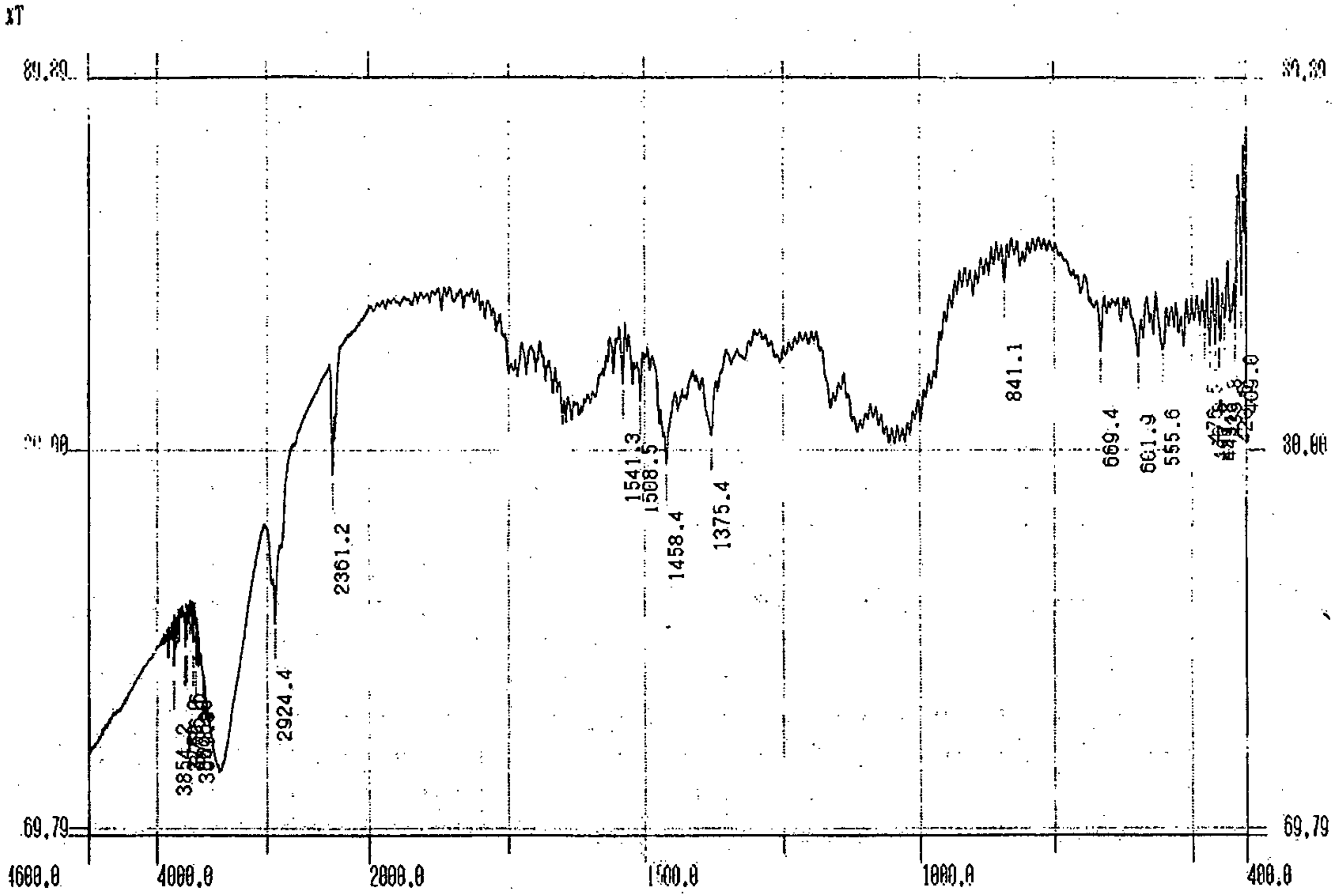


Figure 4.37: Infrared spectrum of maleic acid treated 30 wt% raw jute fiber reinforced polypropylene composites

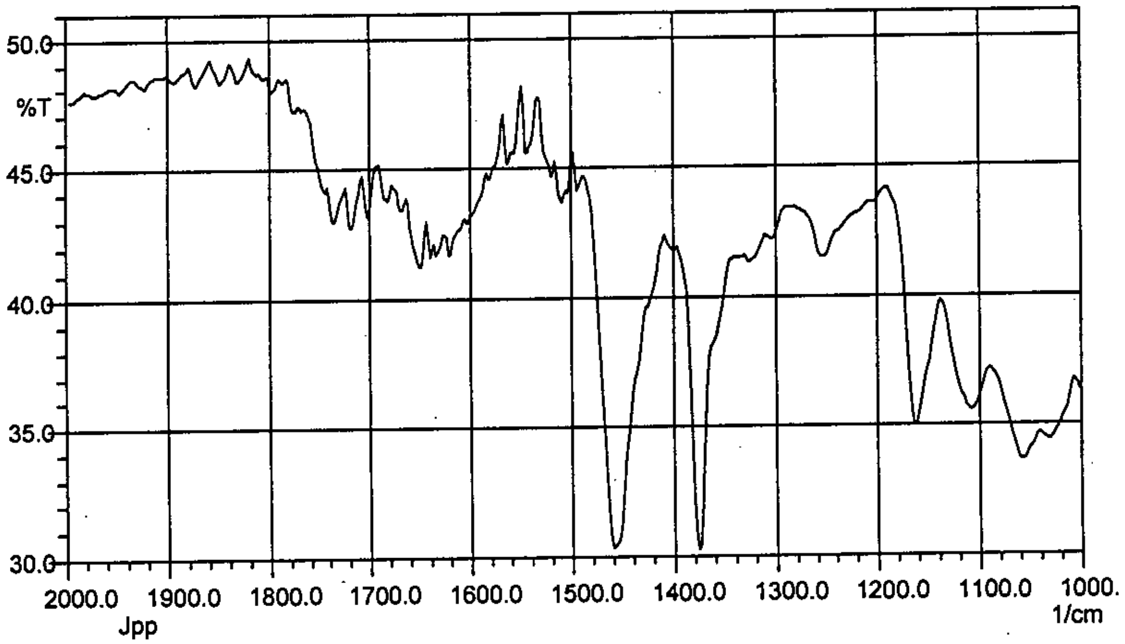


Figure 4.38: The magnified spectrum of the region 1000-2000 cm^{-1} of 30 wt-% raw jute fiber reinforced polypropylene composites

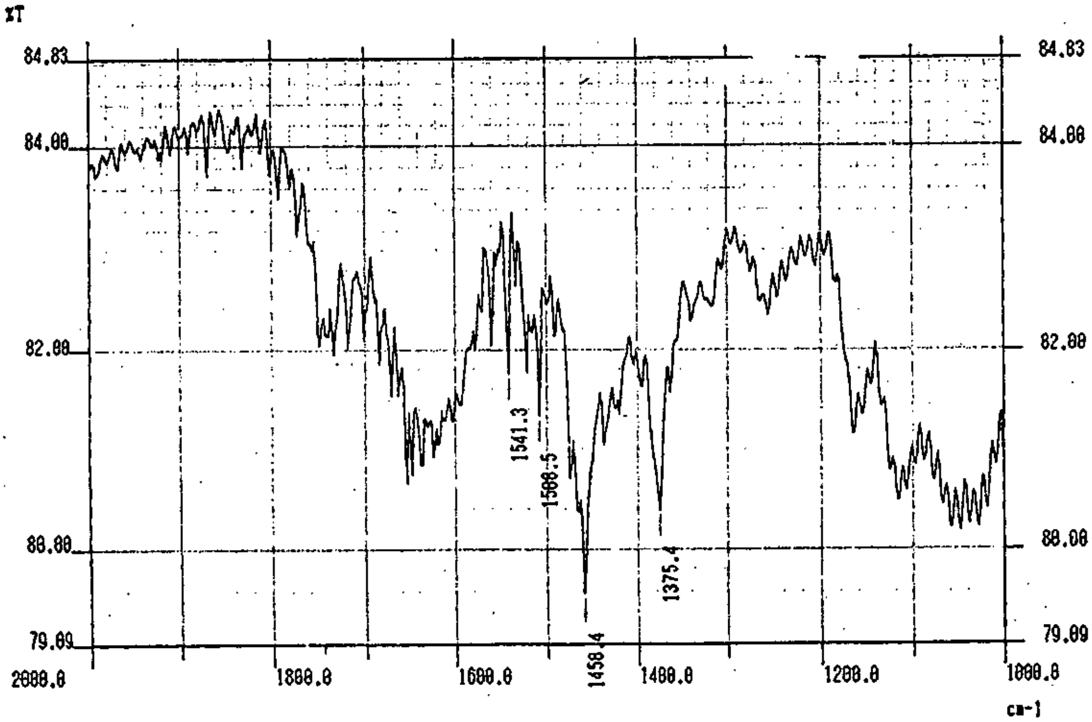


Figure 4.39: The magnified spectrum of the region 1000-2000 cm^{-1} of maleic acid treated 30 wt-% raw jute fiber reinforced polypropylene composites

4.6.3 Mechanical properties of maleic acid treated raw jute fiber reinforced polypropylene composites

To investigate the effect of post-treatment of raw jute reinforced-PP composite materials we have determined the mechanical properties of the composites. The results are discussed in the following section.

