PREPARATION AND PROPERTIES OF KENAF BAST FIBER FILLED (PLASTICIZED) POLY(LACTIC ACID) COMPOSITES

by

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requirements for the degree of

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DEDICATION

To my mum and dad…

For everything…

ACKNOWLEDGEMENTS

Firstly I would like to thank GOD for his generous blessing and undying strength bestowed upon me during the course of this research.

I would like to express my ultimate gratitude and respect to my parents; for without them I wouldn’t have been where I am today. They have always had faith in me and what I was doing, even when I had lost it. Thank you for your unconditional love, support, and sacrifices. Not to forget my caring sister, Subashni, and my loved one, Ramesh, who had always been there without any hesitations whenever I needed them.

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TABLE OF CONTENTS

CHAPTER 1 – INTRODUCTION

CHAPTER 2 – LITERATURE REVIEW

CHAPTER 3 – EXPERIMENTAL

CHAPTER 4 – RESULTS AND DISCUSSION

CHAPTER 5 – CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
CNMR	^{13}C – Nuclear Magnetic Resonance
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DP	Degree of polymerization
DSC	Differential Scanning Calorimetry
DTG	Differential thermogram
FESEM	Field emission scanning electron microscopy
FRIM	Forest Research Institute of Malaysia
FTIR	Fourier transform infrared
KBF	Kenaf bast fiber
KBr	Kalium bromide
MA	Maleic anhydride
MAPE	Maleic anhydride grafted polyethylene
MAPLA	Maleic anhydride grafted poly(lactic acid)
MAPO	Maleated polyolefin
MAPP	Maleic anhydride grafted polypropylene
NaOH	Natrium hydroxide
PCL	Polycaprolactone
PDLLA	Poly(D,L-lactic acid)
PE	Polyethylene
PEG	Poly(ethylene glycol)
PBS	Poly(butylene succinate)
PHB	Poly(hydroxyl butyrate)
PHBV	Poly(hydroxyl butyrate valerate)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
PP	Polypropylene
p-PLA	Plasticized poly(lactic acid)
PS	Polystyrene
TGA	Thermogravimetry analysis
UV	Ultra violet
XRD	X-ray diffraction

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PS	Polystyrene
TGA	Thermogravimetry analysis
UV	Ultra violet
XRD	X-ray diffraction

LIST OF SYMBOLS

%	Percentage
>	More than
≈	Almost equal to
°C	Degree Celsius
CO_2	Carbon dioxide
E’	Storage modulus
E’’	Loss modulus
H_2O	Water
I	Intensity
Ic	Crystallinity index
Mw	Molecular weight
N_2	Nitrogen
phr	Part per hundred resin
rpm	Rotation per minute
T_g	Glass transition temperature
W	Weight
w	Weight fraction
Wt	Water uptake
wt%	Weight percentage
ρ	Density

PENYEDIAAN DAN SIFAT-SIFAT KOMPOSIT POLI(LAKTIK ASID) (DIPLASTIK) TERISI GENTIAN KAYU KENAF

ABSTRAK

Komposit poli(laktik asid) diplastik (p-PLA) terisi gentian kayu kenaf (KBF) telah disediakan dan dikaji secara berperingkat. Pertamanya, poli(laktik asid) (PLA) telah diperlembutkan dengan 5 hingga 20% berat poli(etilena glikol) (PEG) menggunakan pencampur dalaman. Adunan dengan 10% berat PEG dipilih sebagai matriks komposit kerana ia mempunyai kekuatan hentaman dan pemanjangan takat putus yang terbaik. Kedua, PLA dicangkuk maleik anhidrat (MAPLA) berjaya dihasilkan dengan 0.22% pencangkukan melalui kaedah pencangkukan reaktif Komposit p-PLA/KBF telah disebatikan di dalam pencampur dalaman dan diacuan mampat ke bentuk sampel ujian. Kandungan KBF diubah dari 10 hingga 40% berat. Pencirian telah dilakukan melalui ujian tensil dan hentaman, analisis mekanikal dinamik, penyerapan air, penanaman dalam tanah dan pencuacaan semulajadi. Pada pembebanan 40% berat KBF, kekuatan tensil dan modulus masing-masing meningkat sebanyak 120% dan 213%, manakala pemanjangan takat putus dan kekuatan hentaman masing-masing menurun sebanyak 99% dan 52%, berbanding p-PLA tidak terisi KBF. Penambahbaikan sifat-sifat komposit mencadangkan pemindahan tegasan yang berkesan di antara gentian kayu dan matriks. Kajian morfologi membawa kepada anggapan bahawa PEG mengganggu interaksi di antara KBF dan PLA, membentuk antarafasa yang tidak diingini. Kekuatan tensil dan modulus menurun manakala pemanjangan takat putus meningkat apabila 5% berat MAPLA ditambahkan pada sistem komposit. MAPLA dipercayai lebih berinteraksi dengan PEG berbanding KBF, iaitu ia menambahbaik kesan pemplastikan berbanding berfungsi sebagai agen penserasi kepada sistem komposit. Kekuatan tensil dan modulus hanya meningkat apabila 10% berat MAPLA ditambahkan kepada komposit dengan 40% berat KBF, mencadangkan penepuan interaksi antara

MAPLA-PEG, membenarkan lebihan MAPLA berinteraksi dengan KBF. Komposit PLA/KBF dan PP/KBF pada 40% berat KBF juga telah disediakan sebagai perbandingan kepada komposit p-PLA/KBF. Komposit p-PLA mempunyai kekuatan tensil (−38%) dan modulus (−26%) yang lebih rendah tetapi kekuatan hentaman (+20%) yang lebih tinggi berbanding dengan komposit PLA. Walau bagaimanapun, komposit p-PLA/KBF mempamerkan kekuatan tensil yang setanding, modulus (+31%) yang lebih tinggi dan pemanjangan takat putus (−38%) dan kekuatan hentaman (−61%) yang lebih rendah berbanding komposit PP/KBF. Modulus penyimpanan dan kehilangan komposit meningkat dengan peningkatan pembebanan KBF. Ini disebabkan oleh kekakuan KBF yang menyekat mobiliti rantaian polimer. Tan delta meningkat dengan peningkatan pembebanan KBF. Semua komposit tidak mencapai penyerapan air keseimbangan pada akhir ujian. Ini adalah berikutan pengurasan keluar PEG larut air dan pembentukkan retakan mikro disebabkan pembengkakan gentian yang membenarkan penembusan berterusan molekul air ke dalam komposit. Penanaman dalam tanah dan pencuacaan semulajadi menunjukkan kehilangan berat yang lebih tinggi dengan peningkatan pembebanan KBF di dalam kedua-dua komposit p-PLA dan PP, mencadangkan peningkatan tahap degradasi dengan kehadiran KBF. Walau bagaimanapun, komposit p-PLA menunjukkan kehilangan berat jauh lebih tinggi berbanding dengan komposit PP.

