CHAPTER II
LITERATURE REVIEW

2.1 Introduction

The problem of growing global waste, the depletion of fossil fuels and ever increasing prices for crude oil have triggered an interest in renewable resources. Concerns about environmental issues have put pressure for the development of more stringent legislation, which promotes the preservation and protection of the quality of the environment. The pressure for legislation for new technologies for more environmental–friendly products is forcing material suppliers and manufacturers to consider the environmental impact of their products at all stages of their life cycle, including processing, recycling and finally their disposal. The waste disposal problems and criteria for cleaner and safer environment have initiated a great part of the scientific research to biocomposite materials that can be easily degraded or bio assimilated.

Fiber reinforced materials have been used as long as recorded history. Man has used this idea, since the beginning of our civilization when grass and straw were used to reinforce mud brick (Carvalho L.H. 1997). In the past, composites such as coconut fiber/natural rubber latex were extensively used by the automotive industry. However, during the seventies and eighties, cellulose fibers were gradually substituted by newly developed synthetic fibers because of better performance (Mattoso L.H.C. *et al.* 1997). Since then, the use of cellulose fibers has been limited to the production of rope, string, clothing, carpets, and other decorative products. Over the past few years, there has been a renewed interest in using these fibers as reinforcement materials in the plastics industries. This resurgence of interest is due to the increasing cost of plastics (Rowell R. *et al.* 1997), and because of the environmental aspects of using renewable and biodegradable materials. Over the past decade, polymers have replaced many of the conventional metals/materials in various applications. This is possible because of the advantages polymers offer over conventional materials. The most important advantages of using polymers are the ease of processing, productivity and cost reduction. The utilizing of low cost natural fibers which are lightweight offers the potential to replace a large amount of the glass and mineral fillers used for automotive interior and exterior parts.

The interest in using cellulose fibers rather than synthetic fibers such as glass fibers is due to several attractive properties, these fibers can offer a desirable aspect ratio (length divided by effective diameter, L/D) of around 100–200 for good performance after melting process as shown in Table 2.1 (Lee S.M. 1990). The increase in petroleum based–plastic costs couple with the environmental aspects of using renewable and biodegradable materials further make cellulose fibers favorable as reinforcement in composite materials.

Table 2.1 The length of fibers after processed. (Lee S.M. 1990)

Fiber	Fiber Diameter (μm)	Before Processing		After Processing	
		Length (mm)	L/D	Length (mm)	L/D
Glass	13	6.35	488	0.22	17
Carbon	8	6.35	794	0.18	22
Aramid	12	6.35	529	1.33	111
Nylon	25	6.35	254	4.51	180
Cellulose	12	2.00	167	1.20	100

Natural fibers reinforced with thermoplastic and thermoset composites have been embraced by car manufacturers and suppliers for door panels, seat backs, headliners, package trays, dashboards and interior parts, an example is shown in Table 2.2 (Mohanty A.K. *et al.* 2001).

Besides their use in trim parts, natural fibers are used extensively for thermo–acoustic insulation. Such insulating materials, mainly based on cotton fibers recycled from textiles, have relatively high fiber contents of more than 80% by weight. Trim parts in Brazilian trucks, made of a mixture of jute coffee bag wastes and polypropylene bags show that recycling sometimes can lead to advanced applications.

Table 2.2 Example of interior and exterior parts produced from natural materials (Mohanty A.K. *et al.* 2001)

Vehicle Part	**Material Used**
Interior	
Glove box	Wood/cotton fibers molded, flax/sisal
Door panels	Flax/sisal with thermoset resin
Seat coverings	Leather/wool backing
Seat surface/backrest	Coconut fibers/natural rubber
Trunk panel	Cotton fibers
Trunk floor	Cotton with PP/PET fibers
Insulation	Cotton fibers
Exterior	
Floor panels	Flax mat with PP

Another well established field of application is the use of coconut fibers bonded with natural latex for seat cushions. For this application the ability of plant fibers to absorb large amounts of humidity leads to an increased comfort that cannot be reached with synthetic materials. Aside from this kind of developments, fundamentally new applications have not been realized in recent years. An important step towards higher performance applications was achieved with the door panels of the Mercedes–Benz E–Class, Figure 2.1 and Figure 2.2.

The wood fiber materials previously used for the door panels, Figure 2.3 was replaced by a plant fiber–reinforced material consisting of a flax/sisal fiber mat embedded in an epoxy resin matrix. A remarkable weight reduction of about 20% was achieved, and the mechanical properties, important for passenger protection in the event of an accident, were improved. Furthermore, the flax/sisal material can be molded in complicated 3–dimensional shapes, thus making it more suitable for door trim panels than the previously used materials (James H. *et al.* 2006).

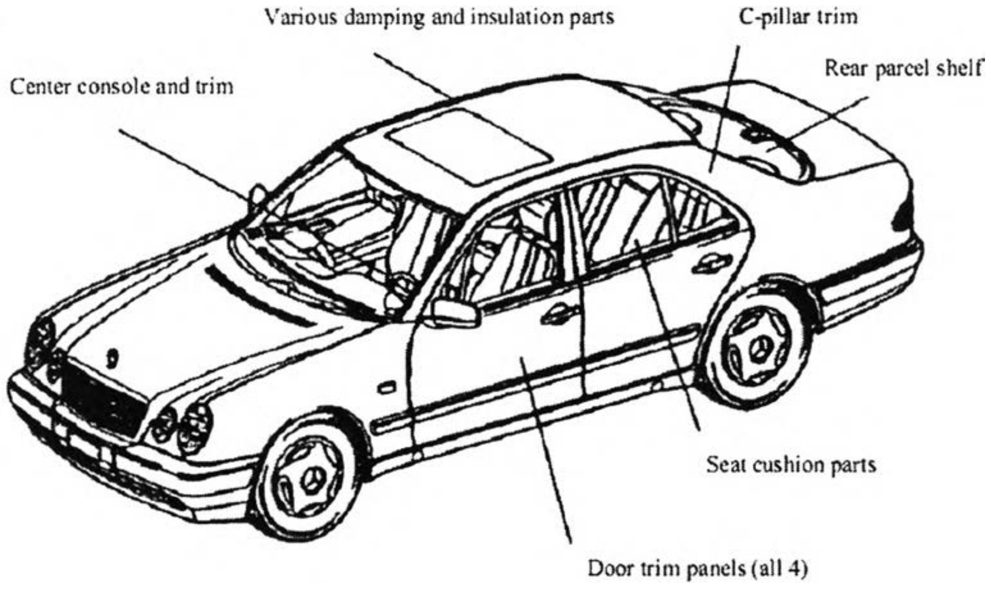

Figure 2.1 Natural fiber applications in the current Mercedes–Benz E–Class (James H. *et al.* 2006).

Figure 2.2 Flax, hemp, sisal, wool and other natural fibers used in 50 Mercedes–Benz E–Class components (James H. *et al.* 2006).

Natural fibers are providing automobile part reinforcement due to advantages drivers as reductions in weight, cost and CO_2, less reliance on foreign oil resources and recyclability. As a result, today most automakers are evaluating the environmental impact of a vehicle's entire lifecycle, from raw materials to manufacturing to disposal. Glass–fiber–reinforced plastics have proven to meet the structural and durability demands of automobile interior and exterior parts. Good mechanical properties and a well–developed, installed manufacturing base have aided in the insertion of fiberglass–reinforced plastics within the automotive industry. However, glass–reinforced plastics exhibit shortcoming such as their relatively high fiber density (approximately 40% higher than natural fibers), difficulty to machine and poor recycling properties. The energy consumption to produce a flax–fiber mat (9.55 MJ/kg), including cultivation, harvesting and fiber separation, amounts to approximately 17% of the energy to produce a glass–fiber mat (54.7 MJ/kg) (James H. *et al.* 2006).

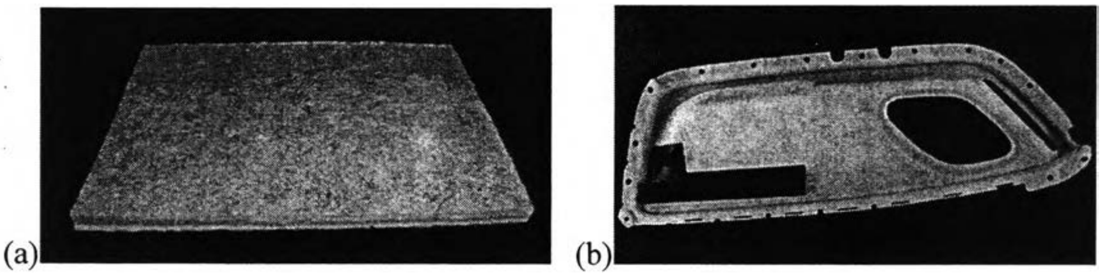

Figure 2.3 (a) A natural fiber mat processed and (b) a door inner panel from natural fiber–reinforced PP, 50% Kenaf with 50% PP (James H. *et al.* 2006).

The automotive market sector is not the only area that has experienced an increase in natural fiber usage. The insertion of natural fibers in the industrial, building and commercial market sectors has experienced a growth rate of 13% compounded over the last 10 years to an annual use of approximately 275 million kilograms (James H. *et al.* 2006).

2.2 Cellulose Fibers

Cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1,4–β–bonded anhydroglucose units which contains alcoholic hydroxyl groups as shown in Figure 2.4. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and intermolecular hydrogen bonds among other cellulose macromolecules as well as with hydroxyl groups from the air which show in Figure 2.5. Therefore, all of the natural fibers are hydrophilic in nature; their moisture content reaches 8–12.6% (Bledzki A.K. *et al.* 1996). There are a wide variety of cellulosic fibers available used to reinforce thermoplastics such as wood fibers (including steam–exploded fibers), a variety of agro–based fibers (such as stems, stalks, bast, leaves and seed hairs) (Razaina M.T. 1998), recycled newspaper, nut shells, starch, and long lingo fibers such as hemp, sisal, kenaf and jute.

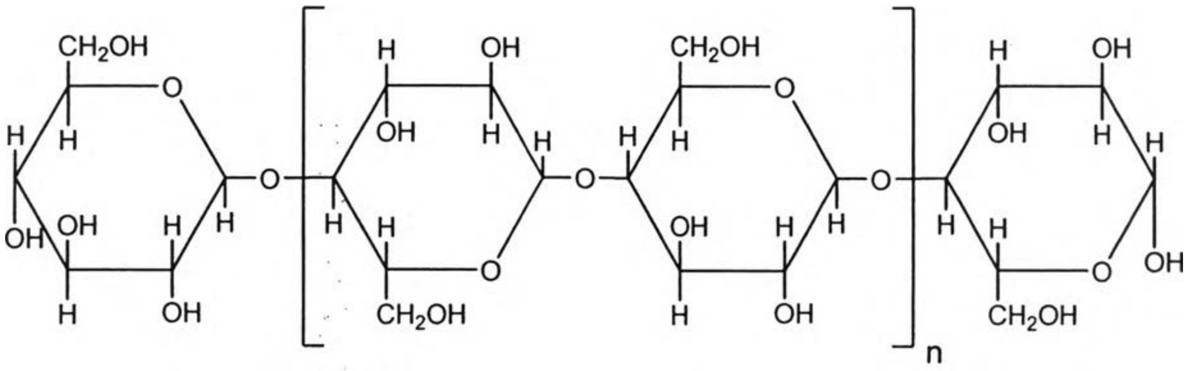

Figure 2.4 The structure of cellulose.

Cellulose fibers present many advantages compared to synthetic fibers which make them attractive as reinforcements in materials. They come from abundant and renewable resources at low cost (as shown in Table 2.3), which ensures a continuous fiber supply and a significant material cost saving to the plastics industry. Cellulose fibers, despite their low strength, can lead to composites with high specific properties because of their low densities.

Unlike brittle fibers, such as glass and carbon fibers, cellulose fibers are flexible and will not fracture when processed over sharp curvature. This enables the fibers to maintain the desired aspect ratio for good performance. Their non–abrasive nature permits a high volume fraction of filling during processing, and this results in high mechanical properties without the usual machine wear problems associated with synthetic fibers especially glass and ceramic. Cellulose fibers are non–toxic, easy to handle and present no health problems like glass fibers that can cause skin irritation and respiratory diseases when the fibrous dust is inhaled. They offer a high ability for surface modification, are economical, require low socio–economic issues. The cellulose fibers as source of raw materials is beneficial because it generates an economic development opportunity for non–food farm products in rural areas.