4.6.3.1 Tensile strength, modulus and elongation at break

The tensile strengths of the maleic acid treated raw jute-PP composites increases slightly with increasing the fiber loading. At 35 wt-% fibers loading, the tensile strength is approximately similar to the PP matrix. It is found that tensile strength of the maleic acid treated raw jute-PP composites increases approximately 2%-10% more than raw jute-PP composites (Fig. 4.40). Tensile modulus of the composites also increases with increasing fiber loading (Fig. 4.41). It is also found that the elongation at break of these composites has been increased in comparing to raw jute-PP composites (Fig. 4.42). This means that ductility of the composites is also increased. But elongation at break decreases with increasing fiber loading. Tensile stress vs strain graph for maleic acid treated 35 wt% raw jute-PP composite comparing with the PP matrix and raw jute-PP composite are shown in the Figure 4.43.

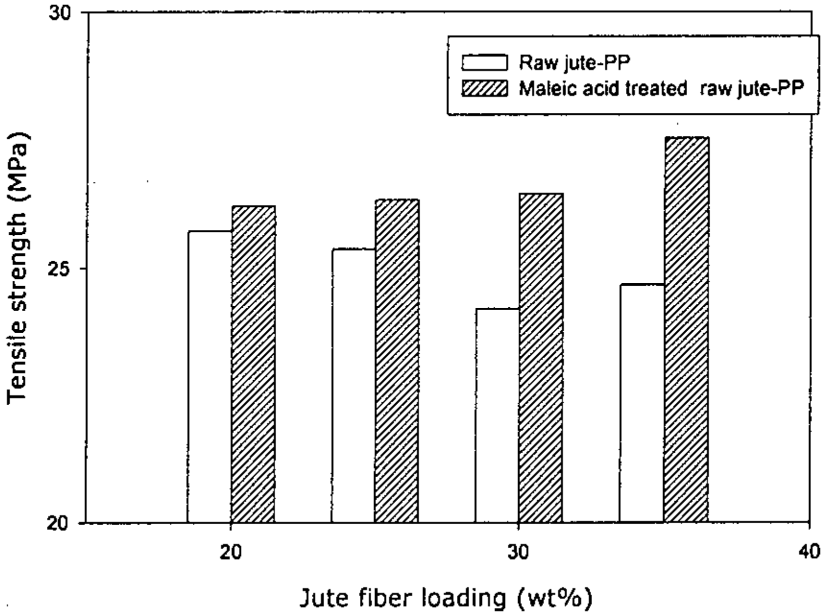


Figure 4.40: Tensile strength vs fiber content (wt%) curves foraw jute-PP composites and maleic acid treated raw jute-PP composites

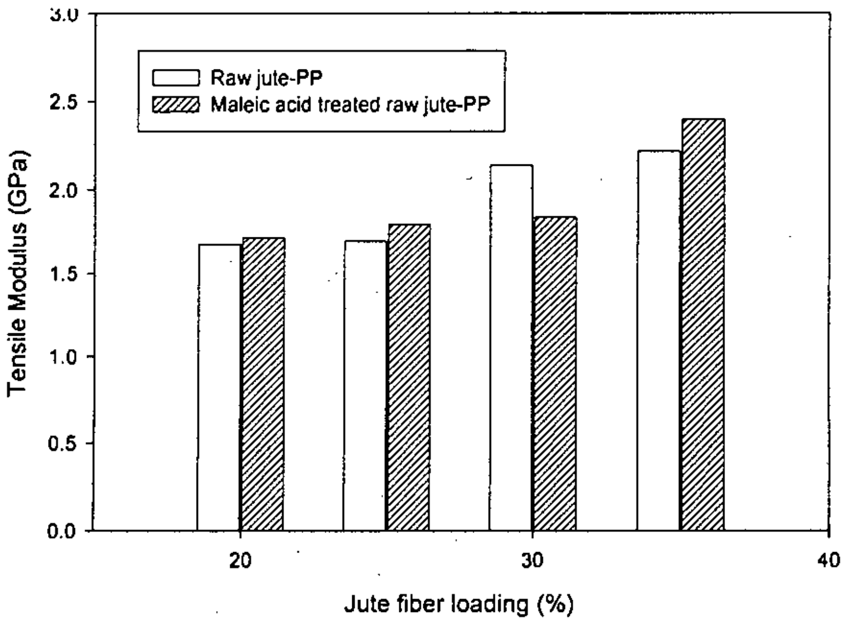


Figure 4.41: Tensile modulus vs fiber loading (wt%) curves for raw jute-PP composites and maleic acid treated raw jute-PP composites

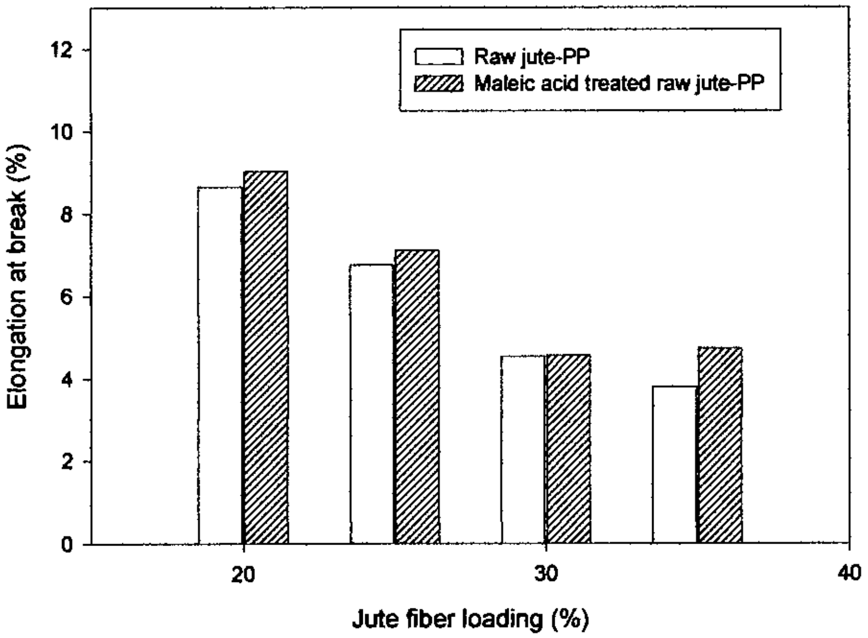


Figure 4.42: Elongation at break vs fiber loading (wt.%) curves for raw jute-PP composites and maleic acid treated raw jute-PP composites

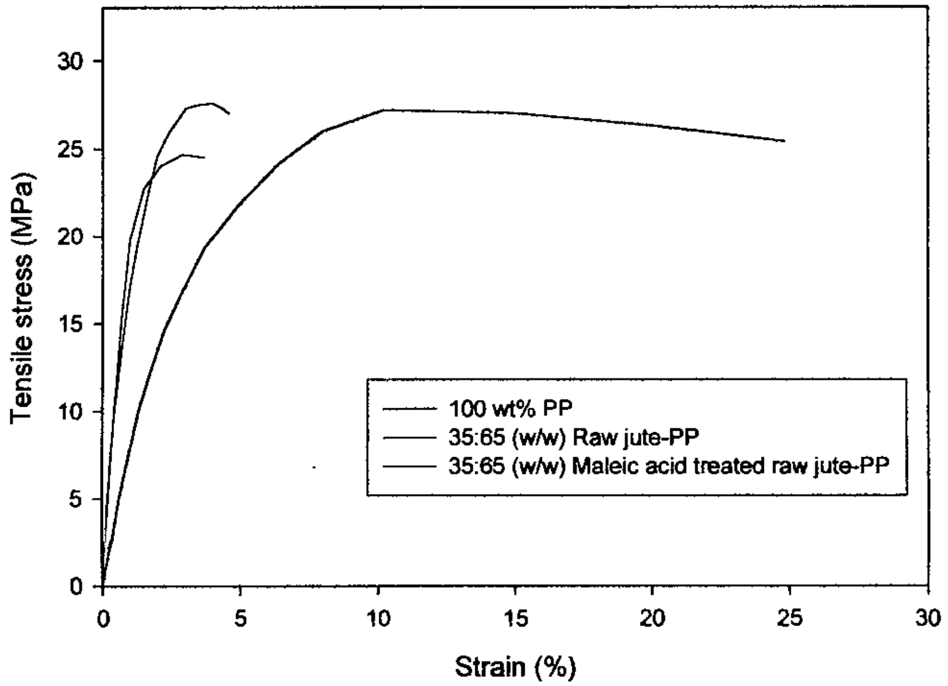


Figure 4.43:Tensile stress vs strain curves for PP matrix, 35 wt% raw jute-PP composite and 35 wt% maleic acid treated raw jute-PP composite

4.6.3.2 Flexural strength and modulus

Flexural strength and modulus of the composites treated with maleic acid have been determined. The obtained results are presented in figure 4.44 and 4.45 respectively. It is observed from the figure that the flexural strength of the maleic acid treated raw jute-PP composites is higher than that of raw jute-PP composites by 7% to 13% (approximately). It is also observed that flexural strength increases with increasing fiber loading. Flexural modulus of these composites also increases with increasing fiber loading. Flexural strength and flexural modulus of these composites shows improved results than that of 100 wt-% PP matrix (Table 4.13).