PREPARATION AND PROPERTIES OF KENAF BAST FIBER FILLED (PLASTICIZED) POLY(LACTIC ACID) COMPOSITES

ABSTRACT

Kenaf bast fiber (KBF) filled plasticized poly(lactic acid) (p-PLA) composites was prepared and examined stage by stage in this study. Firstly, poly(lactic acid) (PLA) was plasticized with 5 up to 20 wt% poly(ethylene glycol) (PEG) via internal mixer. Blend with 10 wt% PEG was chosen as matrix for composite as it showed the best impact strength and elongation at break. Secondly, maleic anhydride grafted PLA (MAPLA) was successfully produced with 0.22% grafting using reactive grafting method, and used as a compatibilizer for the composite system. p-PLA/KBF composite was compounded via internal mixer and compression molded into test specimens. KBF loading was varied from 10 to 40 wt%. Characterization was done by means of tensile and impact testing, dynamic mechanical analysis, water absorption, soil burial and natural weathering. At 40 wt% KBF loading, tensile strength and modulus improved by 120% and 213% respectively, while strain at break and impact strength dropped by 99% and 52% respectively compared to neat p-PLA. Improvement in properties suggests effective stress transfer between fiber and matrix. Morphological studies leads to assumption that PEG interrupts the interaction between KBF and PLA, forming undesirable interphase. Tensile strength and modulus dropped while strain at break improved when 5 wt% MAPLA was added to the composite systems. MAPLA is believed to interact with PEG instead of KBF, enhancing the plasticization effect instead of performing as a compatibilizer for the composite system. Tensile strength and modulus improved only when 10 wt% MAPLA was added to 40 wt% KBF composite, suggesting saturation of MAPLA-PEG interaction, allowing remaining MAPLA to interact with KBF. PLA/KBF and PP/KBF composites were also prepared at 40 wt% KBF loading for comparison with p-PLA/KBF composite. p-PLA composite had lower tensile strength (−38%) and modulus (−26%) but higher impact strength (+20%) than that of PLA composite. However, p-PLA/KBF had comparable tensile strength, higher modulus (+31%) and lower strain at break (−38%) and impact strength (−61%) compared to PP/KBF composite. Storage and loss modulus of p-PLA composites increased with increasing KBF loading. This is due to stiffness of KBF fiber that restricts the mobility of polymer chains. Tan delta decreased with increasing KBF loading. All composites did not reach saturation at the end of test. This was due to leach out of water soluble PEG and formation of micro cracks due to fiber swelling that permit continuous penetration of water molecules into the composite. Soil burial and natural weathering showed higher weight loss with increasing KBF loading in both p-PLA and PP composites, suggesting enhanced degradation with the presence of KBF. However, p-PLA composites showed higher weight loss than PP composites.

CHAPTER 1

INTRODUCTION

1.1 Natural fibers, biodegradable polymers and biocomposites

Natural fiber-reinforced composites, emerging as one kind of benign composite materials, have attracted increasing attention from the standpoint of protection of the natural environments in recent years (John and Thomas, 2008; Liu *et al.*, 2007b; Oksman *et al.*, 2006). These composites have been looked upon as an ecofriendly and economical alternate to glass fiber based composites, owing to the good properties of the natural fibers such as renewability, biodegradability, low cost, low density, acceptable specific mechanical properties, ease of separation, and carbon dioxide sequestration (Huda *et al.*, 2006; Ganster *et al.*, 2006; Ochi, 2008). Natural fiber- reinforced composites have increasing interest in many applications areas including automobile, housing, packaging, and electronic products (Pan *et al.*, 2007; Huda *et al.*, 2006).

The composites from natural fibers and conventional polyolefins, that is, polypropylene and polyethylene, have been extensively studied (Collier *et al.*, 1996; Lei *et al.*, 2007; Tajvidi *et al.*, 2005; Kim *et al.*, 2007). However; combination of few factors such as shortage of landfill space, concerns over emissions during incineration, depletion of petroleum resources; coupled with increasing environmental awareness have spurred the efforts to develop ecofriendly green composites or biocomposites by reinforcing the renewable sources-derived biodegradable plastics with the plant-derived natural fibers (Mohanty *et al.*, 2005; Baiardo *et al.*, 2004; Mehta *et al.*, 2004; Tokoro *et al.*, 2008; Shanks *et al.*, 2006; Alvarez *et al.*, 2004; Tserki *et al.*, 2006; Liu *et al.*, 2005).

One of the most promising biodegradable polymer is poly(lactic acid) (PLA), which is produced from renewable resources, such as corn, sugar beet, wheat or sugarcane (Tokoro *et al.*, 2008; Oksman *et al.*, 2006). PLA has been widely used as a biocompatible polymer for applications in implant materials, surgical suture, and controlled drug delivery systems (Martin and Averous, 2001; Hu *et al.*, 2003a; Ren *et al.*, 2006; Pan *et al.*, 2007). PLA has comparable mechanical properties to number of conventional plastics such as PP and PE, which makes it a reasonable substitute. However, PLA is a material with inherent brittleness and rigid behavior. These problems can be solved by copolymerization, blending with other polymers or adding plasticizer (Jiang *et al.*, 2006; Cao *et al.*, 2003; Pilin *et al.*, 2006).