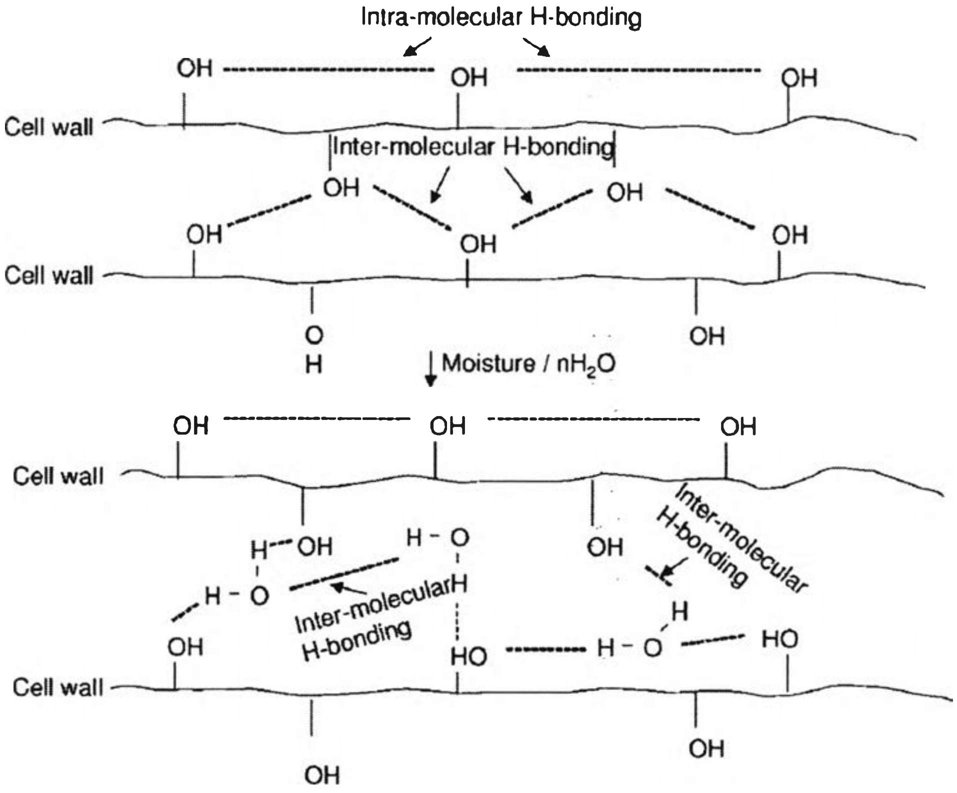

Figure 2.5 Schematic representation of hydrogen bonding in natural fibers.

These mentioned advantages are benefits not likely to be ignored by the plastics industry for use in the automotive, building, appliance, and other applications (Rowell R.M. 2002; Drzal Lawrence T. *et al.* 2003; Li Y. *et al.* 2008). Table 2.4 summarizes all advantages and disadvantages of cellulose fibers.

Despite the advantages mentioned above, the use of cellulose fibers in thermoplastics has not been extensive. Possible reasons that contribute to unsatisfactory final properties of the composites include the limiting of thermal stability at typical melt processing temperatures of about 180–200°C which limit the type of thermoplastics that can be used with the fibers (Nando G.B. *et al.* 1996).

Table 2.3 The annual fiber production and the availability of some cellulose fibers (Lee S.M. 1991)

Fiber	**World Production (tons)**	**India Production (tons)**	**Cost (U.S.$/kg)**
Coir	282,000	160,000	0.03
Banana	100,296	1,632	0.10
Sisal	600,000	3,000	0.05
Palmyrah	Not known	100	0.07
Pineapple	Not estimated	Not estimated	0.05
Glass	–	–	0.33
Carbon	–	–	> 16.00
Stainless Steel	–	–	> 4.00

Poor dispersion characteristics in the non–polar, olefinic thermoplastic melt due to a strong hydrogen force between the fibers. Limiting of the compatibility with many thermoplastic matrices due to their highly hydrophilic character which result in poor mechanical properties of the composites produced. High moisture absorption of the fibers that can affect the dimensional stability of the composite and the interfacial bond strength.

Since, the natural fibers are lignocellulosic in nature and are composed of cellulose, hemicellulose and lignin. The chemical compositions and structural parameters of some fibers are represented in Table 2.5. The amount of cellulose can vary depending on the species and age of the plant.

Table 2.4 The summation of advantages and disadvantages of cellulose fibers over traditional glass fibers (Rowell R.M. 2002; Drzal Lawrence T. *et al.* 2003; Li Y. *et al.* 2008)

Advantages	**Disadvantages**
Low cost	High moisture adsorption
Renewable	Poor microbial resistance
Low density (light weight)	Low thermal resistance
High strength and elasticity modulus	Local and seasonal quality variation
Sound abatement capability	Demand and supply cycles
Non–abrasive	
Low energy consumption	
Thermal incineration possible with high energy recovery	
No residues when incinerated	
Full safe handling and no skin irritations	
Can be stored for long periods of time (with a good prevention from moisture)	
Crops can be used for cleaning soil	
Crops recycle CO_2 from atmosphere	
Fast absorption/desorption of water	
Biodegradability	

Table 2.5 Chemical composition and structural parameters of some natural fibers (Rowell R.M. 2002; Drzal Lawrence T. *et al.* 2003; Li Y. *et al.* 2008)

Type of fiber	**Cellulose (%)**	**Lignin (%)**	**Hemicel-lulose (%)**	**Pectin (%)**	**Wax (%)**	**Moisture content (%)**
BAST						
Jute	61–71.5	12.0–13.0	13.6–20.4	0.2	0.5	12.6
Flax	71.0	2.2	18.6–20.6	2.3	1.7	10.0
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	10.8
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	8.0
Kenaf	31–39	15.0–19.0	21.5	–	–	–
LEAF						
Sisal	67–68	8.0–11.0	10.0–14.2	10.0	2.0	11
PALF	70–82	5.0–12.0	–	–	–	11.8
Henequen	77.6	13.1	4.0–8.0	–	–	–
SEED						
Cotton	82.7	–	5.7	–	0.6	–
FRUIT						
Coir	36–43	41–45	0.15–0.25	3.0–4.0	–	8.0

Since the main drawback of cellulose fibers (CF) is their hydrophilic nature which lowers their compatibility with hydrophobic polymer matrices. The hydrophilic nature of CF leads to biocomposites having high water absorption characteristics that reduce their utility in many applications. High water and moisture absorption of the fibers cause swelling and plasticizing which results in dimensional instability and poor mechanical properties. In order to avoid this drawback, they can be submitted to specific surface modification to minimize their interfacial energy with the often non–polar polymer matrix and provide an efficient hydrophobic barrier. The combination of a plastic matrix and reinforcing fibers gives rise to composites having the best properties of each component. Since the plastics are soft, flexible and lightweight, their combination provides a high strength–to–weight ratio in the resulting composite. Several types of polymers have been used as matrices for natural fiber composites (George J. *et al.* 2001). Both thermosets and thermoplastics are used. The most commonly used thermoset polymers are polyester, epoxies and phenolics. Thermoplastics like polyethylene (PE), polystyrene (PS) and polypropylene (PP) have also been used. These polymers have a different affinity towards the fiber owing to the difference in their chemical structure. The fiber and polymer matrix interaction can be improved by making either chemical or physical modifications to the fiber.

The manufacturer of cellulose fiber composites includes the use of either a thermoset or thermoplastic polymer combined with the cellulose fiber to preform or mat. Thermoplastic offer many advantages over thermoset polymers. One of the advantages of thermoplastic matrix composites is their low processing cost. Another is design flexibility and ease of molding complex parts (Nabi D. *et al.* 1999). Simple methods such as extrusion and injection molding are used for processing of these composites. In thermoplastics, most of the work reported so far deals with polymers such as polyethylene, polypropylene, polystyrene and poly(vinyl chloride). This is mainly because of their low processing temperature, 200°C, which can avoid the thermal degradation of cellulose fibers. In automotive applications, the most common system used today is thermoplastic polypropylene, particularly for non–structural components. Polypropylene is favored due to its low density, excellent processability, mechanical properties, excellent electrical properties and good dimensional stability and impact strength (George J. *et al.* 2001). However, several synthetic thermoplastics are utilized which listed in Table 2.6.

2.3 Modifications of Cellulose Fiber

Cellulose fibers are incompatible with the hydrophobic polymer matrix and have a tendency to form aggregates. These are hydrophilic fibers and thus exhibit poor moisture resistance. Enhanced interfacial adhesion for composites containing cellulose fibers can be achieved either by physical or chemical treatments. The fibers treatment with hydrophobic aliphatic and cyclic structures has been attempted to improve the adhesion between cellulose fibers and polymer matrix.

Table 2.6 Properties of typical thermoplastic polymers used in natural fiber composite fabrication (George J. *et al.* 2001)

Property	**PP**	**LDPE**	**HDPE**	**PS**	**Nylon 6**	**Nylon 6,6**
Density (g/cm^3)	0.899–0.920	0.910–0.925	0.94–0.96	1.04–1.06	1.12–1.14	1.13–1.15
Water Absorption 24 hours (%)	0.01–0.02	<0.015	0.01–0.2	0.03–0.10	1.3–1.8	1.0–1.6
T_g (°C)	−10 to −23	−125	−133 to −100	–	48	80
T_m (°C)	160–176	105–116	120–140	110–135	215	250–269
Heat Deflection Temperature (°C)	50–63	32–50	43–60	Max. 220	56–80	75–90
Coefficient of Thermal Expansion (mm/mm/ °Cx10^5)	6.8–13.5	10	12–13	6–8	8–8.6	7.2–9.0
Tensile Strength (MPa)	26–41.4	40–78	14.5–38	25–69	43–79	12.4–94
Elastic Modulus (GPa)	0.95–1.77	0.055–0.38	0.4–1.5	4–5	2.9	2.5–3.9
Elongation (%)	15–700	90–800	2.0–130	1–2.5	20–150	35– >300
Izod Impact Strength (J/m)	21.4–267	>854	26.7–1068	1.1	42.7–160	16–654

Physical methods, including corona or plasma discharges, are useful for polymers such as polypropylene, polyethylene and polystyrene. Chemical methods cover pre-treatment of fiber surface by a coupling agent, such as isocyanates and silanes, and modification of the matrix by grafting polar moieties, such as acrylic acid, acrylic esters or maleic anhydride on polymer chains.

2.3.1 Physical Modification

The main aim of these treatments is to purify, oxidize, and/or activate the surface of the fibers. They can change the structural and surface properties of the fibers and thereby influence the mechanical bonding with the polymers matrix (Bledzki A.K. *et al.* 1999).

Electric discharge (corona and cold plasma treatment) is another method of physical treatment. These methods are used for cellulose fiber modification to decrease the melt viscosity of cellulose–polyethylene composites.

Corona treatment is one of the most interesting techniques for surface oxidation activation. It changes the surface energy of the cellulosic fibers, which in turn affect the melt viscosity of composites. Sapieha S. *et al.* (1991) explored low–temperature plasma techniques as a mean to form chemically active sites onto the cellulosic surfaces. The active species created during or after corona exposure would initiate graft functionalization when the monomers or their diluted solutions are brought in contact with the surface. Dong S. *et al.* (1993) investigated the effect of corona treating the surfaces of components on tensile properties of wood fiber linear low–density polyethylene composites. Corona treatment results in a significant increase in the strength properties of the composites. Yield stress increases after treatment of one or both of the composite components. Pronounced improvement in ductility has been observed for composites containing 15 to 30% of the corona modified fiber.

Cold plasma (low temperature plasma) is a useful technique to improve the surface characteristics of the fiber and polymeric materials by utilizing ingredients such as electron, ion, radical and excited molecules produced by electrical discharge. This method can be generated under atmospheric pressure in the presence of helium. This method causes mainly chemical implantation, etching, polymerization, free radical formation, crystallization, whereas; sputter etching brings about chiefly physical changes such as surface roughness and leads to increase in adhesion and decreases in light reflection (Bledzki A.K. *et al.* 1999).

γ–Ray treatment has been extensively studied for applications of the extremely high energies associated with γ–irradiation sources to cellulose and its derivatives, but mostly in terms of the degradation mechanism taking place. Takacs E. *et al.* (1999) studied the effect of high–energy irradiation on cotton–cellulose in an inert atmosphere and in the presence of oxygen. A decrease in the degree of polymerization from 1200 to 330 was measured after irradiation with a dose of 15 kGy (dose rate 100 Gy/h) and further gradual decrease was measured when the dose was increased to 100 kGy. At lower doses a slight increase in crease recovery angle was found as compared to the un–irradiated sample. In the FTIR spectra of the same sample the appearance of the absorbance of carbonyl groups (band at 1730–1750 cm^{-1}) was found as a consequence of the oxidative degradation. Cracks on the surface of the fibers were observed by a scanning electron microscope on the samples irradiated with doses higher than 100 kGy.

2.3.2 Surface Chemical Modification

Chemical modification of cellulose fibers aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers. Different chemicals were used in fiber–reinforced composites. The low interfacial bonding between fiber and polymer matrix often reduced their potential as reinforcing agents. Due to the hydrophilic nature of cellulose fibers, chemical modifications are considered to optimize the interface of fibers.

The hydrophilic nature of cellulose fibers leads to high water absorption characteristics biocomposites that reduce their utility in many applications. The presence of a natural waxy substance on the fiber surface contributes immensely to ineffective fiber to polymer matrix bonding and poor surface wetting. The presence of free water and hydroxyl groups reduce the ability of natural fibers to develop acceptable adhesive characteristics with most binder resins. High water and moisture absorption of the fibers cause swelling and a plasticizing effect resulting in dimensional instability and poor mechanical properties. The surface chemical modifications of natural fibers like dewaxing, alkali treatment, vinyl grafting, cyanoethylation, acetylation, bleaching, peroxide treatment, sizing with polymeric isocyanates, treatment with various coupling agents have achieved various levels of success in improving fiber–matrix adhesion in natural fiber composites (Mohanty A.K. *et al.* 2001).