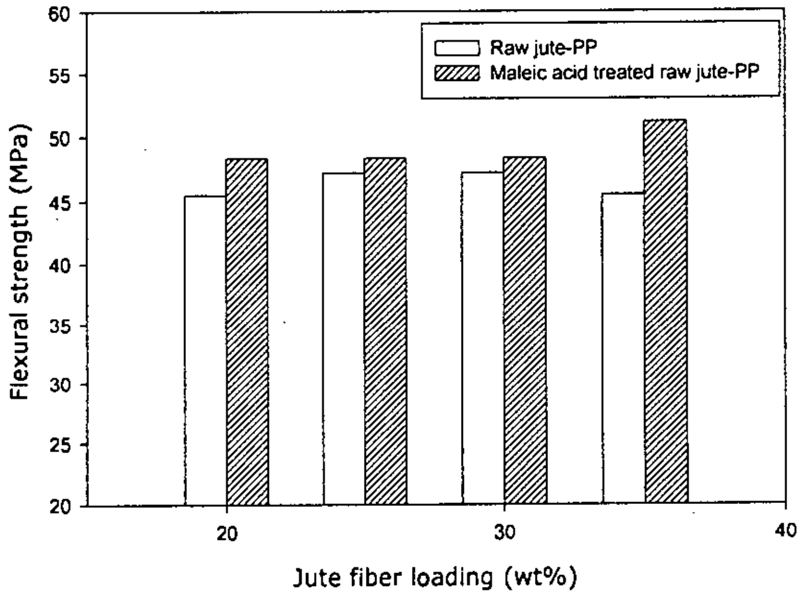


Figure 4.44: Flexural strength vs fiber content (wt%) curves for raw jute-PP composites and maleic caid treated raw jute-PP composites

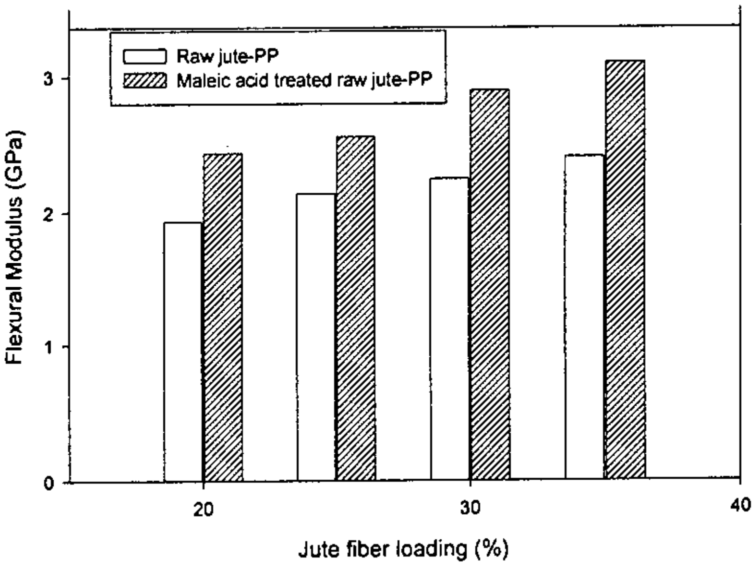


Figure 4.45: Flexural modulus vs fiber loading (wt%) curves for raw jute-PP composites and maleic caid treated raw jute-PP composites

4.6.3.3 Charpy impact strength

Charpy impact strength of the maleic acid treated raw jute-PP composites are shown in Figure 4.46. and Table 4.13. It is found that charpy impact strength of these composites are significantly higher than that of PP polymer matrix. It is also found that charpy impact strength of composite decreases with increasing fiber loading.

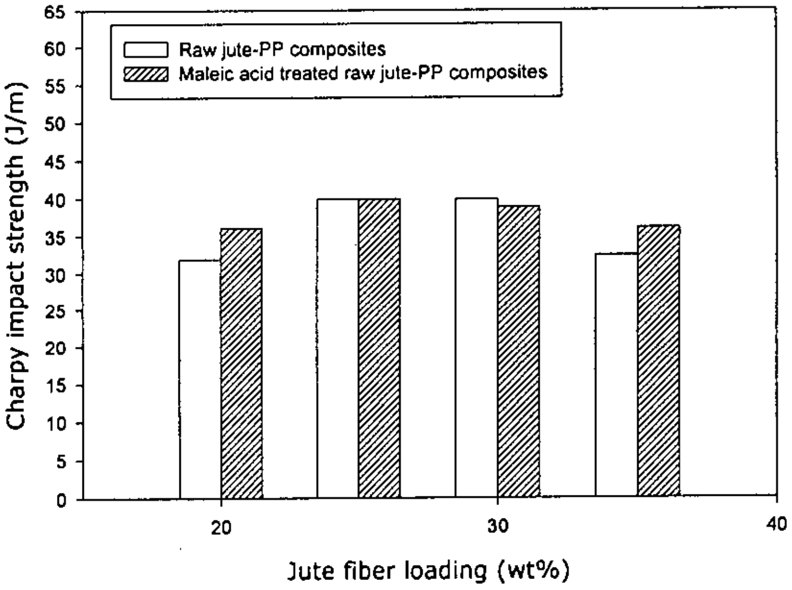


Figure 4.46: Charpy impact strength vs fiber content (wt%) curves for raw jute-PP composites and maleic acid treated raw jute-PP composites

4.6.3.4 Hardness

Rockwell hardness numbers of the composites is shown in Table 4.13. It is found that Rockwell hardness of the maleic acid treated raw jute-PP composites is higher than raw jute-PP composites. Rockwell hardness of the composites is higher than PP polymer matrix. It is also found that Rockwell hardness increases with increasing fiber loading of the composites.

4.6.4 Effect of maleic acid on the mechanical properties of composites

The mechanical properties of 20 wt% to 35 wt% fiber loaded maleic acid treated raw jute-PP composites have been investigated in this study. The values of all the mechanical properties according to series of formulations of the composites are given in the Table 4.13. The mechanical properties of maleic acid treated raw jute-PP composites are more than of raw jute-PP composites. Coupling of maleic acid with raw jute in the raw jute-PP composites enhances the mechanical property by improving the interfacial adhesion between maleic acid treated jute and PP matrix. The hydrophilic nature of maleic acid treated raw jute is weaker than the hydrophilic nature of raw jute as ester group is less polar than hydroxyl group. So hydrophilic nature of maleic acid treated raw jute-PP composites decreases comparing with the raw jute-PP composites which increases the interfacial adhesion of maleic acid treated raw jute with the PP matrix. In the spectroscopic observation it is found that PP polymer structure was changed slightly by the maleic acid treatment that indicates some bridging might be formed between maleic acid and PP matrix by Van der Waals interaction or covalent bond. As a result, the mechanical properties of the maleic acid treated raw jute-PP composites increases with increasing fiber loading.

Table 4.13: Results of mechanical tests of maleic acid treated raw jute reinforced PP composites comparing with the raw jute-PP composites.

Material	Tensile			Flexural		Charpy Impact Strength, J/m	Rockwell Hardness (L Scale)
	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)		
PP only	27.20	0.79	More than 150	42.63	1.28	22.34	66.4
PP-Raw jute (20 wt-%)	25.74	1.68	8.65	45.47	1.93	31.84	77.2
PP- Raw jute (25 wt-%)	25.38	1.70	6.75	47.17	2.14	39.87	80.2
PP- Raw jute (30 wt-%)	24.17	2.14	4.53	47.17	2.25	39.87	82.4
PP-Raw jute (35 wt-%)	24.66	2.22	3.79	45.47	2.41	32.34	85.4
Maleic acid treated PP-Raw jute (20 wt-%)	26.23	1.72	9.02	48.31	2.44	36.10	78.2
Maleic acid treated PP-Raw jute (25 wt-%)	26.35	1.80	7.10	48.31	2.46	39.87	80.2
Maleic acid treated PP-Raw jute (30 wt-%)	26.47	1.84	4.55	48.31	2.98	38.86	85.4
Maleic acid treated PP-Raw jute (35 wt-%)	27.56	2.40	4.72	51.15	3.10	36.10	89.2

4.6.5 Morphological (SEM) characterization of maleic acid treated raw jute fiber reinforced polypropylene composites

Scanning electron microscopy (SEM) is an important tool to study the surface morphology of composite materials. Both physical and chemical interaction of jute fiber and PP and the modification of raw jute-PP composites by coupling reaction produce a significant change in the morphology of composites. Scanning electron micrograph of maleic acid treated 30 wt-% raw jute-PP composite was taken using scratched pieces of fractured tensile test specimen. The micrograph is shown in the Figure 4.47. It is found from the micrograph that PP matrixes are attached on the fiber surfaces due to the improved adhesion and wettability between maleic acid treated fiber and PP matrix. Interfacial interaction between fiber and matrix is found more in the maleic acid treated raw jute-PP composite than untreated raw jute-PP composite (Fig.4.14). Coupling of maleic acid with raw jute which decreases the hydrophilic nature of raw jute might increase this interfacial adhesion and bonding of fiber and PP matrix.