On the other hand, kenaf bast fiber (KBF) has recently been gaining a lot of attention as biomass-based filler, and it is well known as a cellulosic source with ecological and economical advantages, abundant, exhibiting low density, non-abrasiveness during processing, high-specific mechanical properties, biodegradability and cheap pricing (Liu *et al.*, 2005; Ochi, 2008; Aziz and Ansell, 2004). It has been reported that KBF has a significantly high ability to accumulate carbon dioxide. Its photosynthesis speed is at least three times higher than that of usual plants, and it can absorb carbon dioxide 1.4 times that of its own weight (Nishino, 2004; Nishino *et al.*, 2003). KBF has been mainly used for textiles and paper before, and recently composites of KBF and plastics have been studied owing to its promising properties (Liu *et al.*, 2005; Pan *et al.*, 2007; Nishino *et al.*, 2003).

As one of the promising biodegradable thermoplastics at present, the cost of PLA is too high. This high cost has limited its commercial applications to some extent (Yew et al., 2005; Huda *et al.*, 2006). Therefore, it is considered that reinforcing PLA with KBF is possibly an efficient way to enhance its mechanical properties and decrease the cost of PLA-based materials.

While being a very interesting pair with many potential applications, KBF and PLA share an important problem, namely, the weak interfacial bonding between the polar fiber surface and the hydrophobic matrix (Bax and Mussig, 2008; Masirek *et al.*, 2007). The polymer adhesion to the fiber surface controls the stress transfer between the matrix and the reinforcing fibers (Huda *et al.*, 2005). For these cases of polar fibers and hydrophobic matrices, poor mechanical properties can be linked to weak interfacial bonding. This problem of poor interfacial bonding needs to be solved, for good mechanical properties of composite and cost-efficiency of bulk production (Lee and Wang, 2006; Huda *et al.*, 2005). Fiber surface modification or use of compatibilizing agents is the key to solving this problem (Masirek *et al.*, 2007). Compatibilizer, maleic anhydride grafted polymer has been widely studied and used, because the anhydride functionality of maleic anhydride grafted polymer reacts with cellulosic fiber's hydroxyl groups and esterification gives stronger links between the fiber surface and the matrix (Manchando *et al.*, 2003). Whereas, the polymeric chain from the compatibilizer will diffuse into matrix and form entanglements with the matrix at the interphase. This results in a continuous link from the fiber to the matrix (Yang *et al.*, 2007a). Additionally, use of coupling agent is much more economical compared to fiber surface treatments as small amount of coupling agent used could produce desirable properties (Arbelaiz *et al.*, 2006).

In this study, an attempt was made to produce biocomposite from KBF and PLA. Due to the brittle nature of PLA, plasticized PLA (p-PLA) was used instead as the polymer matrix. Poly(ethylene glycol) was used as plasticizer for PLA. Preparation and properties of p-PLA/KBF composites are discussed in this study.

1.2 Research objectives

The present study aims to develop a biocomposites based on KBF and PLA. Mechanical, dynamic mechanical properties and biodegradability of the biocomposites were studied. Main objectives of this study are:

To prepare a suitable matrix for this study by plasticizing PLA with poly(ethylene glycol) (PEG); in order to improve toughness and elongation at break of PLA. Effect of PEG loading (5, 10, 15 and 20 wt%) on the mechanical and dynamic mechanical properties of PLA was studied. The best composition of PLA/PEG imparting good toughness and elongation at break was used as the matrix for the biocomposites.

To prepare and characterize maleic anhydride grafted PLA (MAPLA) to be used as compatibilizer for the biocomposite. This was done as MAPLA is not commercially available at present. MAPLA was prepared by reactive grafting procedure in an internal mixer.

To study the effect of KBF loading and addition of MAPLA on the mechanical and dynamic mechanical properties of the biocomposites. Selected PLA and PP composites were also prepared to be compared to p-PLA biocomposites.

To study the biodegradability of KBF/p-PLA biocomposites by means of water absorption, natural weathering and soil burial test. Water absorption was done for 2 months while others were done for 3 months. PP composites was also prepared and tested as comparison to p-PLA biocomposites.

1.3 Organization of the thesis

There are 5 chapters in this thesis and each chapter gives information related to the research interest.

- **Chapter 1** contains introduction of the project. It covers brief introduction about research background, problem statements, objectives and organization of the thesis.
- **Chapter 2** contains the literature review. It covers brief explanations regarding biodegradable polymers, plant fibers and biocomposites.
- **Chapter 3** contains the information about the materials specifications, equipments and experimental procedures used in this study.
- **Chapter 4** contains results and discussion of this study. It covers material characterizations, plasticization, composite properties and biodegradability studies.
- **Chapter 5** concludes the findings in chapter 4 with suggestion for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

Automotive industry was among the first industries to introduce the use of natural fibers as filler in polymeric matrix, be it thermoset or thermoplastic (Suddell and Evans, 2005). Natural fibers were introduced with intention to yield lighter composites coupled with lower cost compared to existing glass fiber reinforced polymer composites. Natural fibers has lower density (1.2 – 1.6 g/cm^3) compared to glass fiber (2.5 g/cm^3) which ensures production of lighter composites (Huda *et al.*, 2006). Conventional petroleum based plastics such as polypropylene and polyethylene are used extensively with natural fibers such as hemp, jute, sisal and kenaf (Godavarti, 2005).

Recently, there has been interest in combining natural fibers with biodegradable polymers/biopolymers such as poly(lactic acid), poly(3-hydroxybutyrate), poly(caprolactone) and poly(butylene succinate) (John and Thomas, 2008). This interest is a result of growing environmental awareness and government regulations. Depletion of petroleum resources and growing entrapment of non-biodegradable plastics in the food chain and environment has also fueled research of biocomposites or ‘green composites’ utilizing natural fibers and biodegradable plastics (Shanks *et al.*, 2006; Liu *et al.*, 2007). These biocomposites are termed as next generation material as they are compatible with the environment and independent of fossil fuel (Mohanty *et al.*, 2005a).

2.2 Biodegradable polymers

Conventional commodity polymers such as polypropylene, polyethylene, polystyrene and polyvinyl chloride have established their market after decades of studies, research and diversification. However, they posed threat to mankind now as they clog our land fills due to their non-biodegradability and increase environmental pollution caused by the use of plastics and emissions during incineration (John and Thomas, 2008). Utilization of biodegradable polymers offers a solution to this problems faced by mankind.