2.3.2.1 Chemical Coupling Agents

Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix. Generally, chemical coupling agents are the molecules configurations bearing two reactive functions. The first one is to react with the hydroxyl groups of cellulose fiber and the second function is to react with the functional groups of the matrix. The most common coupling agents are silane and isocyanate based compounds. The chemical composition of them allows reacting with the fiber surface, which forms a bridge of chemical bonds between the fiber and the matrix. For cellulose fiber composites, isocyanates were found to be reliable. It is expected that the formation of a primary type of bonds, covalent bonds between cellulose and isocyanate, and a secondary type of weak bonds, between thermoplastics and isocyanates, improve the mechanical properties of wood fiber filled thermoplastics. Pretreatment of fibers by encapsulated coating with silanes or isocyanates and grafting provides better dispersion by reducing the fiber–fiber interaction with the formation of coating on the fiber surface (George J. *et al.* 2001).

F. Corrales *et al.* (2007) have been studying a variety of reagents containing a function able to modify the hydroxyl groups in cellulose fiber and a second moiety to be used in the subsequent elaboration of composites to establish continuous covalent linkage at fiber/matrix interfaces. The chemical modification of jute fibers using oleoyl chloride, a fatty acid derivate, to confer hydrophobicity and resistance to biofibers was investigated. The reaction was applied in two different solvents, pyridine (swelling solvent) and dichloromethane (non–swelling solvent). The characterization methods, an element analysis (EA) and FTIR, have proved the chemical interaction between cellulosic material and the coupling agents. The treatment of lignocellulosic fibers with oleoyl chloride has been undertaken to bring a chemical modification of the substrate by grafting oleoyl moieties on the cellulose backbone as shown in Figure 2.6. The principal characteristic of pyridine is its polar nature and its catalytic capacity for the modification reaction proposed. Thus, the basic character of pyridine allows the molecule to diffuse deeply inside the internal structure of the cellulose fiber increasing its ability to interact with hydroxyl groups and making accessible more hydroxyl groups to the coupling agent. Methylene chloride is a non–swelling solvent for cellulosic fibers, thus the esterification reaction will be limited to the hydroxyl groups located on the external surface of the fiber. The FTIR spectra of jute fibers after the modification reaction showed that the reaction in pyridine leads to a considerable increasing of the carbonyl peak. Almost no modification could be observed for the reaction in dichloromethane.

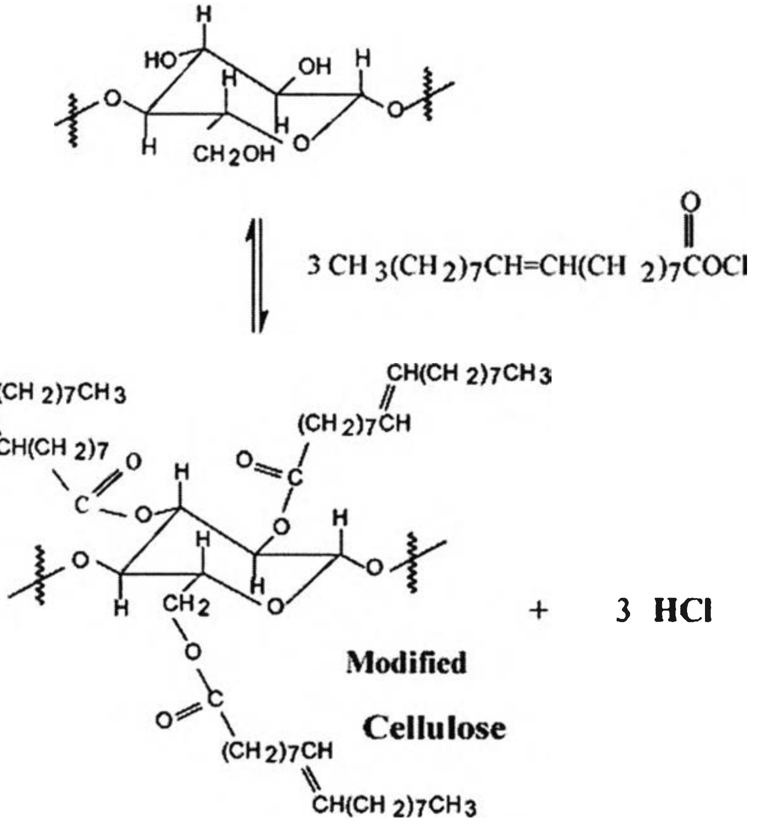

Figure 2.6 The modification reaction of cellulose fiber and oleoyl chloride schematic (Corrales F. *et al.* 2007).

The SEM images were observed for the higher roughness of the fiber surface after chemical modification with oleoly chloride, Figure 2.7. It was assessed that the efficiency of the reaction depends on the solvent polarity and its catalytic capacity which governed the extension of the modification reaction.

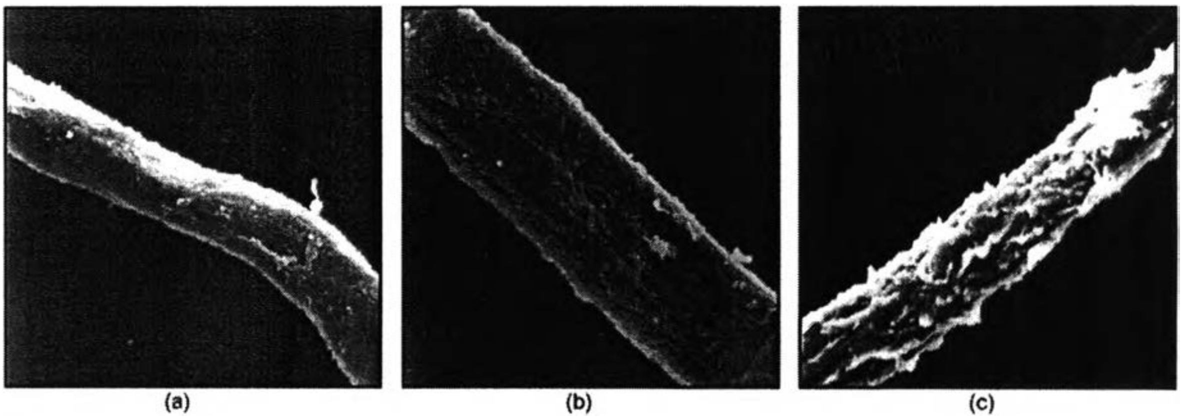

Figure 2.7 SEM microphotography of (a) non–treated jute fibers; (b) modified jute fibers in pyridine for 3 hours; (c) modified jute fibers in pyridine for 24 hours (Corrales F. *et al.* 2007).

Bledzki A.K. *et al.* (1996) studied the structure and properties of natural vegetable fibers (NVF) and showed that the composites made of NFV combine good mechanical properties with low specific mass. The high level of moisture absorption by the fiber, its poor wettability, as well as the insufficient adhesion between untreated fiber and the polymer matrix lead to de–bonding with age. By using a coupling agent, like silanes or sterin acid, the Young's modulus and the tensile strength increased, depend on the resin, up to 50%. The moisture absorption of the composites decreased by about 60%, simultaneously. Bataille P. *et al.* (1989) studied the effect of surface pretreatment of cellulosic fibers and the processing time and temperature on the mechanical properties of the cellulose–containing polypropylene. Treatment of fibers with a coupling agent improves significantly the interfacial adhesion and therefore the mechanical properties of the composite. It was sufficiently high to break and delaminate the cellulosic fibers. Addition of maleic anhydride modified polypropylene improved the properties of resulting composites.

The mechanical properties of polypropylene (PP) composites with various natural fibers such as old newsprint, kraft pulp and hemp were studied by Sain M. *et al.* (2005). The effect of the low molecular weight PP–based coupling agent on the mechanical properties of these natural fiber–filled PP composites was also investigated and the results showed that these modified fibers can be used as an interfacial modifier for enhancing the strength properties of the PP–filled composites. The optimum amount of coupling agent was found to be around 3–4wt% of the composites. Kraft pulp and hemp fiber–filled composite show better tensile, flexural and un–notched impact strength compared to the glass fiber–filled composites at the same fiber loading.

The surface of microfibrillated cellulose (MFC) modified using chemical treatment in an organic solvent was reported by Stenstad P. *et al.* (2008). Succinic and maleic acid groups could be introduced directly onto the microfibrillated cellulose surface as a monolayer by a reaction between the corresponding anhydrides and the hydroxyl group surface of the microfibrillated cellulose. Succinic and maleic anhydrides, shown in Figure 2.9 (a) reacted at the hydroxyls surface of the microfibrillated cellulose under water–free conditions. When succinic anhydride was reacted with microfibrillated cellulose, a layer of acid groups was induced on the fibril surface. This was demonstrated in the FTIR spectra in Figure 2.8 when the peak at 1724 cm^{-1} verified the presence of carboxyl groups after a reaction with succinic anhydride. Similar results were observed, when maleic anhydride was reacted with the hydroxyl groups of microfibrillated cellulose.

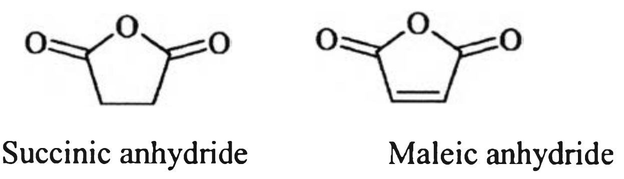

Figure 2.8 Structure of maleic and succinic anhydride.

Vinyl groups can be introduced in addition to the acid groups. This is shown in Figure 2.9 (b) when the FTIR spectra peak at 1722 cm^{-1} confirmed the introduction of acid and the peak at 1636 cm^{-1} indicated the vinyl groups contained in the sample.

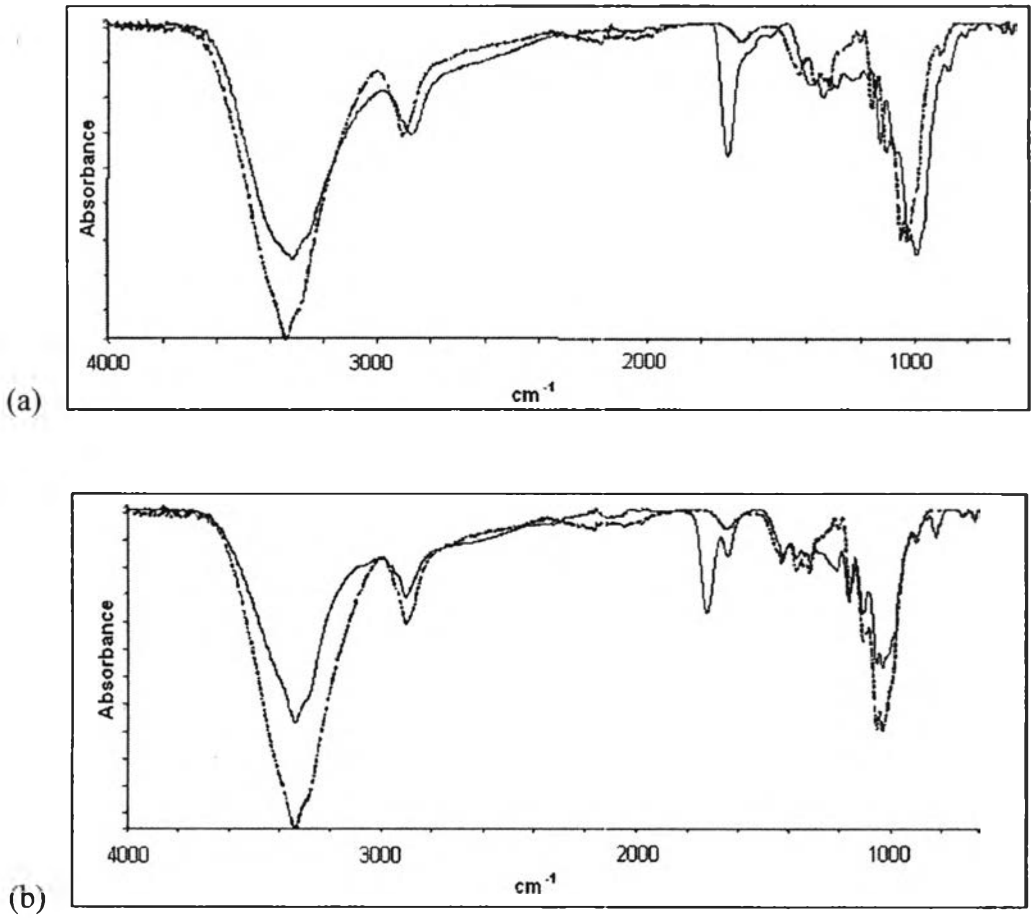

Figure 2.9 FTIR spectra of microfibrillated cellulose; (a) coated with succinic acid compared with that of MFC (dashed line) and (b) coated with maleic acid compared with that of microfibrillated cellulose (dashed line) (Stenstad P. *et al.* 2008).

These vinyl groups could be used as a starting point for grafting reactions with monomers that are water–insoluble. The reactivity of succinic and maleic anhydride was also measured by the zeta potential measurement, as shown in Figure 2.10. The zeta potential, referred to the reactivity, of microfibrillated cellulose coated with succinic anhydride, –40.9 mV, which was much higher than that of maleic anhydride, –32.3 mV. These negative charges of microfibrillated cellulose from the surface modification with anhydrides may have an application in electronic devices.