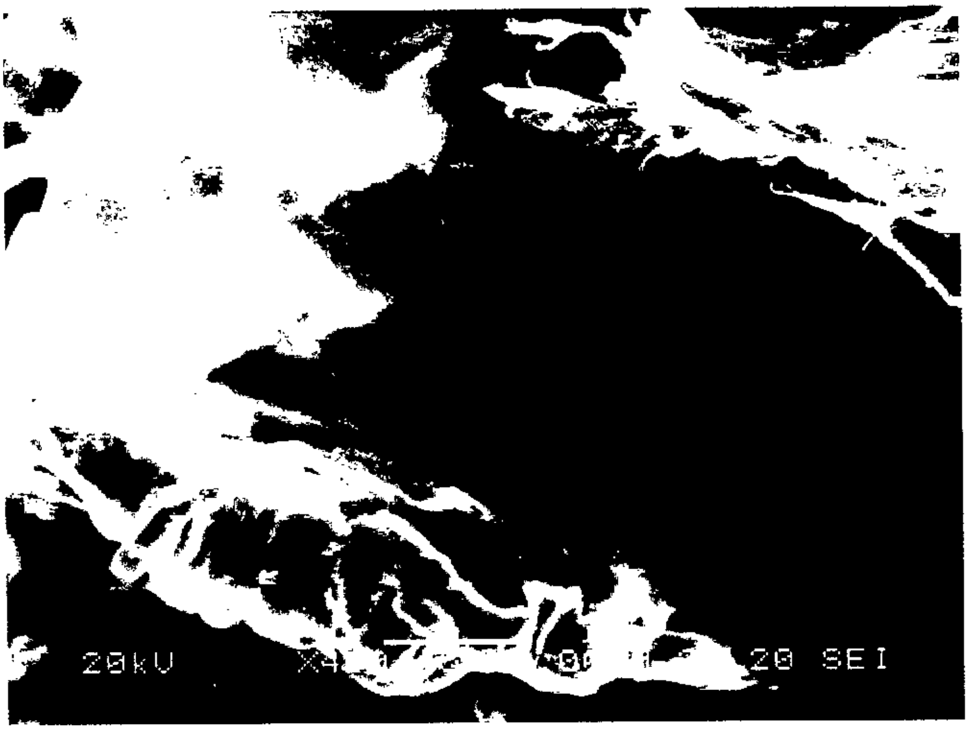


Figure 4.47: SEM micrograph of maleic acid treated 30 wt-% raw jute- PP composite

4.6.6 Water absorption

Water absorption test of maleic acid treated jute reinforced-PP composites have been carried out. The results are presented in Figure 4.48 and Table 4.14. It is observed from the table that water absorption of maleic acid treated raw jute-PP composites are less than that of raw jute-PP composites. The dimensional stabilization of maleic acid treated raw jute-PP composites will be increased due to decreasing of water absorption. This improved result may be due to the effect of polarity of functional group. Organic ester group is less polar than hydroxyl group. So, the coupling of maleic acid with jute decreases the hydrophilic nature of jute, which increases the interfacial adhesion with hydrophobic PP matrix in the composites.

Table 4.14: Water absorption of the maleic acid treated raw jute-PP composites

Composites (Maleic acid treated)	2 h in boiling water (%)	24 h in cold water (%)
PP only	0.099	0.03
PP-Oxidized jute (20 wt-%)	0.74	0.30
PP-Oxidized jute (25 wt-%)	0.78	0.37
PP-Oxidized jute (30 wt-%)	0.83	0.40
PP-Oxidized jute (35 wt-%)	0.90	0.51

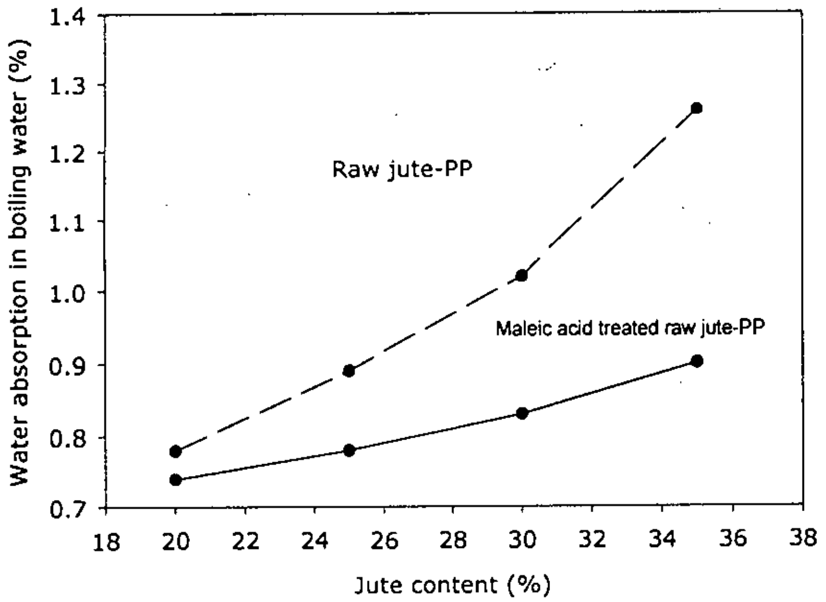


Figure 4.48: Water absorption vs fiber content (wt%) curves for raw jute-PP composites and maleic acid treated raw jute-PP composites

4.7 Comparative results of ultimate tensile strength and water absorption tests for all composites

It is observed from the results of all treated and untreated composites that the maximum tensile strength is obtained at 20 wt-% fiber loading. The highest tensile strength for all composites containing 20 wt-% loaded fiber are shown in the Figure 4.49. It is observed from the figure that urea and urotropine treated oxidized jute-PP composites show higher tensile strength than the PP matrix.

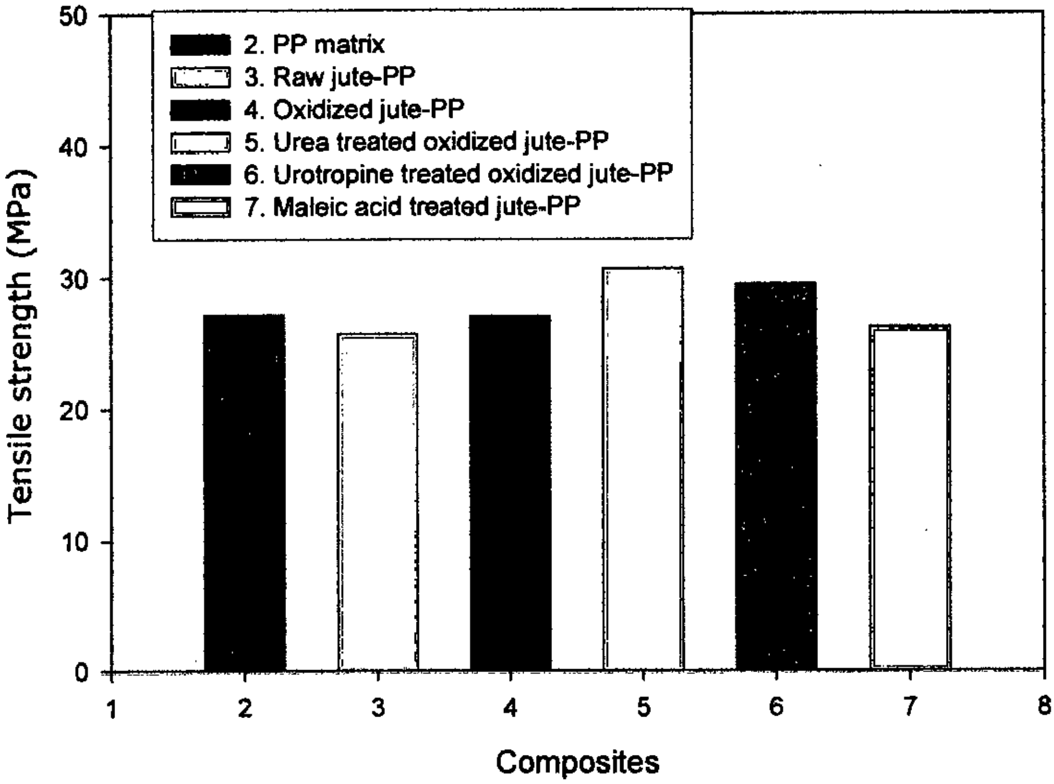


Figure 4.49: comparative tensile strengths of PP matrix and 20 wt-% fiber loaded untreated and treated composites

The tensile strengths of the raw jute-PP composites and oxidized jute-PP composites decrease to a limited extent with increasing fiber loading up to 30 wt-% and the tensile strength of these composites are also less than PP matrix (Table 4.4). It is also observed from the Table 4.4 that the tensile strengths of the raw jute-PP composites and oxidized jute-PP composites start to increase again at 35 wt-% fiber loading. This observation indicates that the tensile strength of the composites might be increased with increasing fiber loading more than 35 wt-%. A. C. Karmaker and J. A. Youngquist[37] reported the improved tensile strength at 50 wt-% jute fiber loaded polypropylene composite than the polypropylene matrix.

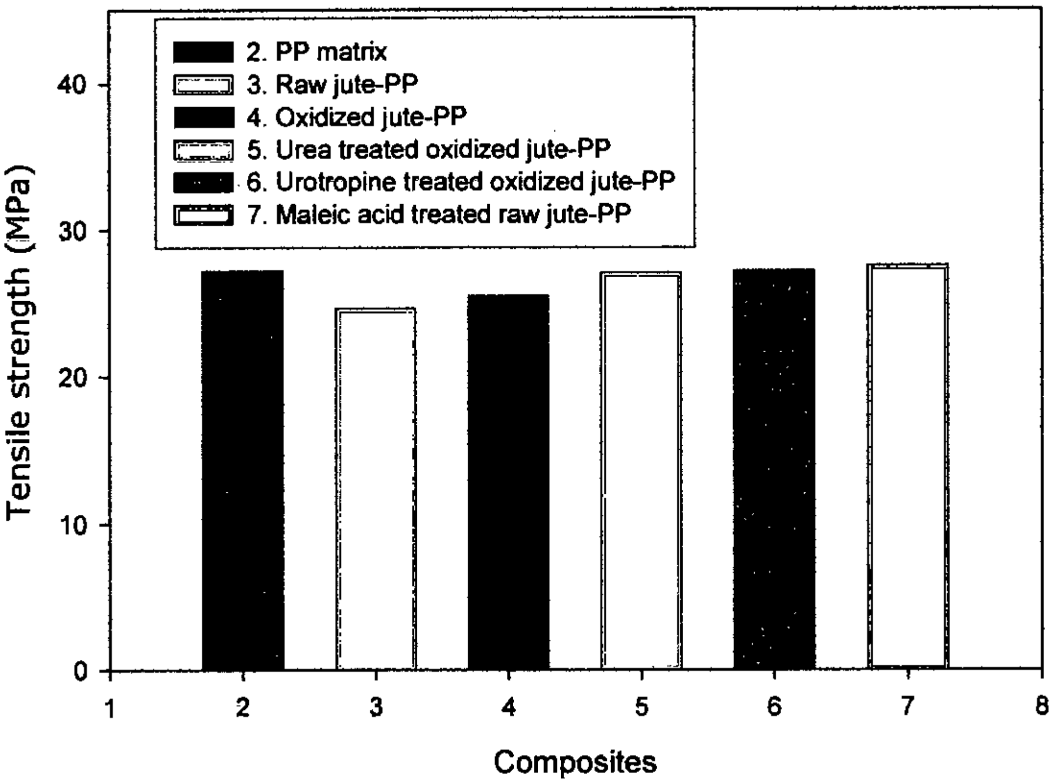


Figure 4.50: comparative tensile strengths of PP matrix and 35 wt-% fiber loaded untreated and treated composites