Rising oil prices helped to stimulate early interest in biodegradable polymers in the 1970s. As for present, concerns over the dwindling availability of landfill sites, environmental regulations, and also the increasing oil prices are reviving interest in these materials (Mohanty *et al.*, 2005). Biodegradable polymers may be defined as polymers that undergo microbially induced chain scission leading to photodegradation, oxidation, and hydrolysis, which can alter the polymer properties and/or microstructure during the degradation process. Another definition states that biodegradable polymers are capable of undergoing decomposition primarily through enzymatic action of microorganisms to carbon dioxide, methane, inorganic compounds, or biomass in a specified period of time (Kolybaba *et al.*, 2003).

Figure 2.1 shows classification of biodegradable polymers and they are classified into four families. Except for petrochemical product family, which is of fossil origin, most biodegradable polymers are obtained from renewable resources or biomass. The biomass product family is agro polymers obtained from biomass by fractionation. The microorganisms and biotechnology families are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants and by synthesis from monomers obtained from biomass. The petrochemical products family are also polyesters but totally synthesized by petrochemical process (John and Thomas, 2008).

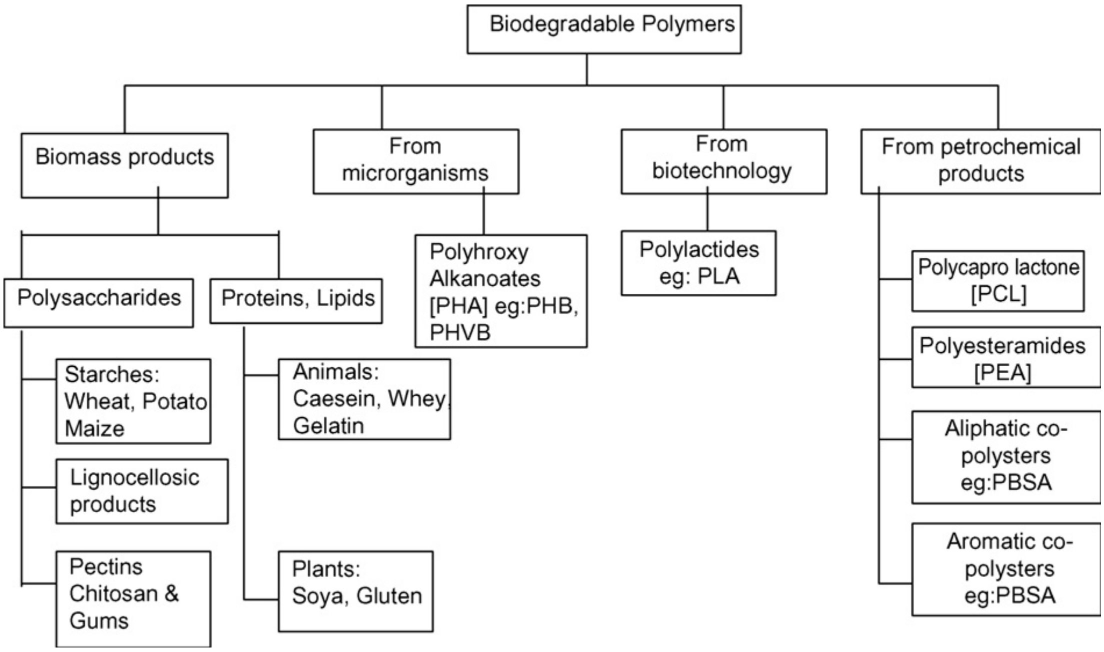


Figure 2.1 Classification of biodegradable polymers (Averous and Boquillon, 2004)

Blending two or more biodegradable polymers are also of interest to produce a new biopolymer designed for specific requirement. For example, blending of starch based polymer or thermoplastic starch with other biodegradable polymer such as poly(lactic acid), poly(vinyl alcohol) or poly(caprolactone) to overcome water sensitivity and brittle behavior of starch (Chiou *et al.*, 2005).

2.2.1 Poly(lactic acid)

Poly(lactic acid) (PLA) is one of the extensively studied biodegradable thermoplastic polymer (Ren *et al.*, 2006). PLA belongs to the family of aliphatic polyester commonly made from α–hydroxy acids. PLA can be produced from lactic acid (2-hydroxy propionic acid) through fermentation of renewable resources such as corn starch and sugarcane (Bax and Mussig, 2008). Lactic acid is the simplest hydroxy acid with an asymmetric carbon atom and exists in two optically active configurations; L(—) lactic acid and D(+) lactic acid (Figure 2.2) (Gupta and Kumar, 2007). It is a highly water-soluble, three-carbon chiral acid that is naturally occurring and is most commonly found in the L(—) form (Henton *et al.*, 2005). Both D(+) and L(—) enantiomers are produced in bacterial systems, thus lactic acid can be obtained by fermentation, selecting suitable microorganism, e.g. homo-lactic organisms such as various optimized or modified strains of *Lactobacilli* are used to produce stereoregular L-lactic acid. However, lactic acid obtained by the chemical process is a racemic mixture of D- and L-isomers (Gupta and Kumar, 2007; Garlotta, 2002).

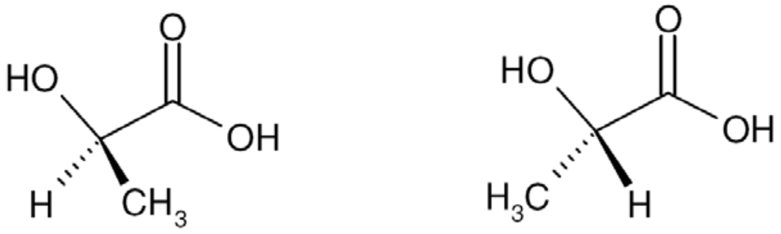


Figure 2.2 Different isomeric forms of lactic acid; left: L-lactic acid and right: D-lactic acid (Gupta and Kumar, 2007)

Two different routes of polymerization can be followed to produce PLA from lactic acid monomers, as depicted in Figure 2.3. Lactic acid is condensation polymerized to yield low molecular weight, brittle, glassy polymer, which, for most part is unuseable for any application unless external coupling agents are used to increase the molecular weight of the polymer (Garlotta, 2002). Polymer obtained by this direct condensation is low in molecular weight due to difficulty in removing water from highly viscous reaction mixture (Gupta and Kumar, 2007). The back biting equilibrium reaction of these resulting low molecular weight forms the six member lactide ring (Garlotta, 2002).