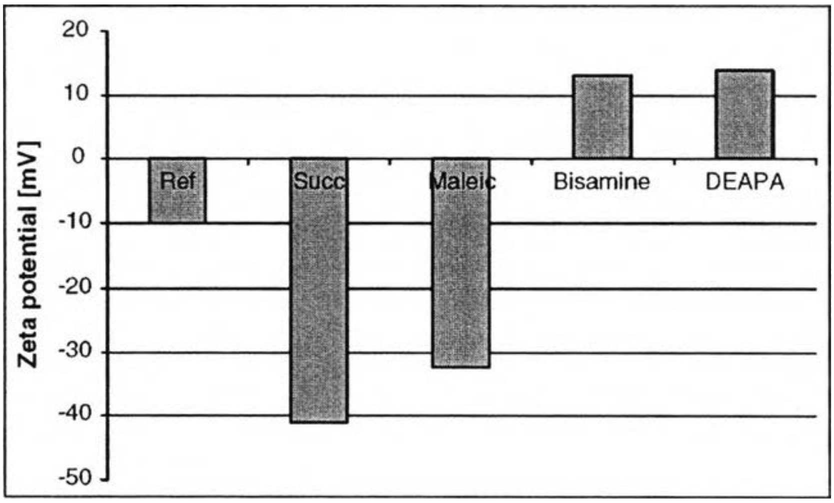

Figure 2.10 Zeta potentials at pH 7.0 of unmodified microfibrillated cellulose (Ref), microfibrillated cellulose coated with succinic acid (Succ), maleic acid (Maleic), di-isocyanate followed by reactions with bis– (3–aminopropyl) amine (Bisamine) and with 3– (diethylamino) propylamine (DEAPA) (Stenstad P. *et al.* 2008).

Rensch H.P. *et al.* (1992) modified chemithermomechanicalpulp (CTMP) with various isocyanates such as n–butyl isocyanate (BUI), phenyl isocyanate (PHI), hexamethylene di–isocyanate (HMDI) and poly(methylene) poly(phenyl) isocyanate (PMPPIC) in dimethylformamide (DMF) in the absence of catalyst. Their effect on the thermoanalytical behavior of CTMP was investigated. Aliphatic isocyanates such as BUI and HMDI showed a low potential of reaction with CTMP, compared to aromatic isocyanates with equal functionality like MDI and PHI. The use of MDI and its oligomeric modification PMPPIC as a coupling agent resulted in an increased thermal stability of modified pulp compared to untreated pulp. Treatment with the aromatic diisocyanate MDI, however, resulted in an increased reduction of water uptake.

Gandini A. *et al.* (1998) treated the various cellulosic substrates including powders, long fibers and sheets with coupling agents 3–isopropenyl–αα'–dimethylbenzyl isocyanate (TMI) and 2–isocyanatoethyl methacrylate (IEM), shown in Figure 2.11, in a dry non–swelling medium. These heterogeneous reactions introduced a small but significant number of polymerizable moieties at the surface of the cellulose. In a second step, the free radical polymerization of styrene or methyl methacrylate was carried out in the presence of these modified celluloses. It was shown that the alkenyl functions appended onto their surface took part in the chain growth thus giving a continuous path of covalent bonds between the solid substrate and the polymer matrix.

3–isopropenyl–αα′–dimethylbenzyl isocyanate

2–isocyanatoethyl methacrylate

Figure 2.11 The structure of 3–isopropenyl–αα′–dimethylbenzyl isocyanate (TMI) and 2–isocyanatoethyl methacrylate (IEM) coupling agents.

The grafting of cellulose fibers with different coupling agents in order to reinforce the elements in composite materials was studied by Ly B. et al. (2008). Pyromellictic dianhydride (PPDI), benzophenone–3,3′,4, 4′–tetracarboxylic dianhydride (BPDA), 1,4–phenylene diisocyanate (PPDI) and 4,4′–diphenylmethane diisocyanate (MDI) were used to graft fibers. The chemical structure of these four coupling agents is shown in Figure 2.12.

The chemical modification of Avicel seems to improve the quality of the fibers/matrix interface. Cellulose particles were successfully modified using six different di–functional molecules. The stiff backbone of these grafted agents ensured that one reactive group was preserved and directed outwards from the fiber surface. The grafting and the preservation of the second function were proven by FTIR, elemental analysis and XPS analysis techniques. The FTIR spectra displayed the appearance of isocyanate function (2275 cm^{-1}) in the case of PDI and MDI modification. In both anhydride and isocyanate grafting, the presence of a peak at 831 cm^{-1} associated with the presence of a di–substituted aromatic ring confirmed the occurrence of chemical bonds between cellulose and the four coupling agents. The urethane linkage signal, which should appear due to the reaction of the isocyanate with the cellulose hydroxyl groups, was masked by a large signal at 1634 cm^{-1}.

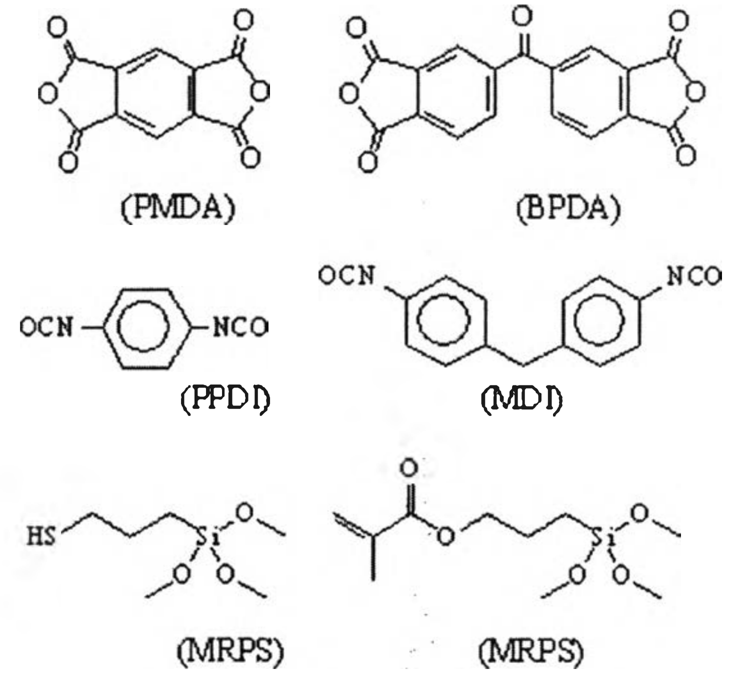

Figure 2.12 Chemical structure of the coupling agents used for cellulose surface modification (Ly B. et al. 2008).

The elemental analyses of samples are given in Table 2.7. Most importantly, it confirms the presence of nitrogen for PPDI–treated cellulose but no significant difference could be noticed for the other grafting agents, because there is no significant difference in oxygen and carbon atom content between the coupling agents and the cellulosic substrate.

XPS analyses were carried out in order to ascertain more precisely the chemical composition of the surface. The XPS spectra of cellulose before and after treatment are given in Figure 2.13. Theoretically, pure cellulose exhibits two peaks in the full XPS spectra, carbon and oxygen, with an O/C ratio of 0.83.

Table 2.7 Elemental analysis of Avicell before and after modification with different coupling agents (Ly B. et al. 2008)

Samples	**C (%)**	**H (%)**	**O (%)**	**N (%)**	**Si (%)**
Avicel	42.4	6.5	49.3	–	–
PMDA_Av	43.2	6.4	49.4	–	–
BPDA_Av	45.2	5.9	49.5	–	–
PPDI_Av	44.5	6	48.4	1.1	–
MPS_Av	42.9	6.4	50.9	–	0.1

The XPS spectra of unmodified Avicell and ksp displayed the expected two signals (oxygen and carbon atoms at around 532.6 and 285 eV, respectively in Figure 2.13 (a) and (b)). For modified cellulose samples, new peaks appeared, namely: the nitrogen signal at around 400 eV, for PDI and MDI, respectively (Figure 2.13 (g) and (h)), those corresponding to silicon atoms in MPS and MRPS at 102 and 150 eV, respectively (Figure 2.13 (i) and (j)) and that associated with the presence of sulfur atom at 160 eV, for MRPS (Figure 2.13 (j)).

The effect of chemical treatment on the tensile properties of sisal fiber–reinforced LDPE (Low Density Polyethylene) composites was investigated by Kuruvilla J. *et al.* (1996). Treatments using chemicals such as sodium hydroxide, isocyanate (Cardanol derivative of toluene diisocyanate, CTDIC), permanganate and peroxide were carried out to improve the bonding at the fiber–polymer interface. The reaction path way for the preparation of the urethane derivative of cardanol is given in Figure 2.14.

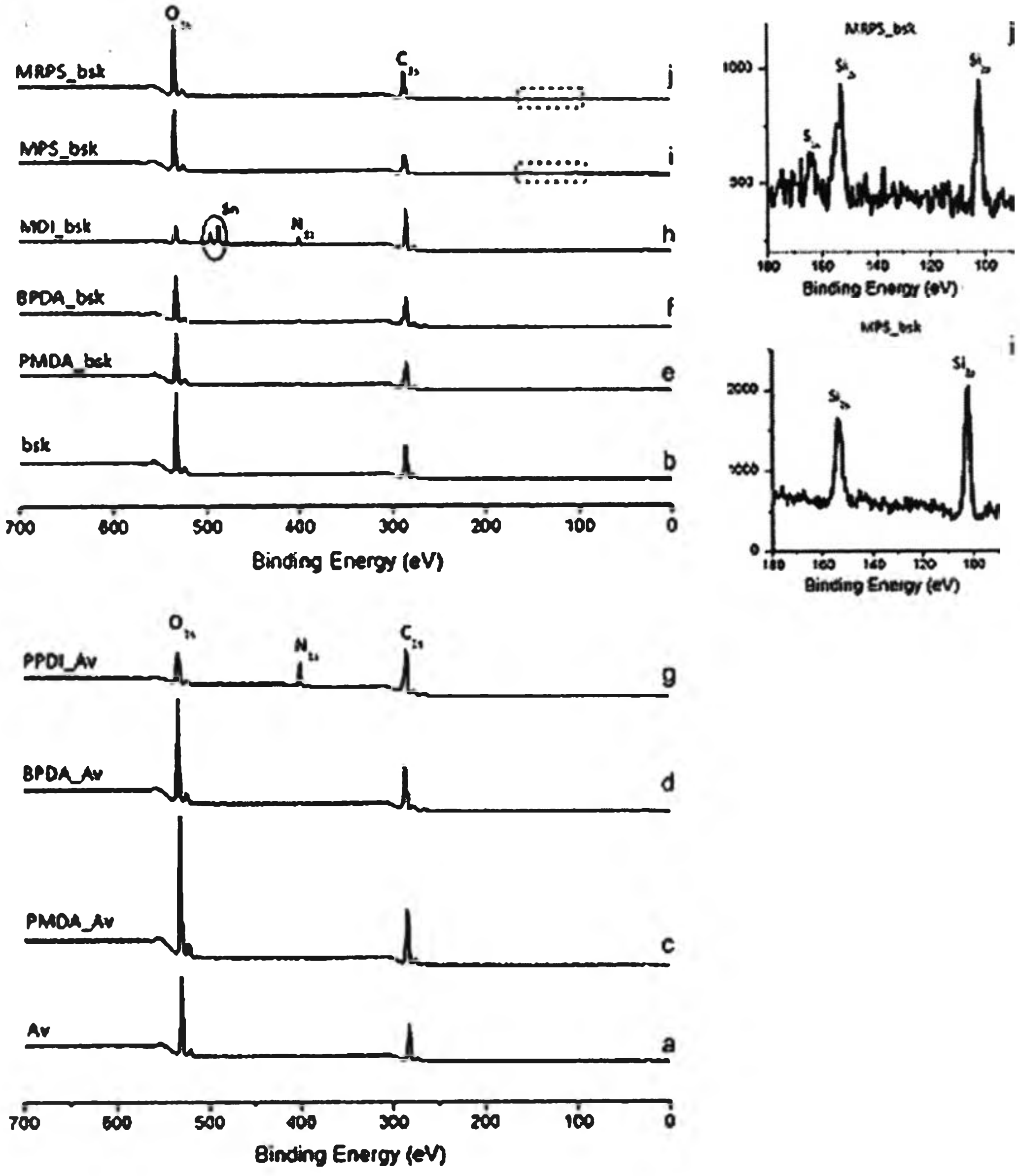

Figure 2.13 Full XPS spectra of cellulose surface, before and after modification with different coupling agents (Kuruvilla J. *et al.* 1996).

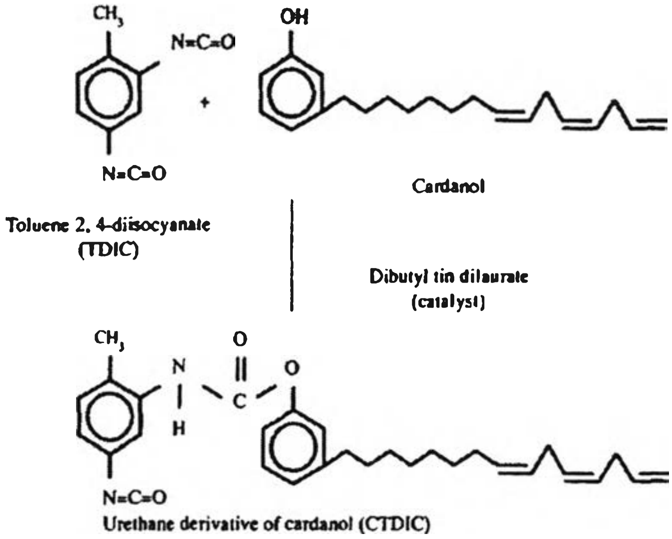

Figure 2.14 The reaction pathway for the preparation of urethane derivative of cardanol (Kuruvilla J. *et al.* 1996).