The tensile strengths of composites containing 35 wt-% loaded fiber are shown in the Figure 4.50. It is evident from the figure that there is no appreciable change in the tensile strengths of PP matrix, urea and urotropine treated oxidized jute-PP composites and maleic acid treated raw jute-PP composites. However, lower tensile strength is obtained for raw jute-PP and oxidized jute-PP composites. These results have been explained in the previous part of the result and discussion section.

The results of water absorption tests for all composites are shown in the figure 4.51. It is observed from the figure that the resistances of water absorption for oxidized jute-PP composites, urotropine treated oxidized jute-PP composites and maleic acid treated raw jute-PP composites are higher than those of raw jute-PP and urea treated oxidized jute-PP composites. These results have been explained in the previous part of this section on the basis of hydrophilic and hydrophobic functional groups in the composites.

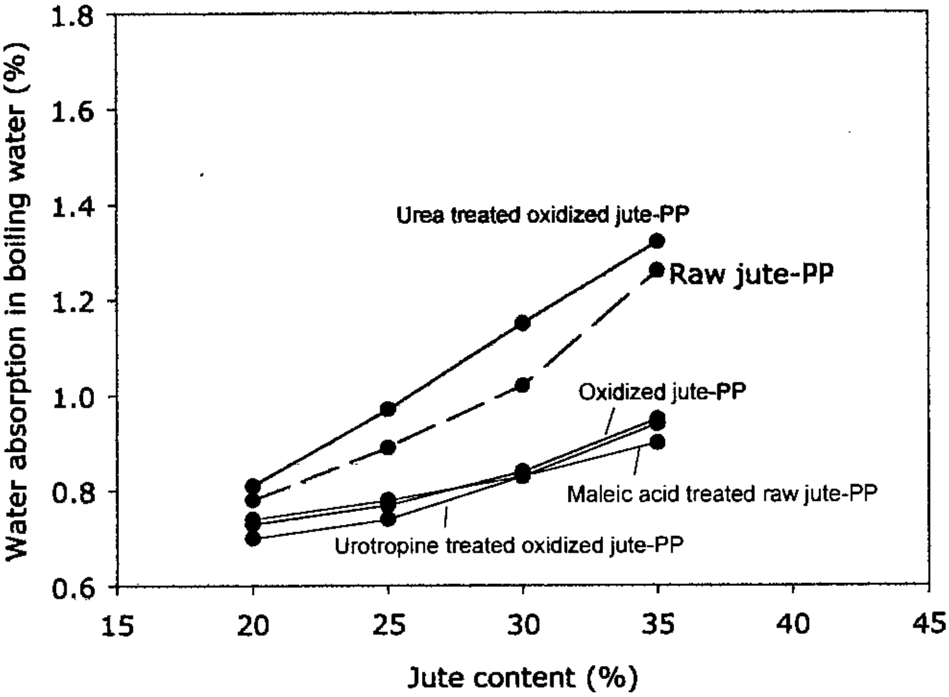


Figure 4.51: Water absorption vs fiber content (wt%) curves for all untreated and treated jute-PP composites

CHAPTER 5: SUMMARY AND CONCLUSION

This study refers to the experimental determination and theoretical interpretation of a series of works on "Studies on the Effects of Additives on the Physico-mechanical Properties of Jute Reinforced Composites." The total work of this study is summarized below:

(1) Cellulose in raw jute fibers can be oxidized at C_2 and C_3 position of anhyroglucose unit to form reducing oxycellulose (dialdehyde) by sodium periodate. The dialdehyde derivative of cellulose in jute is found to be more active to the coupling agent like urea and urotropine than the cellulose in jute.

All the mechanical properties of the oxidized jute-PP composites are higher than those of raw jute-PP composites. Tensile modulus, flexural modulus, Charpy impact strength and hardness of the raw and oxidized jute-PP composites are significantly higher than polypropylene (PP). Flexural strength of the composites increases up to 30 wt-% fiber loading than unfilled PP matrix. Tensile strength, elongation at break and Charpy impact strength of the composites decreases with increasing fiber loading. Tensile modulus, flexural modulus and hardness of these fibers loaded composites increases with increasing fiber loading.

Morphological studies of these composites show better interfacial bonding between fiber and matrix for oxidized jute-PP composites than raw jute-PP composites. Water absorption properties of the composites also show better result for oxidized jute-PP composites than raw jute-PP composites, which will improve the dimensional stability of the composites.

From these observation, it can be concluded that modification of jute fibers by sodium periodate oxidation enhances the physico-mechanical properties of the jute reinforced composites. The absence of intermolecular hydrogen bonding of dialdehyde cellulose in oxidized jute improves the adhesion between fiber and PP matrix in the composites interface. As a result oxidized jute fibers dispersed more uniformly in the composites than raw jute fibers.

(2) Both the FT-IR spectroscopic and SEM analyses indicate that coupling reaction has occurred between aldehyde group of oxidized jute with urea molecule. Reaction conditions were investigated to get highest mechanical properties. Urea treated oxidized jute-PP composites shows the better mechanical properties than raw jute-PP composites and oxidized jute-PP composites. Tensile strength, elongation at break and Charpy impact strength of the composites decreases with increasing fiber loading. Tensile modulus, flexural modulus and hardness significantly increase with increasing fiber loading. Coupling of urea with oxidized derivative of cellulose might enhance to give these results. With increase of fiber content at percentage (above 30 wt%) the mechanical properties are found to be decreased. This may be due to nonformation of chemical bonds between PP and treated jute. Better mechanical properties of the composite may be obtained by converting the hydrophobic PP into hydrophilic PP or by maleating the PP with maleic anhydride.

Improved interfacial bonding is achieved by urea coupling reaction. Polarity of amide group increases the water absorption which might be the cause of dimensional instability of the urea treated composites.

From this observation it can be recommended that moisture-protecting coating is needed for the use of urea treated composites. For this purpose nitrogen containing less hydrophilic larger molecule might give better positive coupling reaction with oxidized jute thereby would enhance the dimensional stability of composite materials.

(3) Both the FT-IR spectroscopic and SEM analyses indicate that coupling reaction has occurred between aldehyde group of oxidized jute with urotropine molecule. Reaction conditions were investigated in order to get better mechanical properties in the composites. Urotropine treated oxidized jute-PP composites shows the better mechanical properties than raw jute-PP composites, oxidized jute-PP composites and PP matrix. Tensile strength, elongation at break and Charpy impact strength of the composites decreases with increasing fiber loading. Tensile modulus, flexural modulus and hardness significantly increase with increasing fiber loading. Coupling of urotropine might enhance to give these results. With increase of fiber content at percentage (above 30 wt%) the mechanical properties are found to be decreased. This may be due to nonformation of chemical bonds between PP and treated jute. Better mechanical properties of the composite may be obtained by converting the hydrophobic PP into hydrophilic PP or by maleating the PP with maleic anhydride.

Improved interfacial bonding is achieved by urotropine coupling reaction. Water absorption results indicate that urotropine coupling lowers the moisture absorption, hydrophilic nature, of the jute-PP composites, which has higher dimensional stability. It can be recommended from this observation that nitrogen containing larger molecule will give positive coupling reaction with the oxidized jute, which is a great indication of possible research in this area to find out more improve coupling reaction to prepare more better jute reinforced composites.

(4) FT-IR and SEM analyses indicate that esterification has occurred between cellulosic hydroxyl groups of jute with maleic acid in aqueous media. The reaction was carried out in aqueous media at lower reaction conditions of time and temperature to prepare monoester. FT-IR spectroscopic analyses indicate that streic hindrance, mild reaction conditions and the presence of excess maleic acid slows down the reverse hydrolysis of the products. It is found that all the mechanical properties of maleic acid treated jute-PP composites are slightly more than that of raw jute-PP composites. But the properties increase significantly with increasing fiber loading at 35 wt-%.

SEM observation and water absorption test gives better result for maleic acid treated jute-PP composites. Maleic acid treated raw jute-PP composites reduce the hydrophilic nature of the composites, which enhances the dimensional stability of the composites.

Finally, it can be concluded that positive results are obtained by the oxidation of jute fibers and coupling reactions of composites with urea, urotropine and maleic acid. Improved injection moulded jute-PP composites have been prepared. Oxidation reaction of jute by pre-treatment and coupling reaction of composites by post-treatment with urotropine and maleic acid reduces the hydrophilic nature of the jute-PP composites, which is needed for their dimensional stabilization. So, it can be said that chemical modification of jute by various ways may improve the quality of jute-PP composites which might have bright future in Bangladesh.