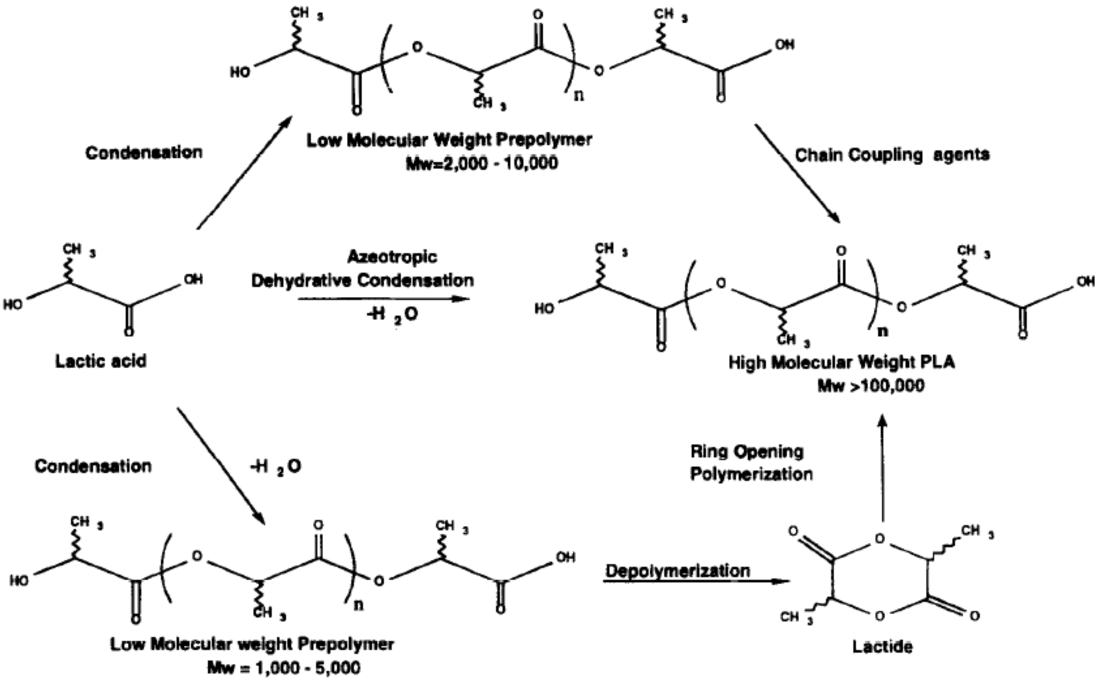


Figure 2.3 Synthesis methods for high molecular weight PLA (Lunt, 1998)

Controlled depolymerization of low molecular weight polymer can be done to produce crude lactides which have to be purified and undergo ring opening polymerization (in the presence of catalyst) to yield high molecular weight polymer. Since lactic acid is found in two stereoisomerism forms, therefore lactides are found in three stereoisomerism forms, which are DD-lactide, LL-lactide and DL-lactide/meso-lactide (Figure 2.4). Ring opening polymerization can be further divided into two, which is cationic and anionic ring opening polymerization. Purification of crude lactides is essential in order to remove impurities such as water, lactic acid and oligomers, which could interfere with polymerization reaction, resulting in low molecular weight polymer with high degree of racemization. This ring opening polymerization technique is a solvent free process adapted by Cargill Dow, the present major producer of PLA. This method was the only method of producing pure, high molecular weight PLA until Mitsui Toatsu Chemicals commercialized a process wherein lactic acid and catalyst are azeotropically dehydrated in a refluxing, high-boiling, aprotic solvent under reduced pressures to obtain PLA with weight average molecular weights greater than 300, 000 (Gupta and Kumar, 2007; Garlotta, 2002; Lunt, 1998).

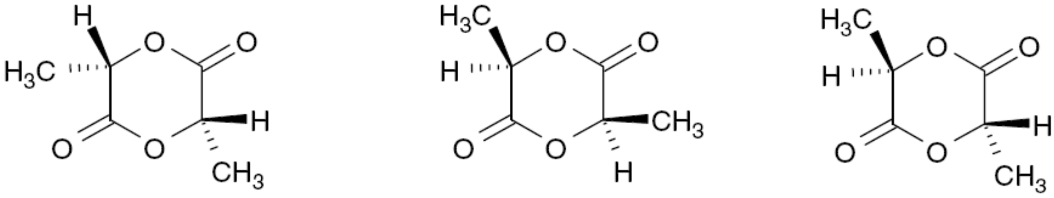


Figure 2.4 Different isomers of lactides, left: DD-lactide, middle: LL-lactide, right: DL-lactide/meso-lactide (Gupta and Kumar, 2007)

Generally, commercial PLA grades are copolymers of L-lactide and D-lactide. The optical purity, defined as (L% - D%), strongly affects the properties. Optically pure PLA is isotactic and highly crystalline. Decreasing the optical purity reduces the degree of stereoregularity and crystallinity. Poly(L-lactide) (PLLA) with more than 15% D-lactide and vice versa is amorphous (Hu *et al.*, 2003a). Random copolymers made from meso-lactide result in an atactic primary structure referred to as poly(meso-lactide) and are amorphous. Random optical copolymers made from equimolar amounts of D-lactide and L-lactide are commonly referred to as PDLLA or poly(*rac*-lactide). PDLLA is also essentially atactic, but the primary structure is segregated into optical doublets of the lactyl group, and it is also amorphous (Henton *et al.*, 2005).

PLA is a thermoplastic that can be processed like polyolefin plastics such as polypropylene (PP) and polyethylene (PE). PLA can be processed by conventional processing methods such as injection molding, sheet extrusion, blow molding, thermoforming or fiber spinning (Jacobsen *et al.*, 1999; Oksman *et al.*, 2003).

PLA has been extensively used for ages in biomedical fields for applications such as sutures, drug delivery and orthopedic implants (Velde and Keikens, 2002). However, ease of processing and good mechanical properties coupled with its biodegradability has made PLA an interesting new candidate to substitute non-biodegradable commodity polymers such as PP, PE and PS (Ren *et al.*, 2006). One of the industry that found PLA as a viable candidate is packaging industry. Figure 2.5 shows a few application of PLA in packaging industry.