The hydroxyl groups in cellulose fiber are relatively unreactive, since they form strong hydrogen bonds. The possible reaction between free isocyanate groups in CTDIC and cellulose fiber is illustrated in Figure 2.15. The linkage of isocyanate and fiber was due to the formation of a chain of covalent chemical bonds.

The tensile properties of CTDIC treated, alkali treated and untreated sisal–PE composites, 30% fiber loading, is shown in Table 2.8. It was found that CTDIC treated fiber composites show superior tensile strength and modulus than alkali treated and untreated composites. By treating the cellulose fiber surface with CTDIC, the hydrophilic nature of cellulose can be reduced. The long chain structure of CTDIC linked to the cellulosic fiber makes the fiber hydrophobic, compatible and highly dispersible in PE matrix. This will result in a strong interfacial bond between fiber and PE matrix. The SEM photomicrographs support the strong fiber–matrix adhesion in sisal–LDPE composites. A hypothetical chemical structure of cellulose fiber–CTDIC–PE in the interfacial is given in Figure 2.16.

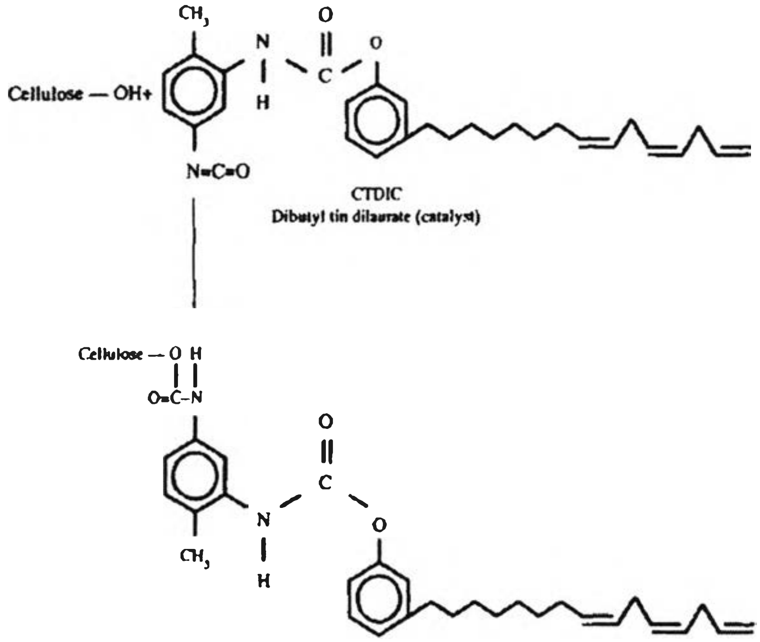

Figure 2.15 A possible reaction between free isocyanate groups in CTDIC and cellulosic sisal fiber (Kuruvilla J. *et al.* 1996).

Table 2.8 Variation of tensile properties of LDPE–sisal composites with fiber treatments (fiber length = 5.8 mm, fiber content = 30%) (Kuruvilla J. *et al.* 1996)

Composites	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
Untreated	31.12	3086	2
Alkali treated	34.27	3328	1
Isocyanate treated	41.5	4066	4

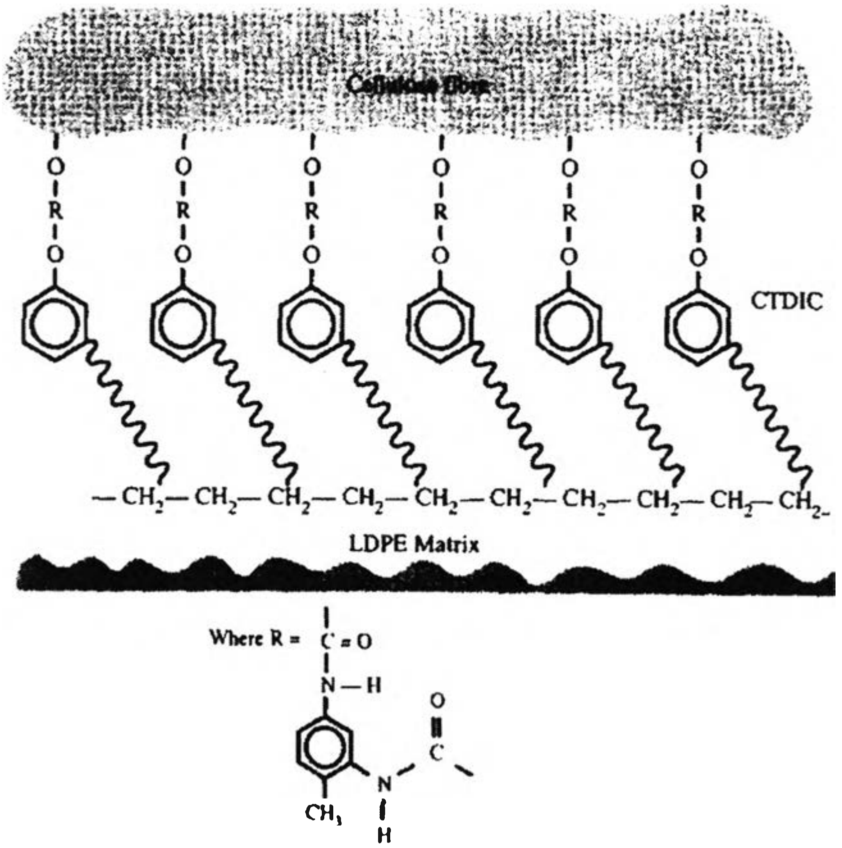

Figure 2.16 A possible hypothetical structure of sisal fiber–CTDIC–PE in the interfacial area (Kuruvilla J. *et al*. 1996).

Chui G. G et al. (2008) investigated the effect of m–isopropenyl–α,α–dimethylbenzyl isocyanate grafted polypropylene (m–TMI–PP) on the interfacial interaction of wood–flour/polypropylene (WF/PP). WF/PP composites prepared by a twin–screw/single–screw extruder system. The experimental results demonstrated that m–TMI–PP greatly improved the interfacial interaction between WF and PP. The interaction among WF, PP and m–TMI–PP is illustrated in Figure 2.17.

The mechanical properties of WF/PP materials influenced by m–TMI–PP are shown in Table 2.9. The loading of 6% m–TMI–PP effectively increased mechanical properties compared with the WF/PP composite.

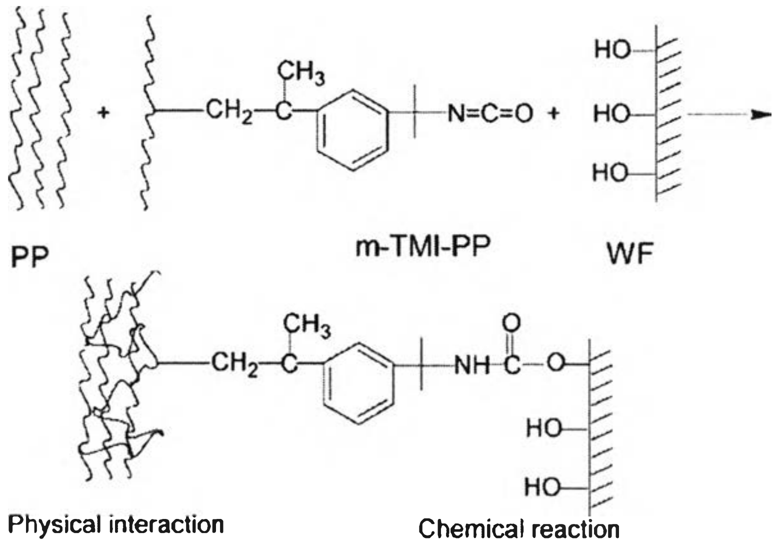

Figure 2.17 Schematic hypothesis of interfacial interaction for WF/m–TMI–PP/PP (Chui G. G et al. 2008).

Table 2.9 Mechanical properties of WF/PP and its composites

Sample	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Unnnotched Izod impact strength (kJ/m^2)
PP	23.1	29.2	1.3	18.21
WF/PP	29.8	41.3	3.2	10.49
WF/m–TMI–PP/PP	39.1	95.8	5.4	13.79

The SEM micrographs of the composites are given in Figures 2.18. The WF/PP image, Figure 2.18 (a), indicates poor mechanical strength between their surfaces. On the other hand, WF/m–TMI–PP/PP image, Figure 2.18 (b), shows the improvement of WF and PP interface. The WF was embedded in the PP matrix phase and good adhesion between WF and PP were obtained. According to DSC results, m–TMI–PP makes PP crystallization temperature and crystallization degree decrease compared with WF/PP composites. The WF/m–TMI–PP/PP achieves slightly higher thermal stability and char residue than WF/PP by TGA results.

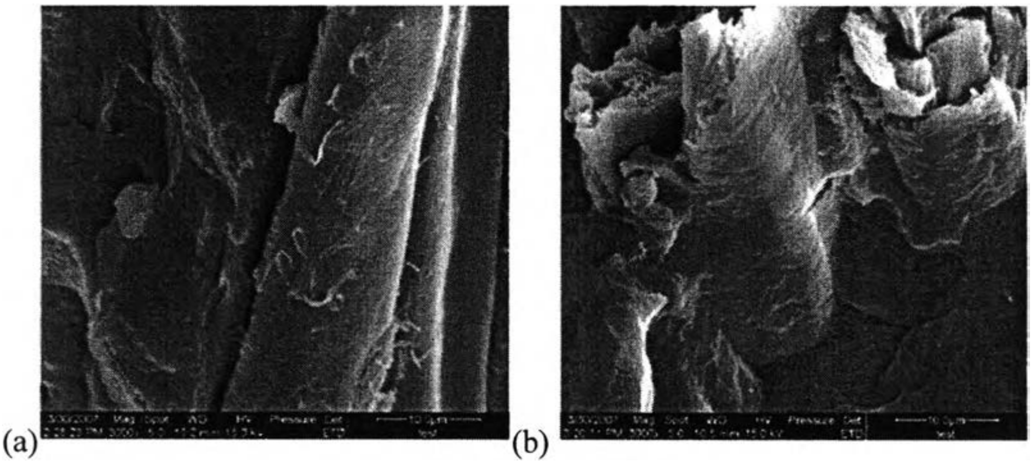

Figure 2.18 SEM micrographs of (a) WF/PP and (b) WF/m–TMI–PP/PP (Chui G. G et al. 2008).

Composites of highly crystalline cellulosic microfibers (30% by weight) with polypropylene (PP) as well as with maleic anhydride grafted polypropylene (MAPP) prepared by using 1,6–diisocyanatohexane (DIC) as a Compatibilizing agent were studied by Wulin Q. et al. (2005). The results of these composites show that the tensile strength and Yong's modulus were improved intensively by using DIC. The enhancement is proposed to be due to stronger interfacial adhesion caused by the reduction of the polarity and hydrophilicity of cellulose fiber in PP–based composites, compared to more chemically bound MAPP chains on cellulose fiber in MAPP–based composites. The SEM micrograph of PP and cellulose composites clearly shows the large gaps and voids between the PP matrix and cellulose fiber, Figure 2.19. When cellulose fiber was surface pretreated with DIC and compounded with a PP or MAPP matrix, the reactions are proposed as shown in Figure 2.20 Composite materials obtained by compounding and molding cellulose fibers from sugar cane bagasse with low–density polyethylene (HDPE) were studied by Pasquini D. *et al.* (2008). The fibers were used after chemical modification with octadecanyl (OC) and dodecanoly (DC) chloride acids. The morphology, thermal properties and the water absorption behavior of the composites were tested. It appeared that the surface chemical modification of cellulose fibers resulted in an improvement of the interfacial adhesion with the HDPE matrix and higher dispersion level.

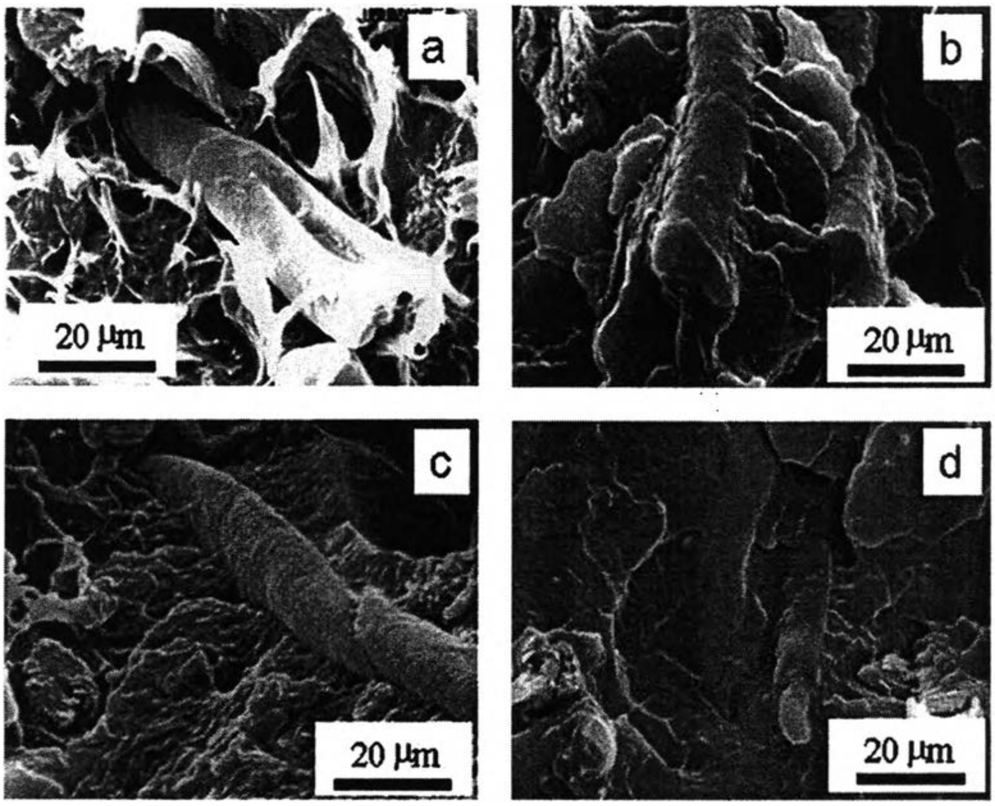

Figure 2.19 SEM photographs of fractured surfaces of (a) neat PP and PP–based composites with DIC content of, (b) 1.0, (c) 2.5 and (d) 5.0 phr (Wulin Q. et al. 2005).