REFERENCES

1. G. W. Ehrenstein and J. Kabelka, Reinforced Plastics, In *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A 23, Fifth Edition, VCH Publishers, Editors: B. Elvers, S. Hawkins and G. Schulz, 1992.
2. L. M. Matuana, J. J. Balatinez, R. N. S. Sodhi and C. B. Park, Surface characterization of esterified cellulosic fibers by XPS and FTIR Spectroscopy, *Wood Science and Technology*, Vol. 35, pp.191-201, 2001.
3. R. D. Gilbert, *Cellulosic polymers, blends and composites.* New York : Hanser Publishers, pp.115-130, 1994.
4. http://www.jute.org/plant_1.htm
5. R. Kozlowski, Potential and diversified uses of green fibers, In *3rd International Wood and Natural Fiber Composites Symposium*, Kassel, Germany, September 19-20, 2000.
6. R. M. Rowell and H. P. Stout, Jute and Kenaf, In *Handbook of Fiber Science and Technology*, Volume IV, Fiber Chemistry, Edited by: M. Lewin and E. M. Pearce, New York, 1985. htpp://www.rmmn.org/documnts/pdf1998/rowel98e.pdf
7. F. El-Hosseiny and D. Page, The mechanical properties of single wood pulp fibers: Theories of strength, *Fibre Sci Technol*, Vol.8, pp. 21- 31, 1975.
8. R. T. Woodhams, G. Thomas and D. K. Rodgers, Wood fibers as reinforcing fillers for polyolefin's, *Polym. Eng. Sci.* Vol. 24, pp. 1166-1171, 1984.
9. P. Zadorecki and A. J. Michell, Future prospects for wood cellulose as reinforcement in organic polymer composites, *Polym. Compos.*, Vol.10, pp. 69-77, 1990.
10. Literature Review: Thermoplastic Composite Materials http://wwwscholar.lib.vt.edu/theses/available/etd-110499-135025/unrestricted/Etbody.pdf

11. C. J. Wolf, Thermoplastics, In *KIRK-OTHMER Encyclopedia of Chemical Technology*, Fourth Edition, Vol. 7, 1998.

12. A. Bismarck, I. A. Askargorta and J. Springer, Surface Characterization of Flax, Hemp and Cellulose Fibers; Surface Properties and the Water Uptake Behavior, *Polymer Composites*, Vol. 23, No. 5, pp. 872-894, October 2002.

13. K. S. Whiteley, T. G. Heggs, H. Koch and W. Immel, Polyolefins, In *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A 21 Fifth Edition, VCH Publishers, Editors: B. Elvers, S. Hawkins, G. Schulz, 1992.

14. P. O. Olesen and D. V. Plackett, Perspectives on the Performance of Natural plant fibers. htpp://www.ienica.net/**fibres**seminar/olesen.pdf

15. http://www.jute.org/jute_diversified_prod.htm

16. http://www.jute.org/Taxonomical%20Characteristics.pdf

17. R. M. Rowell, A new generation of composite materials from agro-based fiber, In *Proceedings of the 3rd International Conference on frontiers of Polymers and Advanced Materials*, kualumpur, Malaysia, January 16-20, 1995.

18. D. R. Moore and A. Cervenka, Future requirements in the characterization of continuous fiber-reinforced polymeric composites (IUPAC Technical Report), *Pure Appl. Chem.*, Vol. 74, No. 4, pp. 601- 628, 2002.

19. http://www.jute.org/agriculture_3.htm

20. M. Andersson and A-M. Tillman, Acetylation of jute: Effects on strength, rot resistance, and hydrophobicity, *Journal of Applied Polymer Science*, Vol. 37, No. 12, pp. 3437-3447, March 2003.

21. P. Chow, Z. Bao, J.A. Youngquist, R. M. Rowell, J. H. Muehl and A. M. Krzysik, Effects of two fiber treatments on properties of hemlock hardboard, *Forest Products Journal*, Vol. 46, N0. 7/8, pp. 62-66, March 1995.

22. P. Chow, Z. Bao, J. A. Youngquist, R.M. Rowell, J. H. Muehl and A. M. Krzysik, Properties of hardboards made from acetylated aspen and southern pine, *Wood and Fiber Science*, Vol. 28(2), pp. 252-258, April, 1996.

23. M. M. Huque , M. A. Kabir and M.U. Ali, Comparative studies of some physico-mechanical properties of alkali and diazonium salt treated jute fiber, *Journal of Polymer Plastics Technology and Engineering* , Vol. 42, No.5, pp.935-946, 2003.

24. M. M. Hassan, M. R. Islamand and M. A. Khan, Effect of Pretreatment with Ultraviolet Radiation on the Mechanical Performance of Photografted Jute Yarn with 3-(Trimethoxysilyl) Propylmethacrylate, In *3rd USM-JIRCAS Joint International Symposium*, Penang, Malaysia, 9th to 11th March 2004.

25. M. B. Ahmad, M. A. Khan, W. M. Z. W. Yunus and M. Z. A. Rahman, Grafting of 2-hydroxy ethyl methacrylate (HEMA) onto oil palm fiber using potassium permanganate as initiator, In *Proceedings USM-JIRCAS Joint International Symposium*, pp. 87-194, 20th to 22nd March 2001.

26. D. Ray, B. K. Sarkar, A. K. Rana and N.R. Bose, Effect of alkali treated jute fibers on composite properties, *Bull. mater. Sci.*, Vol. 24, No. 2, pp.129-135, April 2001.

27. G. W. Beckermann, K.L. Pickering and N. J. Foreman, The Processing, Production and Improvement of Hemp-Fiber Reinforced Polypropylene Composite Materials, In *The 2nd International Conference on Structure, Processing and Properties of Materials. SPPM 2004*, Dhaka, Bangladesh, pp.257-265, 25- 27 February 2004.

28. M. D. H. Beg and K. L. Pickering, Effect of Fiber Pre-Treatment on the Mechanical Properties of Wood/ Polypropylene Composites, In *The 2nd International Conference on Structure,*

Processing and Properties of Materials. SPPM 2004, Dhaka, Bangladesh, pp.240-247, 25-27 February 2004.

29. A. K. Mohanty, M. A. Khan and G. Hinrichsen, Surface modification of jute and its influence on performance of biodegradable jute-fabric / biopol composites, *Composites Science and Technology*, Vol. 60, pp.1115-1124, 2000.
30. B. V. Kokta, R. G. Raj and C. Daneault, Use of wood flour as filler in polypropylene: Studies on mechanical properties, *Polym.-Plast. technol. eng.* Vol. 28(3), pp. 247-259, 1989.
31. T. G. Rials, U. S. Forest Service, Interfacial structure and properties of wood/ polypropylene composites. http://www.srs.fs.usda.gov/pubs/ja/jarials001.pdf
32. M. A. Khan, F. Mina and L. T. Drzal, Influence of silane coupling agents of different functionalities on the performance of jute-polycarbonate composite, In *3rd International Wood and Natural Fibre Composites Symposium*, Kassel, Germany September 19-20, 2000.
33. A. K Rana, A. Mandal, B. C. Mitra, R. Jacobson, R. Rowell, and A. N. Banerjee, Short Jute-Fibre Reinforced Polypropylene Composites: Effect of Compatibilizer, *Journal of Applied Polymer Science*, Vol. 69, pp.329-338, 1998.
34. M. M. Hassan, M. R. Islam and M. A. Khan, Effect of additives on the improvement of mechanical and degradable properties of photografted jute yarn with acryl amide, *Journal of Polymers and the Environment*, Vol.14 (4), pp.139-1145, 2002.
35. J. Gassaan and A.K. Bledzki, Possibilities for improving the mechanical properties of jute / epoxy composites by alkali treatment of fibers , *Composite Science and Technology*, Vol. 59 , pp.303-309 , 1999.

36. A. K. Bledzki, O. Faruk and M. M. Huque , Physico-mechanical studies of wood fiber reinforced composites, *BSME-ASME Int. on Thermal Engineering,* Dhaka, Bangladesh, 31 Dec. 2001-2 Jan. 2002.

37. A.C. Karmaker and J. A. Youngquist, Injection molding of polypropylene reinforced composites with short Jute fibers, *Journal of Applied Polymer Science*, Vol.62, pp.1147- 1151, 1996.

38. S. N. Alam, K. L. Pickering, and A. Fernyhough, The Characterization of Natural Fibers and Their Interfacial and Composite Properties, In *The 2nd International Conference on Structure, Processing and Properties of Materials. SPPM 2004,* Dhaka, Bangladesh, pp.248-256, 25-27 February 2004.

39. M. Kazayawoko, J. J. Balatinecz and L. M. Matuana, Surface modification and adhesion mechanisms in wood fiber-polypropylene composites, *Journal of Materials Science*, Vol. 34, pp-6189-6199, 1999.

40. R. Karnani, M. Krishnan and R. Narayan, Biofiber-Reinforced Polypropylene Composites, *Polymer Engineering and Science*, Vol. 37, No.2, pp-476-483, 1997.

41. M. L. Hassan, R. M. Rowell, N. A. Fadl, S. F. Yacoub and A. W. Christiansen, Thermoplasticization of Bagasse. II. Dimensional Stability and Mechanical Properties of Esterified Bagasse Composite, *Journal of Applied Polymer Science*, Vol. 76, pp. 515-586, 2000.