Mechanical properties of PLA are similar to those of commodity plastics such as PP and PE; but PLA also exhibits inherent brittle behavior similar to polystyrene (PS). PLA shows high elastic modulus and tensile strength in the range of 3.2 to 3.7 GPa and 55 to 70 MPa, respectively (Baiardo *et al.*, 2003; Jiang *et al.*, 2006). However, low impact toughness and elongation at break have been limiting factors to diversification in applications of PLA (Shibata *et al.*, 2006; Oksman *et al.*, 2003). Numbers of method have been studied to modify the stiff and rigid behavior of PLA. Among them are copolymerizations, blending with other polymers or plasticizer.

Figure 2.5 PLA as packaging materials

Successful use of PLA as sutures in biomedical field has triggered research in diversifying the use of PLA in this field. Main targets were drug delivery and bone/internal fixations. However, stiff and brittle behavior of PLA has made it difficult to be used in these areas. To overcome this problem, lactic acid was copolymerized with other monomers such as ε-caprolactone, glycolide or ethylene oxides (Lan *et al.*, 2004; Kricheldorf, 2001). Maglio *et al.* (2004) studied the effect of copolymerization of lactic acid monomer with ε-caprolactone and ethylene oxides monomers. With copolymerization, both lactic acid-ε-caprolactone and lactic acid-ethylene oxides based diblock and triblock copolymer shows improved ductility and toughness. Chen *et al.* (2003a) successfully synthesized multiblock PLLA-PEG copolymer with ductile behavior with elongation at break reaching 500% compared to PLLA which is only 4.2%.

Copolymerization process of PLA is still in the beginning level of implementation. Many studies are being carried out to develop low cost PLA copolymers (Teng *et al.*, 2004). Commercial availability of these copolymers is also scarce. Therefore, blending PLA with other polymers presents a more practical and economical measure to obtain product with desired properties (Jiang *et al.*, 2006). Blending can effectively alter the resultant properties which depend sensitively on the mechanical properties of the components as well as the blend microstructure and the interface between the phases (Broz *et al.*, 2003). PLA/poly(ε-caprolactone) (PCL) blends have been extensively studied. This two polymers form immiscible blends. Various compatibilizer such as P(LA-*co*-CL), triphenyl phosphate and polyoxypropylene-polyoxyethylene were used to improve miscibility between PLA and PCL (Chen *et al.*, 2003b; Wang *et al.*, 1998; Broz *et al.*, 2003). Blends with compatibilizer displayed homogenous dispersion of the PCL minor phase in the PLA matrix, resulting in better mechanical properties compared to those of neat PLA. Other types of polymers has also been blended with PLA, such as poly(vinyl acetate-*co*-vinyl alcohol) (Park and Im, 2003), poly(butylene adipate-*co*-terephtlate) (Jiang *et al.*, 2006), polyethylene (Anderson and Hillmyer, 2004) and poly(hydroxyl ester ether) (Cao *et al.*, 2003).

Currently, most of the available biodegradable polymers are expensive and blending of these polymers would still mean expensive final product. In this case, use of plasticizer would be a wiser choice (Ren *et al.*, 2006). Plasticizer are widely used in plastic industry to reduce brittleness, improve flow, impart flexibility and increases toughness, tear resistance and impact resistance of the polymer. Plasticizers are also capable of reducing glass transition temperature of glassy polymer (Wu and McGinity, 1999). Wu and McGinity (1999) also quoted that degree of plasticization depends mainly on type and amount of plasticizer to ensure a uniform and reproducible product. The effects of plasticization are the result of the plasticizer's ability to weaken polymeric intermolecular attractions thus allowing the polymer molecules to move more readily, which increases the flexibility of the polymer. Increasing the amount of plasticizer could lead to an increase in free film elongation and a decrease in tensile strength and Young's modulus (Rahman and Brazel, 2006).

Among plasticizers used for PLA are triacetin (Ljunberg and Wesslen, 2002 : Ljunberg *et al.*, 2003), poly(1,3-butylene glycol adipate) (Ren *et al.*, 2006), acetyl tri-n-butyl citrate (Baiardo *et al.*, 2003), poly(1,3-butanediol), dibutyl sebacate, acetyl glycerol monolaurate (Pilin *et al.*, 2006), glycerol, PEG monolaurate, oligomeric lactic acid (Martin and Averous, 2001), citrate ester (Labreque *et al.*, 1997) and PEG with different molecular weight (Hu *et al.*, 2003a;b;c; Lai *et al.*, 2004; Kulinski and Piorkowska, 2005; Sheth *et al.*, 1997). Use of PEG (Figure 2.6) as plasticizer for PLA has been studied extensively compared to other plasticizers. This is due to PEG's efficiency in increasing elongation at break and softness of PLA. However, miscibility of PLA/PEG is dependent on PEG's molecular weight and content. Miscibility of PLA/PEG is limited when molecular weight of PEG decreases and/or PEG content increases. Macroscopic phase separation occurs beyond the limiting PEG content and molecular weight. For example, Pilin *et al.* (2006) observed macroscopic phase separation when PLA was plasticized with 20 wt% PEG 200 (molecular weight 200) and 30 wt% PEG 400 (molecular weight 400).

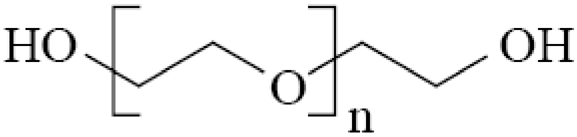


Figure 2.6 Chemical formula of PEG (Pilin *et al.*, 2006)

PLA is unique polymer as it is derived from renewable resources and also biodegradable. Degradation of PLA happens within weeks to months in a composting condition depending on its molecular weight, moisture and temperature. The degradation occurs by two step degradation process which is: 1) degradation by hydrolysis (primary reaction) followed by 2) bacterial attack on the fragmented residue to biomass, carbon monoxides, carbon dioxide and water. In the primary step hydrolysis is catalyzed by water (Figure 2.7) forming lower molecular weight lactic acid oligomers and no microorganism are involved (Lunt, 1997; Oksman *et al.*, 2003). Gonzales *et al.* (1999) mentioned that the primary reaction proceeds at a faster rate at the core compared to surface due to catalytic effect of degradation product. Formation of carboxylic acid end group catalyzes further hydrolysis. Low molecular weight lactic acid oligomers are believed to leach out when they reach a certain molecular weight when immersed in aqueous media (Gonzales *et al.*, 1999; Henton *et al.*, 2005; Tsuji and Ikarashi, 2004; Priokakis *et al.*, 2004).