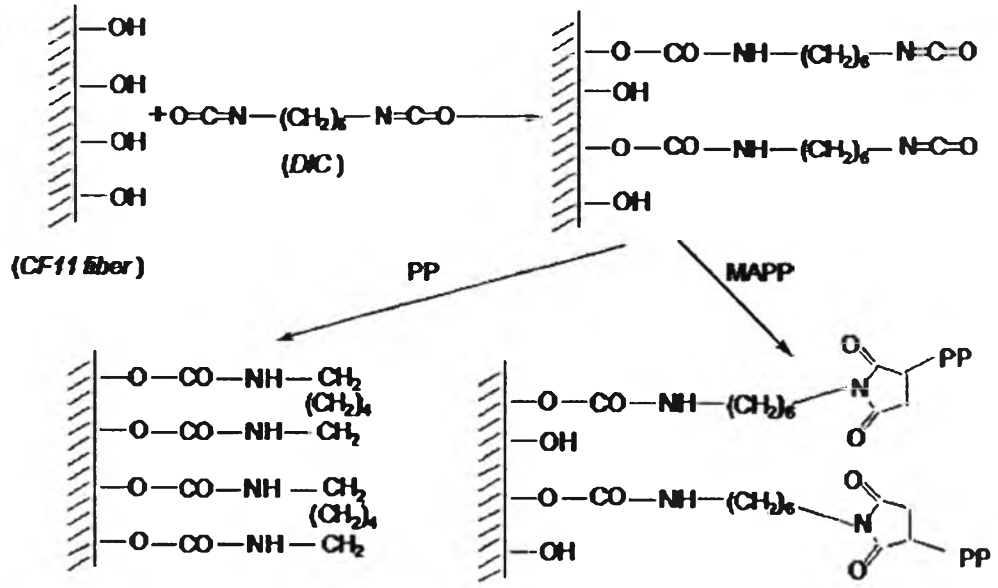

Figure 2.20 The reactions of DIC compatible with PP or MAPP (Wulin Q. et al. 2005).

The SEM micrographs of the fracture surface for the composite samples are shown in Figure 2.21. The unmodified fibers are pulled out practically intact from the matrix (Figure 2.21 (a)). This observation clearly indicates that the interfacial adhesion between cellulose fibers and matrix was poor. The presence of fiber aggregates provides an evidence of the poor dispersion of the filler within the polymeric matrix. On the other hand, the SEM micrographs of modified fibers (Figure 2.21 (b) and (c)) seem to provide good evidence of cellulose dispersion without fiber aggregates formation and strong interfacial adhesion provided by the cellulose fibers breaking during fracture.

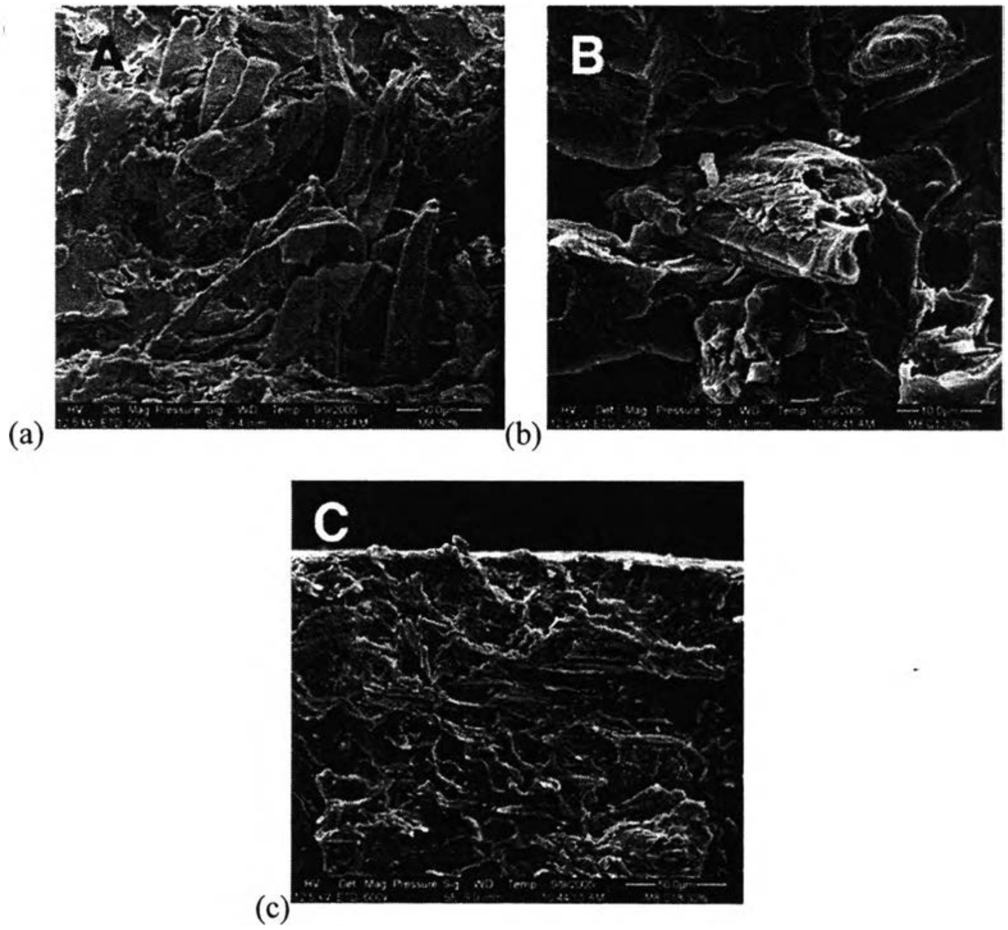

Figure 2.21 Scanning electron micrographs of fractured surface of cellulose fibers/LDPE composites: (a) 30 wt% of SMC (organosolv/methanol–supercritical carbon dioxide cellulose) fibers, (b) 30 wt% of SMC–DC fibers and (c) 30 wt% of SMC–OC fibers (Wulin Q. et al. 2005).

The addition of unmodified cellulose fibers in LDPE matrix promotes the most considerable reduction in the tensile strength as shown in Figure 2.22. For the modified cellulose fibers with octadecanoyl and dodecanoyl based composites, the reduction in the tensile strength was less pronounced. This behavior suggests the interfacial adhesion between the matrix and the fiber is higher, and that the dispersion level of the filler in polymer matrix is improved.

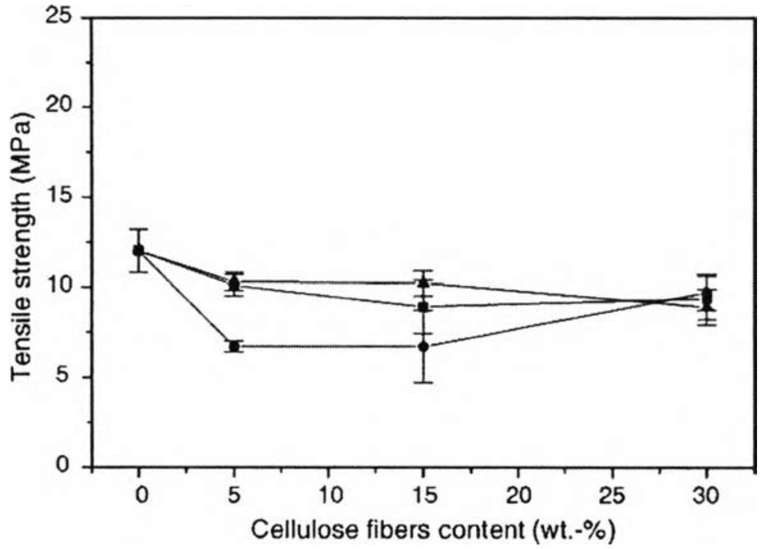

Figure 2.22 The tensile strength of unmodified SMC (●), modified SMC–DC (■), and SMC–OC (▲) cellulose fibers filled LDPE composites versus filler loading.

The water absorption for the different composite specimens immersed in water was evaluated as a function of time. The diffusion coefficient of water (D) and water uptake at equilibrium (WU) values are presented in Table 2.10. Both of the D and WU increased with increasing cellulose fibers content. These also resulted in a better water resistance. Discrimination between the two chemical treatments towards the water sensitivity is noted. The WU is higher for cellulose fiber modified by dodecanuyl compared to octadecanuyl based composites. However, the despite improved the compatibility between filler and matrix modified fiber–based composites, it did not show an improvement of the mechanical performances compared to the unmodified fibers.

Table 2.10 The water uptake at equilibrium (WU) and diffusion coefficient of water (D) for LDPE based composites when immersed in water at room temperature

Filler	**Fiber Content (wt%)**	**Water Immersion**	
		WU (%)	**D ($cm^2/s \times 10^{-13}$)**
–	0	0.18	0.881
SMC	5	0.81	0.693
	15	2.07	5.46
	30	4.66	12.27
SMC–DC	5	0.9	1.31
	15	1.53	4.08
	30	3.69	12.47
SMC–OC	5	0.93	1.8
	15	1.44	1.77
	30	3.18	12.47

2.3.2.2 Graft Copolymerization

A number of studies have focused on the use of acrylic or maleic anhydride grafted polypropylene as coupling agents for the composites of polypropylene with cellulose fiber materials.

Sanidi A.R. *et al.* (1994) reported the results of using recycled newspaper fibers as a reinforce filler in polypropylene. They used maleic anhydride–grafted polypropylene (MAPP) and acrylic acid–grafted polypropylene (AAPP) as coupling agents and found that both coupling agents improved the interaction between the hydrophobic PP and the highly polar fibers, tensile and impact strengths. However, the coupling agents with both high molecular weight and high acid content produced the highest mechanical properties.

Joly C. *et al.* (1996) found that partial masking of cellulose fiber with maleic anhydride (MAH) grafted polypropylene (PP) reduced the water absorption in cotton fiber composites. The effectiveness of MAH–PP copolymers as a coupling agent in jute–PP composites was also studied by Gassan J. *et al.* (1997). They found that the fiber treatment time and the MAH–PP concentration influenced the mechanical properties of the composites. Flexural strength of the composites with MAH–PP treated fibers was higher than that of unmodified fibers, and increased with fiber loading. SEM investigations confirmed that the increase in properties is caused by improved fiber–matrix adhesion. There was less inclination for fibers to pull out of the matrix.

Amash A. *et al.* (1998) tested the compatibility of maleic anhydride–modified polypropylene (MAPP) composites with natural fibers and its efficiency to improve the fiber–matrix. The grafting reaction of silane–coupling agents on cellulose fibers was been tested and it was demonstrated that the reaction between ≡Si–OR′ (where R′ is an alkyl moiety) from silane–coupling agent and the hydroxyl from cellulose takes place with trace amounts of water and at high temperatures only (Belgacem M.N. *et al.* 2005).

The optimization of acrylonitrile grafted onto cellulosic material, isolated from bamboo was performed by using ceric ammonium nitrate (CAN) as an initiator to generate the free radical on cellulose surface. The variety of the process parameters such as duration of soaking of cellulosic material in ceric ammonium nitrate solution, ceric ammonium nitrate concentration, polymerization time, temperature of reaction and acrylonitrile concentration were also investigated to study their influence on percent grafting and grafting efficiency (Khullar R. *et al.* 2008). The percent grafting for this sample was 210.3% and grafting efficiency was 97%. The FTIR spectra of the cellulosic material derived from bamboo observed the characteristic absorption bands for the nitrile group (–C≡N), at 2245 cm^{-1}, with an increase in intensity, thereby indicating that grafting of acrylonitrile had occurred. The SEM images depict the transformation in surface morphology of bamboo fiber on being subjected to grafting with acrylonitrile. Figure 2.23 shows the different surface of untreated and treated bamboo fibers. The uneven surface of fiber indicated the chemical bonding between acrylonitrile and bamboo fiber surfaces. The water sorbency of the fibers was expressed as the water retention value (WRV). The WRV decreased on the grafting indicating increased hydrophobic nature of the grafted fibers.