42. J. A. Murshidi and S. Zakaria, Benzylated oil palm empty fruit bunch (EFB) for obtaining thermoplastic property: Study of its thermal properties, In *Proceedings USM-JIRCAS Joint International Symposium*, pp. 436-441, 20th to 22nd March 2001.

43. R. M. Rowell, Opportunity for value-added bio-based composites, In *Pacific Rim Bio-Based Composites Symposium*, Rotorua, Newzealand, pp-244-252, 9-13 November 1992.
44. R. M. Rowell and C. M. Clemons, Chemical modification of wood fiber for thermoplasticity, compatibilization with plastics and dimensional stability, In *Proceedings, International Particleboard/ Composite Materials Symposium*, T. M. Maloney, ed., Pullman, WA, April, 1992.
45. R. M. Rowell, Chemical Modification of Agro-resources for Property Enhancement, Ch-11, pp-351-375. http://www.fpl.fs.fed.us/documnts/pdf1997/rowel97g.pdf
46. H. Matsuda and M. Ueda, Preparation and utilization of esterified woods bearing carboxyl groups. IV. Plasticization of esterified woods, *Mokuzai Gakkaishi*, Vol. 31(3), 215, 1985.
47. B. Ilschner, J. K. Lees, A. K. Dhingra and R. L. Mccullough, Composite Materials, In *Ullmann's Encyclopedia of Industrial Chemistry,* Vol. A7, Fifth Edition, VCH Publishers, Editors: B. elvers, S. Hawkins, G. Schulz, 1992.
48. R. Wolf and B. L. Kaul, Plastics Additives, In *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A20, Fifth Edition, VCH Publishers, Editors: B. elvers, S. Hawkins and G. Schulz, 1992.
49. J. A. Brydson, *Plastics Materials*, Seventh Edition, Published by Butterworth-Heinemann, 1999.
50. Joel R. Fried, *Polymer Science and Technology*, Published by Prentice-Hall of India Private Limited, New Delhi, 2000.
51. P. Kandachar, Agricultural fibers for product design & development http://www.thinkcycle.org/tcpapers/?paper_id=16090

52. B. English, P. Chow, and D. S. Bajwa, Processing into Composites, Chapter 8, In *Paper and Composites from Agro-Based Resources*, Edited by R. M. Rowell, R. A. Young and J. K. Rowell, Lewis Publishers.
53. R. M. Rowell, Chemical Modification of Lignocellulosics, In *Proceedings of the International Workshop on Frontiers of Surface Modification and Characterization of Lignocellulosic Fibers*, Sweden, May 30-31, 1996.
54. R. M. Rowell, A. R. Sanadi, D. F. Caulfield and R. E. Jacobson, Utilization of Natural Fibers in Plastic Composites: Problems and Opportunities, In *Lignocellulosic-Plastics Composites*, Edited by: A. I. Leao, F. X. Carvalho and E. Frollini, 1997. htpp://www.fpl.fs.fed.us/documnts/pdf1997/rowel97d.pdf
55. S. Das, A. K. Saha, P. K. Choudhury, R. K. Basak, B. C. Mitra, T. Todd, S. Lang and R. M. Rowell, Effect of Steam Pretreatment of Jute Fiber on Dimensional Stability of Jute Composite, *Journal of Applied Polymer Science*, Vol. 76, pp.1652–1661, 2000.
56. Resin and Compounds, *Modern Plastics Encyclopedia*, McGraw-Hill, New York, pp.269, 1993.
57. Material Design Material Selector Issue, *Thermoplastic Molding Compounds,* Penton Publishing, OH, pp. 184, 1994.
58. P. Chow, T. C. Bowers, D. S. Bajwa, J. A. Youngquist, J. H. Muehl, N. M. Stark, A. M. Krzysik and L. Quang, Dimensional stability of composites from plastics and cornstalk fibers, In *Fifth International Conference on Wood-plastic Composites*, The Madison concourse Hotel, Madison, Wisconsin, May 26-27, 1999.

59. N. Sombatsompop and K. Chaochanchaikul, Effect of moisture content on mechanical properties, thermal and structural stability and extrudate texture of poly(vinyl chloride) / wood sawdust composites, *Polym. Int.*, Vol. 53, pp.1210-1218, 2004.

60. V.G. Yachmenev, D. V. Parikh and T.A. Calamari, Thermal Insulation Properties of Biodegradable, Cellulosic-Based Nonwoven Composites for Automotive Application, *Journal of Industrial Textiles*, Vol. 31, No. 4, pp. 283-296, April 2002.

61. M. Lucka and A. K. Bledzki, Effect of acetylation on the structure and properties of flax fiber, In *3rd International Wood and Natural Fiber Composites Symposium*, Kassel, Germany, September 19-20, 2000.

62. J. Gassan and A. K. Bledzki, Effect of Moisture Absorption Desorption on the Mechanical Properties of Silanized Jute-Epoxy Composites, *Polymer Composites*, Vol. 20, No. 4, pp.604-611, August 1999.

63. M. A. Khan, M. M. Hassan and L. T. Drazal, Effect of 2-hydroxy ethyl methacrylate (HEMA) on the mechanical and thermal properties of jute-polycarbonate composite, *Composites: Part A: Applied Science and Manufacturing*, Vol. 36, pp. 71-78, 2005.

64. L. Yinghai, L. Zhanjun, L. Xiaohui and D. Kuilin, Grafting of poly(methyl acrylate) onto cellulose by potassium diperiodatocuprate (III) initiating system, *CJI*, Vol. 5, No. 3, pp.18,March,2003.
htpp://www.chemistrymag.org/cji/2003/05018pe.htm

65. Interface modification in jute/ polypropylene composites htpp://www.ipfdd.de/whatsnew/JB2004/06lang5.pdf

66. L. K. Poh, S. Zakaria, S. Ahmad and M. Deraman, A study on the thermal properties and suprastructure of benzoylated palm empty fruit bunch fibers, In *Proceedings USM-JIRCAS*

Joint International Symposium, pp.140-145, 20th to 22nd March 2001.

67. K. M. I. Ali, M. A. Khan and M. M. Husain, Wood-Plastic Composite with Methylmethacrylate in presence of Novel Additives, *Poly.-Plast. Technol. Eng.,* Vol. 33, No. 4, pp.477-487, 1994.
68. H. D. Rozman, G. S. Tay, and A. Abusamah, The Effect of Glycol Type, Glycol Mixture, and Isocyanate/ Glycol Ratio on Flexural Properties of Oil Palm Empty Fruit Bunch-Polyurethane Composites, *Journal of Wood Chemistry and Technology*, Vol. 23, Nos. 3 & 4, pp. 249-260, 2003.
69. R. M. Rowell, A. Sanadi, R. Jacobson and D. Caufield, Properties of Kenaf/ Polypropylene Composites, Chapter 32, In: *Kenaf Properties, Processing and Products*, Mississippi State University, Ag & Bio Engineering, pp. 381-392, ISBN 0-9670559-0-3, 1999.
70. A. R. Sanadi, D. Feng, and D. F. Caulfield, Highly Filled Lignocellulosic Reinforced Thermoplastic: Effect of Interphase Modification, In *Proceedings of the 18th RisØ International on Materials Science: Polymer Composites-Expanding the Limits*, Editors: S. I. Andersen, P. BrØndsted, H. Lilholt, A. Lystrup, J. T. Rheinlander, B. F. SØrensen and H. Toftegaard, RisØ National Laboratory, Roskilde, Denmark, 1997.
71. P. Chow, D. S. Bajwa, and W. Lu, Injection-Molded Composites from Kenaf and Recycled Plastic, In *Proceedings of 1st Annual American Kenaf Society Meeting*, San Antonio, TX, February 1998.
72. K. Joseph, R. D. T. Filho, B. James, S. Thomas, and L. H. Carvalho, A Review on Sisal Fiber Reinforced Polymer Composites, *Revista Brasileira de Engenharia Agricola e Ambiental*, Vol. 3, No. 3, pp. 367-379. 1999.

73. X. Li, S.A. Panigrahi, L.G. Tabil, and W.J. Crerar, Flax Fiber-reinforced composites and the effect of chemical treatments on their Properties, American Society of Agricultural Engineers (ASAE), Paper Number: MB04-305 htpp://umanitoba.ca/faculties/afs/biosystems engineering/2004%20regional%20conference/mb04-305.pdf
74. F. Zhang, T. Endo, R. Kitagawa, H. Kabeya and T. Hirotsu, Synthesis and characterization of a novel blend of polypropylene with *Chlorella, J. Mater. Chem.,* Vol.10, pp. 2666-2672, 2000.
75. T. J. Kim, Y. M. Lee and S. S. Im, The Preparation and Characterization of Low-Density Polyethylene Composites Containing Cellulose Treated With Cellulase, *Polymer Composites*, Vol. 18, No. 3, pp. 273-282, June 1997.
76. A. Sanadi, Lignocellulosic/ Plastic composites htpp://www.fpl.fs.fed.us/documnts/pdf1998/sanad98a.pdf
77. R. M. Rowell, The State of Art and Future Development of Bio-Based Composite Science and Technology Towards the 21st Century, In *Proceedings, the fourth Pacific rim bio-based composites symposium*, Indonesia. pp. 1-18, November 2-5, 1998.
78. M. Idicula, N. R. Neelakantan, and S. Thomas, Mechanical Properties of Short Banana/ Sisal Hybrid Fiber Reinforced Polyester Composites, In *Proceedings USM-JIRCAS Joint International Symposium*, pp. 368-373, 20th to 22nd March 2001
79. Z. Mohamad, H. Ismail and A. A. Bakar, Rice Husk Powder Filled Polystyrene/ Styrene Butadiene Rubber Blends: Chemical Treatment, In *3rd USM-JIRCAS Joint International Symposium*, Penang, Malaysia, 9th to 11th March 2004.