Numbers of studies have been carried out to understand microbial degradation of PLA. Tokiwa and Jarerat (2004) used the plate count and clear zone methods to evaluate the distribution of polyester degrading microorganism in different soil environment and found that PLA-degraders have a limited distribution and rather scarce in the environment compared with those that degrade PHB, PCL and PBS. It was found that PLA degrading strains phylogenetically belong to *Pseudonocardiaceace* family and related genera, including *Amycolatopsis*, *Lentzea*, *Kibdlesporangium*, *Streptoalloteichus* and *Saccharothrix*. However, it is not easy to isolate these genera that are able to degrade PLA as they are rare in the environment. Out of 14 fungal strains tested, only two strains of *F. moniliforme* and one strain of *Penicillium roqueforti* could assimilate lactic aacid and racemic oligomer products of PLA but no degradation was observed on PLA. To date, *Tritirachium album* is the only L-PLA degrading fungus that has been reported so far (Tokiwa and Jeraret, 2004; Tokiwa and Calabia, 2007; Tokiwa and Calabia, 2006).

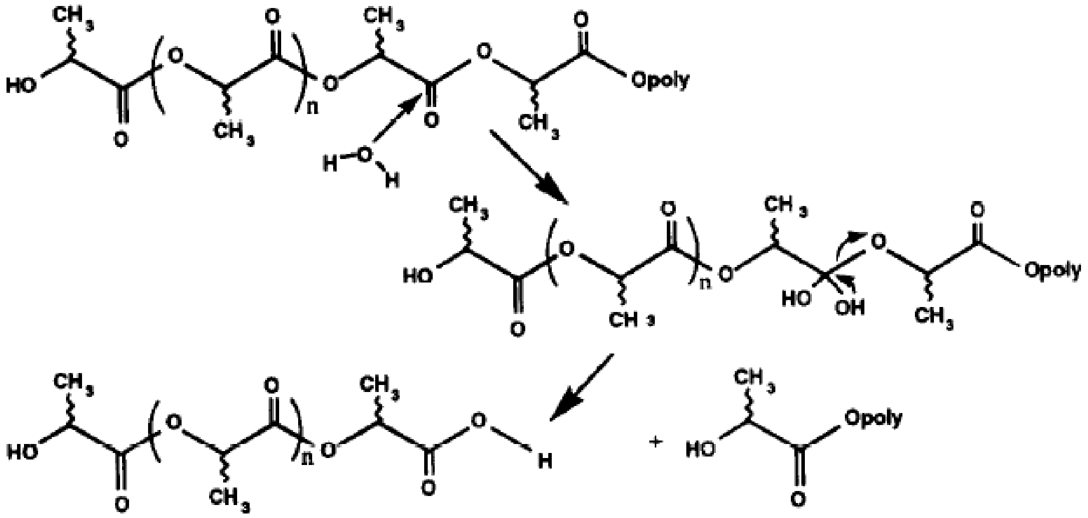


Figure 2.7 Hydrolytic degradation in PLA (Lunt, 1997)

2.3 Plant fibers

Natural fiber can be subdivided into few categories depending on their origins as displayed in Figure 2.8. Vegetable fibers are also known as plant fibers. All plant fibers are composed of cellulose while animal fibers consist of protein. Plant/vegetable fibers can be further divided into few categories as displayed in Figure 2.8 (John and Thomas, 2008; Bismarck *et al.*, 2005).

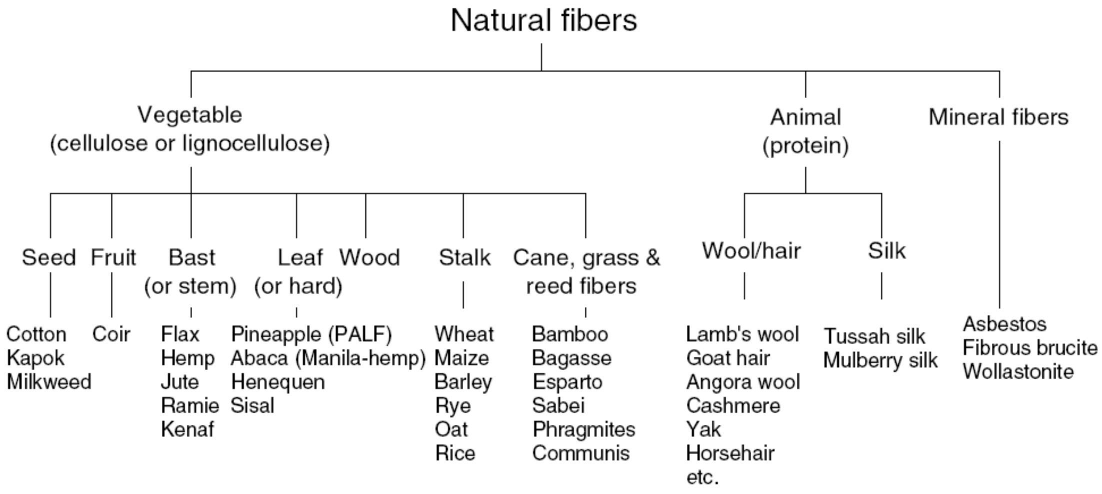


Figure 2.8 Classification of natural fibers (Bismarck *et al.*, 2005)

Plant fiber has been found useful by human kind since the start of human kind. We first started to use fibers for ropes and textiles by collecting raw materials from the wild. Later generation learned to cultivate useful crops for domestic use. Hemp and linen fragments were found in Neolithic sites in Syria, Turkey, Mesopotamia (present-day Iraq), and Persia (present-day Iran), and have been carbon dated back to 8000−6000 B.C. Religious Hindu scripts reported the cultivation of cotton as early as 1500 B.C. Much later, in A.D. 105, Ts'ai Lun of the imperial court of China found a way to make paper sheets using mulberry and other bast fibers along with fishnets, old rags, and hemp waste. The ancient Egyptians wrapped their corpses in linen cloth for thousands of years. Tomb paintings and hieroglyphs show and describe the production of flax, retting, spinning, and weaving as well as the treatment and dyeing of linen cloths. In Central Europe, the Swiss lake dwellers started flax cultivation and the production of linen more than 4000 years ago (Hon, 1994; Bismarck *et al.*, 2005).