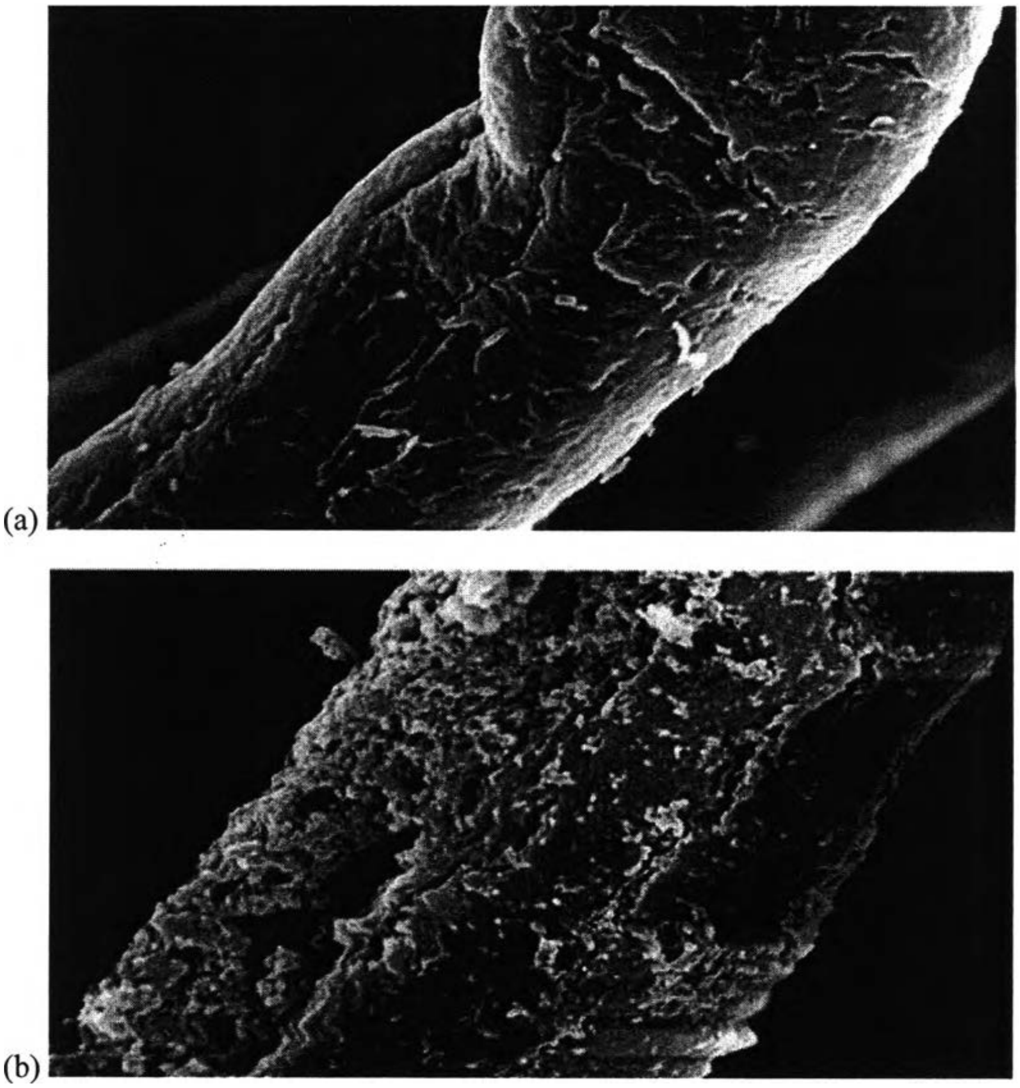

Figure 2.23 Scanning electron micrographs of (a) cellulosic material and (b) acrylonitrile grafted cellulosic material (Khullar R. *et al.* 2008).

Lori'a–Bastarrachea M.I. *et al.* (2001) studied the grafting of Poly (acrylic acid) (PAA) onto cellulosic microfibers. The grafting was carried out with a two-step procedure. First, vinyl–terminated ethoxy silane was deposited on the surface of the fiber. This was followed by a grafting polymerization reaction in aqueous media of acrylic acid with different concentrations of potassium persulfate (KPS), which act as an initiator. The grafted copolymer was characterized by Fourier transform infrared spectroscopy. Strong evidence that the grafting reaction was successful was given by the presence of the band, with a maximum at 1732cm^{-1} as shown in Figure 2.24, which was characteristic of carbonyl group absorption which was not initially present in the cellulosic fibers. The water absorption of the cellulosic microfibers grafted with PAA was three times greater than the water absorption of the ungrafted microfibers.

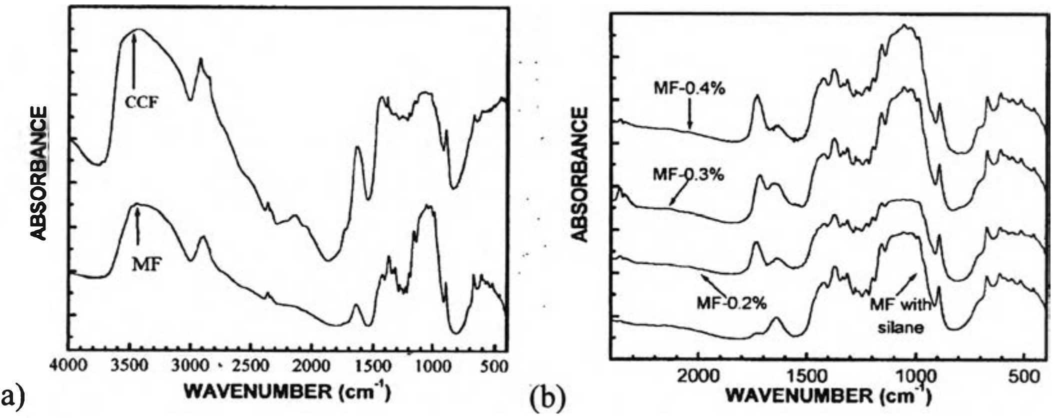

Figure 2.24 FTIR spectra of (a) cellulosic MF and CCF before grafting (b) silane–treated MF and PAA–grafted MF with several initiator concentrations (Lori'a–Bastarrachea M.I. *et al.* 2001).

The grafting copolymerization of styrene onto cellulosic material isolated from Agave Lechuguilla and Fourcroydes, using the ceric ammonium nitrate (CAN) with nitric acid as an initiator, under various concentrations of components, reaction conditions and pretreatment of starting material with aqueous NaOH was investigated by Cruz R.A. *et al.* (1999). For both fibers, the mechanically most stable fibers were obtained under the following reaction conditions: 0.4 g of fiber, 0.25 M of styrene, 0.025 M of ceric ammonium nitrate and 0.25 M of nitric acid at a reaction time of 4 hours and 50°C reaction temperature.

The characterization of grafted products by means of FTIR and SEM indicates the presence of the styrene grafts. Figure 2.25 shows the representative FTIR spectra of fibers isolated from Agave Lechuguilla and the grafted product. In the grafted sample case, further signals at 3025–3080 cm^{-1} and 1599–1450 cm^{-1} are clearly indicate the polystyrene units.

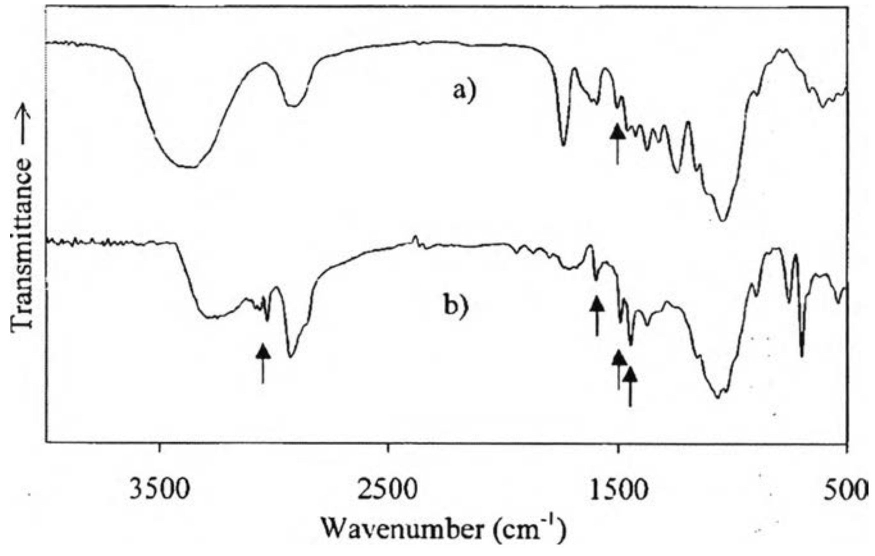

Figure 2.25 FTIR spectra of (a) cellulosic material isolated from Agave Lechuguilla and (b) styrene–grafted Agave Lechuguilla fiber (9%) (Cruz R.A. *et al.* 1999).

The morphologies of Avage Lechuguilla fiber and styrene grafted Agave Lechuguilla fiber are shown in Figure 2.26. The smoother surface of the Agave Lechuguilla fiber which comes from the growth and deposition of the grafted styrene on the surface is clearly visible.

The DSC investigations show that grafting makes the materials from Agave Lechuguilla and Fourcroydes thermally more stable as illustrated in Figure 2.27. A weak endothermic peak around 80°C is due to the evaporation of water. The DSC curve of Agave Lechuguilla–grafted fibers are characterized by the two weak exothermic peaks around 280–300°C and 370°C which is assigned to hemicellulose and cellulose composition, respectively.

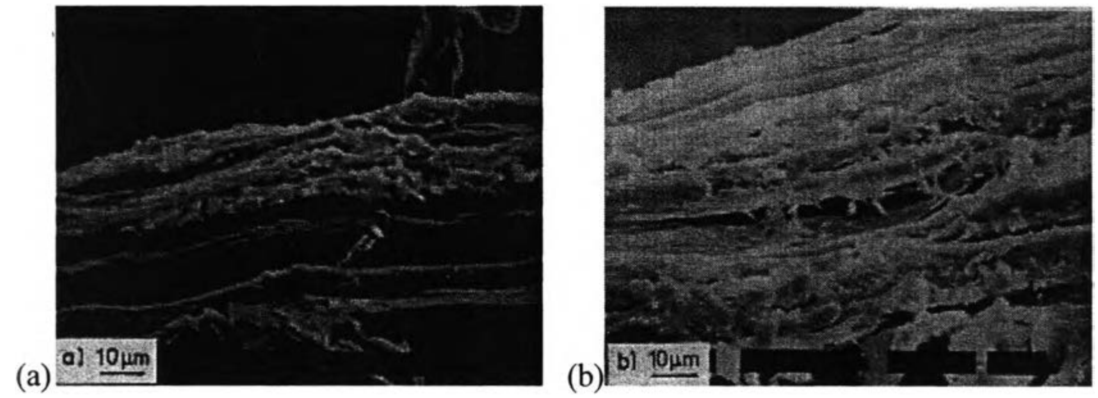

Figure 2.26 Scanning electron microscopic pictures of (a) cellulosic material isolated from Agave Lechuguilla and (b) styrene–grafted Agave Lechuguilla fiber (9%) (Cruz R.A. *et al.* 1999).

A strong endothermic peak at 400–300°C appears which is characteristic for the decomposition of the styrene grafts. The decomposition temperature of cellulose is about 50°C higher than the unmodified material meaning that the grafting makes the cellulose of Agave Lechuguilla fibers thermally more stable.

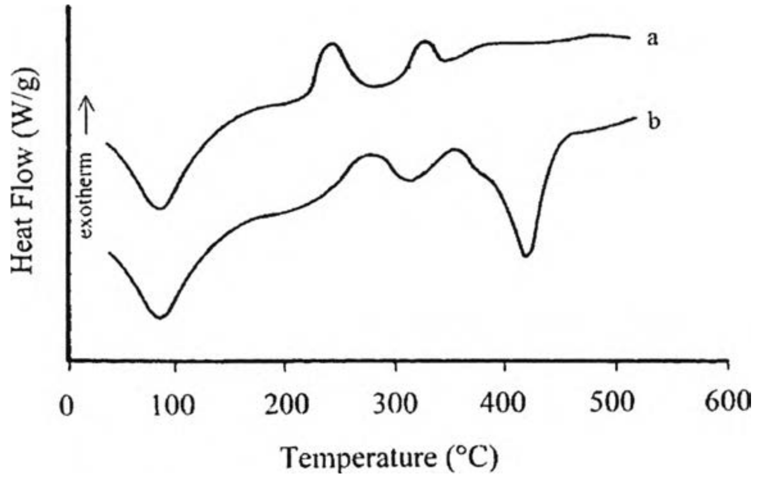

Figure 2.27 DSC curves of (a) cellulosic material isolated from Agave Lechuguilla and (b) styrene–grafted Agave Lechuguilla fiber (9%) (Cruz R.A. *et al.* 1999).

Thompson T.T. *et al.* (2005) investigated a surface treatment on cellulosic microfibers (CM) using the reaction of two vinyl epoxides, 1,2–epoxy–5–hexane (E5H) and 1,2–epoxy–7–octane (E7O), with a solvent of 1,4–dioxene in the grafting of poly(acrylic acid). There is an interest in the grafting of poly(acrylic acid), PAA, onto cellulose fibers due to the possibility of developing materials that present high water sorption properties. In medical applications, cellulose materials grafted with PAA could be used as an adsorbent sponge for body fluid.

Initially, it was possible to attain a larger PAA grafting percentage using an initiator concentration of 0.4% with respect to the cellulosic microfibers. Figure 2.28 shows the reaction used for PAA grafted onto cellulosic microfibers. This reaction produced a cellulosic microfiber with a double bond on the surface which is able to react with the acrylic acid using KPS as an initiator.