80. B. D. Park and J. J. Balatinecz, Mechanical Properties of Wood-Fiber/ Toughened Isotactic Polypropylene Composites, *Polymer Composites*, Vol. 18, No. 1, pp. 79-89, February 1997.

81. C. M. Clemons, D. F. Caulfield and A. J. Giacomin, Dynamic Fracture Toughness of Cellulose Fiber-Reinforced Polypropylene: Preliminary Investigation of Microstructural Effects, *Journal of Elastomers and Plastics*, Vol. 31, pp.367-378, October 1999.

82. K. Takemura, Effect of water absorption on static and creep properties for jute fiber reinforced composite. htpp://www.witpress.com,ISBN 1-85321-717-5

83. B. V. Kokta, Wood Fiber Reinforced Thermoplastics Composites: Effect of Compounding, Molding and Fiber Length on Resulting Properties: Pilot Plant Trials, In *3rd International Wood and Natural Fibre Composites Symposium*, Kassel, Germany, September 19-20, 2000.

84. C. Santulli and W. J. Cantwell, Impact Damage Characterization on Jute Reinforced Composites, *Journal of Materials Science and Letters*, Vol.20, pp.471–473, February 2001. www.kluweronline.com/article.asp?PIPS=337022&PDF=1

85. A. R. Sanadi, D. F. Caulfield, N. M. Stark and C. C. Clemons, Thermal and mechanical analysis of lignocellulosic polypropylene composites, In *The Fifth International Conference on Wood Fiber-Plastic Composites,* Madison, Wisconsin, May 26-27, 1999.

86. ASTM Standard D 638-01, Standard Test Methods for Tensile Properties of Plastics. In *Annual Book of ASTM Standard*, Vol. 08.03, 2002.

87. ASTM Standard D 790-00, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical

Insulating Materials. In *Annual Book of ASTM Standard*, Vol. 08.01, 2002.

88. ASTM Standard D 6110-97, Standard Test Methods for Determining the Charpy Impact Resistance of Notched Specimens of Plastics. In *Annual Book of ASTM Standard*, Vol. 08.03, 2002.
89. ASTM Standard D 785-98, Standard Test Method for Rockwell Hardness of Plastics and Electrical Insulating materials. In *Annual Book of ASTM Standard*, Vol. 08.01, 2002.
90. ASTM Standard D 570-98, Standard Test Method for Water Absorption of Plastics, In *Annual Book of ASTM Standard*, Vol. 08.01, 2002.
91. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, Second Edition, John Wiley & Sons, Inc., New York.
92. M. N. Haque, H. P. S. A. Khalil and C. A. S. Hill, Chemical Modification of Wood Flour and Thermomechanical Pulp Fibre with Acetic Anhydride, htpp://www.ind.usm.my/ti/E-Journal/html-vol1/..%5Cpdf-vol1- journal%5CAkhalil.pdf)
93. P. Garside and P. Wyeth, Identification of Cellulosic Fibers by FTIR Spectroscopy I: Thread and Single Fiber Analysis by Attenuated Total Reflectance. http://eprints.soton.ac.uk/14069/
94. X. H. Li, Y. Z. Meng, S. J. Wang, A. V. Rajulu and S. C. Tjong, Completely Biodegradable Composites of Poly(propylene carbonate) and Short, Lignocellulose Fiber *Hildegardia populifolia*, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 42, pp. 666-675, 2004.
95. G. Parthasarthy, M. Sevegney and R. M. Kannan, Rheooptical Fourier Transform Infrared Spectroscopy of the Deformation Behavior in Quenched and Slow-Cooled Isotactic Polypropylene

Films, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 40, pp.2533-2551, 2002.

96. M. Sakayanagi, B. Pharm, Y. konda, K. Watanabe, Y. Harigaya, Identification of Pressure-Sensitive Adhesive Polypropylene Tape, *J Forensic Sci.*, Vol. 48, No. 1, January 2003.
97. T. Miyamoto and H. Inagaki, Structural and Steric Isomerism of Polypropylenes, *Journal of Polymer Science: Part A-2*, Vol. 7, pp. 963-981, 1969.
98. J. Garbarczyk and S. Borysiak, Crystallisation of Isotactic Polypropylene at Surfaces of Cellulose Natural Fibers, In *3rd International Wood and Natural Fiber Composite Symposium*, Kassel, Germany, 19-20th September 2000.
99. C. M. Clemons, A. J. Giacomin and D. F. Caulfield, Spherulitic Structure in Cellulose-Fiber Reinforced Polypropylene, In *The Fifth International Conference on Wood Fiber-Plastic Composites*, Madison, Wisconsin, 26-27th May 1999.
100. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Fifth Edition, Prentice-Hall of India Private limited, New Delhi-110001, 1990.
101. M. J. Saad, Z. A. M. Ishak and H. D. Rozman, Empty Fruit Bunch (EFB)-Polypropylene Composites: The Effect of Chemical Modification of EFB with Maleic Anhydride (MAH) on the Tensile Properties and Dimensional Stability, In *Proceedings USM-JIRCAS Joint International Symposium*, pp. 209-223, 20th to 22nd March 2001.
102. G. S. Tay, A. Abusamah and H. D. Rozman, Tensile Properties of Polyurethane (PU) Composites Based on Epichlorohydrin Modified Oil Palm Empty Fruit Bunch (EFB), In *3rd USM-JIRCAS Joint International Symposium*, Penang, Malaysia, 9th to 11th March 2004.

103. M. L. Hassan, R. M. Rowell, N. A. Fadl, S. F. Yacoub and A. W. Christiansen, Thermoplasticization of Bagasse. I. Preparation and Characterization of Esterified Bagasse Fibers, *Journal of Applied Polymer Science*, Vol. 76, pp. 561-574, 2000.

104. K. Oksman and C. Clemons, Mechanical Properties and Morphology of Impact Modified Polypropylene-Wood Flour Composites, *Journal of Applied Polymer Science*, Vol. 67, pp. 1503-1513, 1998.

105. H. Ismail, Salmah and A. A. Bakar, The Effect of PPMaH and LICA on Properties of Paper Sludge Filled PP/ EPDM Composites, In *3rd USM-JIRCAS Joint International Symposium*, Penang, Malaysia, 9th to 11th March 2004.

106. J. J. Schemenauer, T. A. Osswald, A. R. Sanadi and D. F. Caulifield, Melt Rheological Properties of Natural Fiber-Reinforced Polypropylene, *ANTEC 2000 Society of Plastic Engineers Conference*. 2:2206-2210, 2000.

107. S. Joseph, M. S. Sreekala, Z. Oommen, P. Koshy and S. Thomas, A Comparison of the Mechanical Properties of Phenol Formaldehyde Composites Reinforced with Banana Fibers and Glass Fibers, *Composites Science and Technology*, Vol. 62, pp. 1857-1868, 2002.

108. L. A. Pothan, Z. Oommen and S. Thomas, Dynamic Mechanical Analysis of Banana Fiber Reinforced Polyester Composites, *Composite Science and Technology*, Vol. 63, pp. 283-293, 2003.

109. Y. Xue, D. Veazie, C. Glinsey, M. Wright and R. M. Rowell, Mechanical Properties of Wood Fiber Composites Under the Influence of Temperature and Humidity, In *The Seventh International Conference on Wood Fiber-Plastic Composites*, Madison, Wisconsin, USA, May 19-20, 2003.

110. A. K. M. Masud, J. Suzuki and K. Isogimi, Aramid Short Fiber/Up Composite and Their Mechanical Properties, In *Proc. Int. Conf. on Structure, Processing and Properties of Materials, SPPM'97*, Dhaka, Bangladesh, Paper No. 9, pp. D67-D76, 15-17 November, 1997.

111. C. L. Tien, M. Millette, M. Lacroix and M. A. Mateescu, Modified alginate matrices for the immobilization of bioactive agents, *Biotechnol. Appl. Biochem.*, Vol. 39, pp. 189–198, 2004.
http://www.babonline.org/bab/039/0189/bab0390189.htm

112. A. J. Kirby, I. V. Komarov, Vi. A. Bilenko, J. E. Davies and J. M. Rawson, Structure and chemistry of a zwitterionic amine–aldehyde adduct, *Chemical Communications*, Vol.18, pp. 2106-2107,DOI:10.1039/b206639d,2002.
http://www.rsc.org/publishing/journals/CC/article.asp?doi=b206639d

113. Edward M. Hawes, *N*+-Glucuronidation, a Common Pathway in Human Metabolism of Drugs With a Tertiary Amine Group, *Drug Metabolism and Disposition*, Vol. 26, No.9, pp. 830-837, September,1998.
http://dmd.aspetjournals.org/cgi/content/full/26/9/830#B69

114. L. A. Fasce, P. A. Frontini, S. C. Wong and Y. W. Mai, Polypropylene Modified with Elastomeric Metallocene-Catalyzed Polyolefin Blends: Fracture Behavior and Development of Damage Mechanisms, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 42, pp. 1075-1089, 2004.

115. A. Boudenne, L. Ibos, M. Fois, E. Gehin and J. C. Majeste, Thermo physical Properties of Polypropylene/ Aluminum Composites, *Journal of Polymer Science: Part B: Polymer Physics*, Vol.42, pp. 722-732, 2004.