The FTIR spectra for CM, CM treated with E5H and CM treated with E7O are shown in Figure 2.29. The O–H stretching band, 3100–3500 cm^{-1}, does not show large changes due to the introduction of the epoxide moieties. However, it is possible to see an increment in the band corresponding to 1640 cm^{-1} that indicates an increase in H–O–H interactions when the epoxide is deposited on the fibers surface. This is ascribed to an extra OH group in the epoxide. The absorbance peak at 1727 cm^{-1} in both CM treated with epoxides is attributed to the formation of an aldehyde when the epoxide reacts with cellulose microfibers.

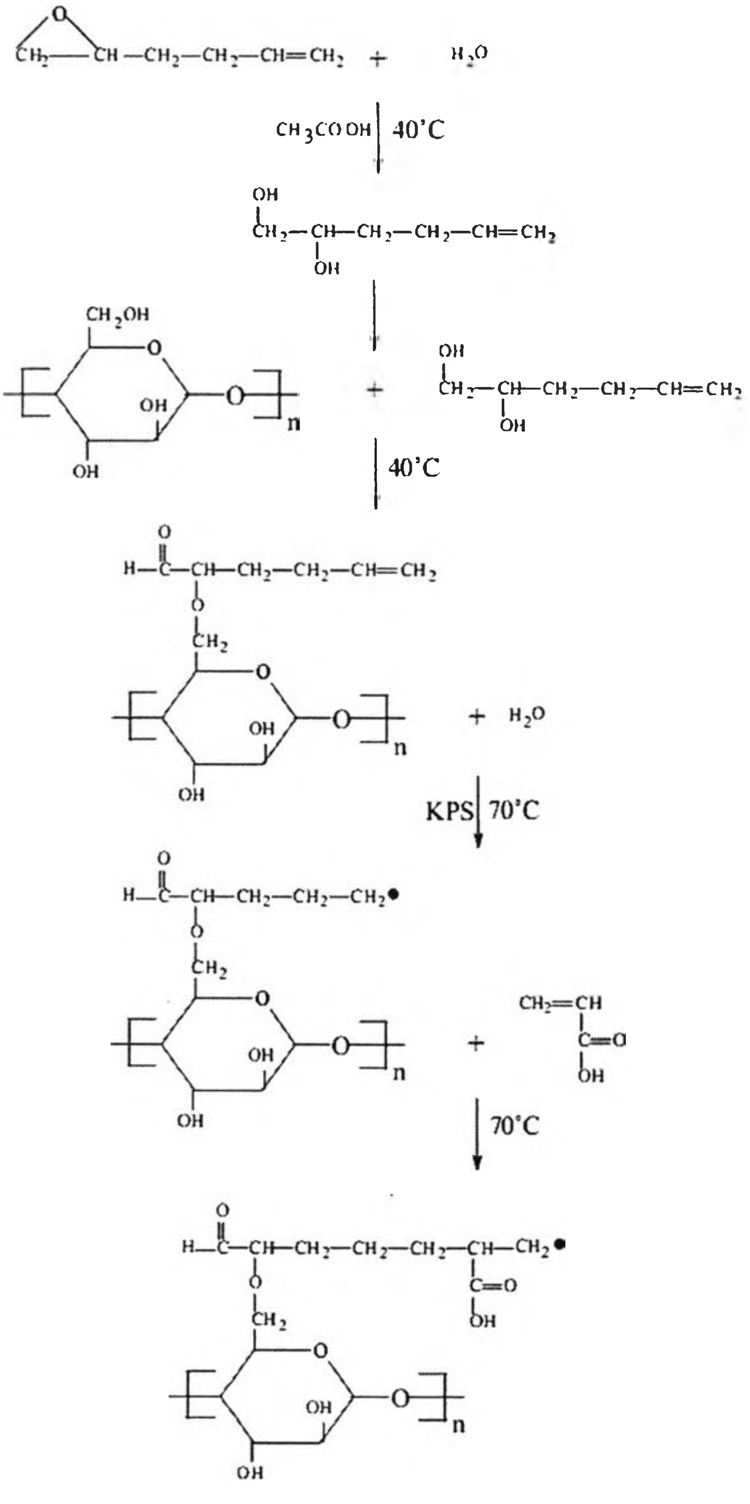

Figure 2.28 Reaction scheme for PAA grafting onto CM using an epoxide (Thompson T.T. *et al.* 2005).

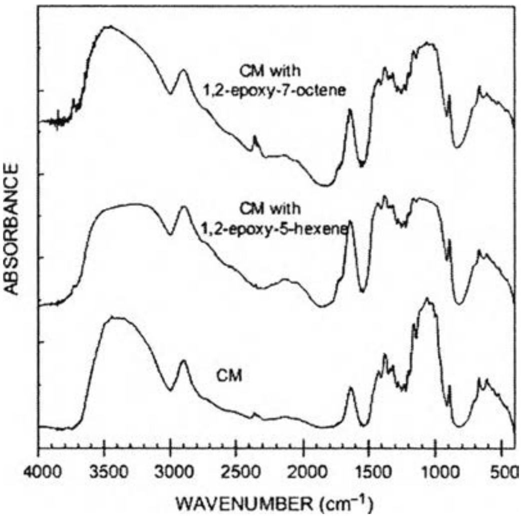

Figure 2.29 FTIR traces for CM, CM treated with 1–epoxy–5–hexene and 1,2–epoxy–7–octane (Thompson T.T. *et al.* 2005).

The thermogravimetrical analysis shows a better stability of the grafted CM with PAA than the CM treated with epoxide and unmodified CM, shown in Figure 2.30. The sorption measurement confirmed that PAA grafted CM, 14.17 g of water/ g of cellulose, has a water sorption capacity that is three times greater than CM, 4.17 g of water/ g of cellulose, without grafting.

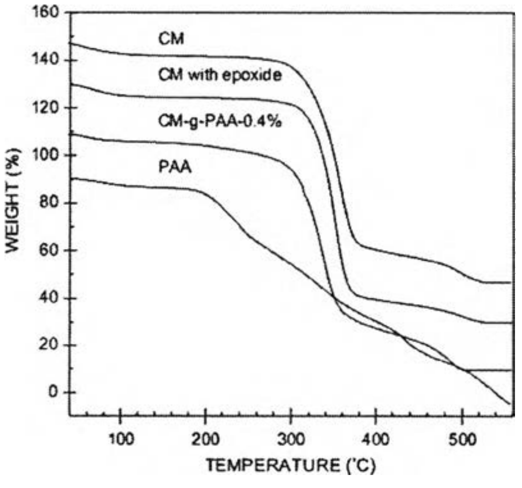

Figure 2.30 Thermograms of CM, CM–PAA grafted (4% of KPS) and PAA (Thompson T.T. *et al.* 2005).

The modification of cellulosic fibers in order to improve and increase the consistency of their performance in biodegradable materials was reported by Ouajai S. *et al.* (2004). The amount of grafting was controlled by an initiator concentration and monomer/fiber ratio.

As a vinyl monomer, acrylonitrile has the potential to graft onto cellulose fiber using different initiating systems such as ionic and radical initiators. The graft copolymerization can take place in heterogeneous or homogeneous reactions, with or without solvent inclusion. The introduction of hydrophobic groups onto cellulose and the further modification to hydrophobic character after grafting, the free solvent system initiated by free radical from azo–bis–isobutylonitril (AIBN) for grafting cellulose at low grafting level was studied.

The effect of AIBN concentration on the grafting yield showed an increase with AIBN concentration. This result suggests that AIBN was mostly responsible for the generation of free radicals on the cellulose backbone for the initiation of the graft copolymerization. The grafting yields were also increased with acrylonitrile monomer to hemp fiber ratio. The higher ratio provided a better yield because of the low adsorption ability of acrylonitrile on fiber. The availability of acrylonitrile molecules in the fiber was less, so that the grafting yield was lower.

The FTIR spectra of acrylonitrile grafted hemp fibers are shown in Figure 2.31. The band at 2243 cm^{-1} arising from the stretching vibration of $C{\equiv}N$ was used for characterization of the modified hemp.

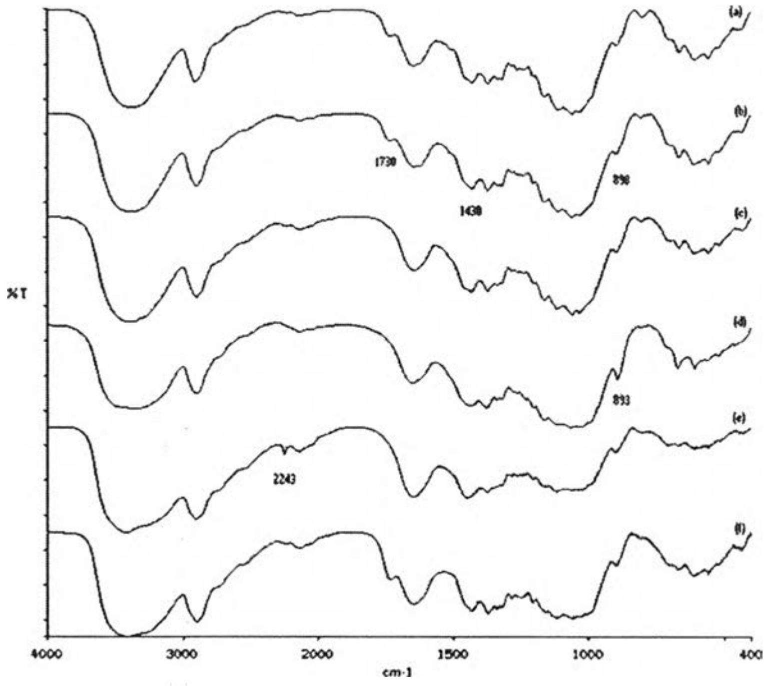

Figure 2.31 Infrared spectra of hemp and flax fibers for measurements of lateral crystallinity. (a) Untreated hemp, (b) acetone–extracted hemp, (c) 8% NaOH–treated hemp, (d) 20% NaOH–treated hemp, (e) 2.94% acrylonitrile–grafted hemp and (f) untreated flax (Ouajai S. *et al.* 2004).

The mechanical properties of acrylonitrile grafted–hemp showed a variation with the amount of grafting. However, the grafting produced little degradation of the mechanical properties. As shown in Figure 3.32, the amount of grafting is directly correlated with the thickness of the acrylonitrile grafted–layer on fiber, providing more structure and increased surface area for adhesion with polymer matrix and improved environmental resistance.

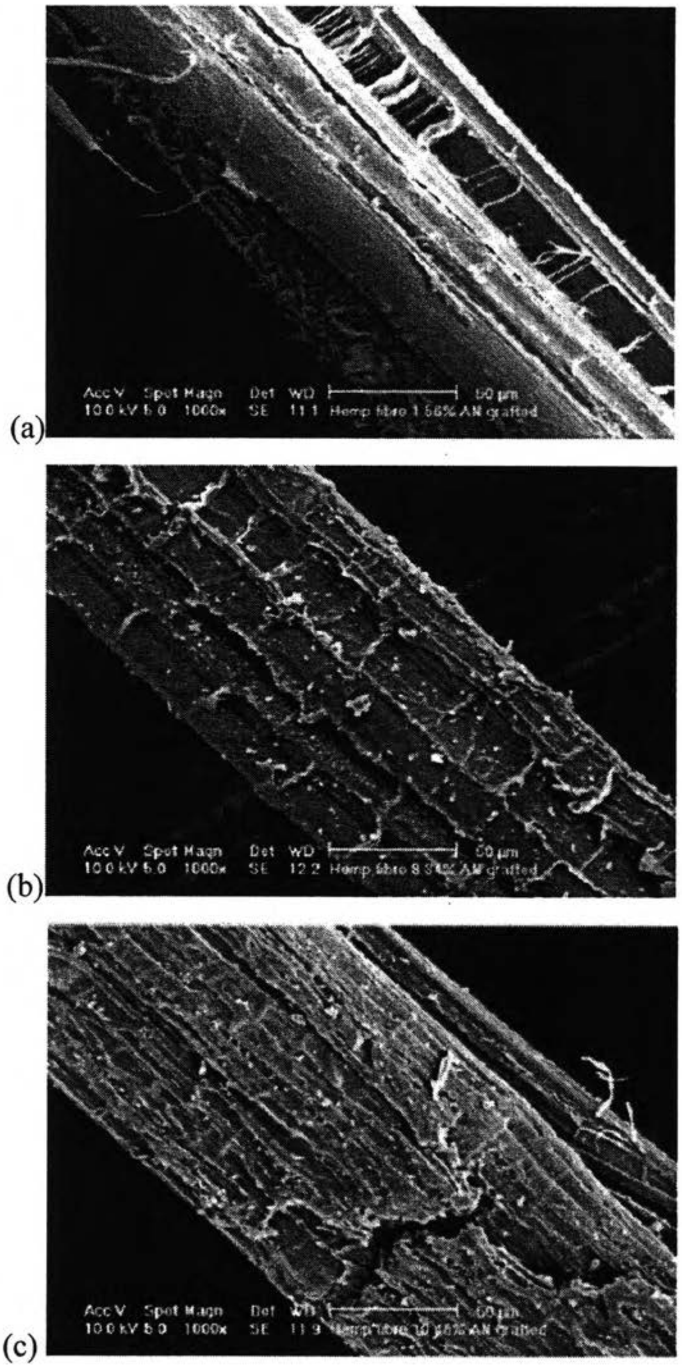

Figure 2.32 SEM photomicrographs of acrylonitrile–grafted hemp: (a) 1.56% grafted, (b) 8.34% grafted and (c) 10.46% grafted (Ouajai S. *et al.* 2004).