Ingenious fiber crops, such as flax, hemp, and nettle, possessed great agricultural importance for the production of textile fibers until the late 19th century.

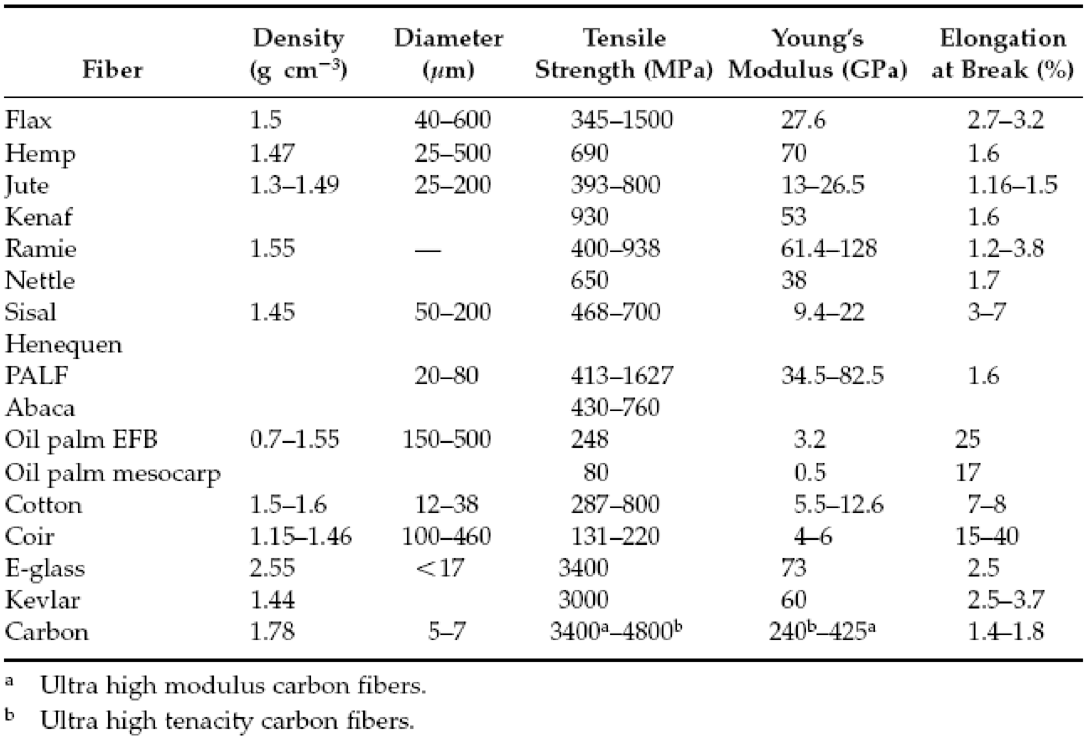
However, the mechanization of cotton harvest, processing, and development, and the growing demand for and production of cheap synthetic textile fibers destroyed the production of traditional fiber crops. Gradually, they became less significant and almost vanished in Western Europe and North America (Hon, 1994; Bismarck *et al.*, 2005).

Lately, plant fibers have made a grand come back as load bearing constituent in composite materials. Number of research has been done to utilize different types of plant fibers in plastic material to mainly develop composite with comparable specific properties to glass fiber reinforced plastic composites; especially in automotive industry (Joshi *et al.*, 2004). In Germany, car manufacturers have used plant fiber plastic composite to make automotive components, as they are recyclable and biodegradable. The door panels in the Mercedes have been made from plastics reinforced with flax fibers. Canadian companies are using the flax fibers in a polypropylene matrix to create moldable material to form the rear-shelf panel of the 2000 Chevrolet Impala. Driving factor for this is renewability and biodegradability of plant fibers (George *et al.*, 2001).

2.3.1 Advantages and disadvantages of plant fibers

Plant fibers is well known for their low price, economical production with few requirements for equipment and low specific weight (low density), which results in a higher specific strength and stiffness when compared to glass reinforced composites (Table 2.1) (Bismarck *et al.*, 2005). Plant fibers are nonabrasive to mixing and molding equipment, which can contribute to significant equipment maintenance cost reductions. They also present safer handling and working conditions compared to synthetic reinforcements such as glass fibers. The processing atmosphere is friendly with better working conditions and therefore there will be reduced dermal and respiratory irritation compared to glass fibers (Gaceva *et al.*, 2007). The most interesting aspect about plant fibers is their positive environmental impact. Plant fibers are a renewable resource with production requiring little energy and biodegradable. They are carbon dioxide neutral i.e. they do not return excess carbon dioxide into the atmosphere when they are composted or combusted (Joshi *et al.*, 2004; Mohanty *et al.*, 2002). Plant fibers also possess high electrical resistance. Thermal recycling is also possible. The hollow cellular structure provides good acoustic insulating properties. The worldwide availability is an additional factor (Li *et al.*, 2007; George *et al.*, 2001).

Table 2.1 Properties of plant fibers and synthetic fibers (Bismarck *et al.*, 2005)



Fiber	Density (g cm^{-3})	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
Flax	1.5	40–600	345–1500	27.6	2.7–3.2
Hemp	1.47	25–500	690	70	1.6
Jute	1.3–1.49	25–200	393–800	13–26.5	1.16–1.5
Kenaf			930	53	1.6
Ramie	1.55	—	400–938	61.4–128	1.2–3.8
Nettle			650	38	1.7
Sisal	1.45	50–200	468–700	9.4–22	3–7
Henequen					
PALF		20–80	413–1627	34.5–82.5	1.6
Abaca			430–760		
Oil palm EFB	0.7–1.55	150–500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5–1.6	12–38	287–800	5.5–12.6	7–8
Coir	1.15–1.46	100–460	131–220	4–6	15–40
E-glass	2.55	<17	3400	73	2.5
Kevlar	1.44		3000	60	2.5–3.7
Carbon	1.78	5–7	3400[a]–4800[b]	240[b]–425[a]	1.4–1.8

[a] Ultra high modulus carbon fibers.
[b] Ultra high tenacity carbon fibers.

A major drawback of plant fibers is their nonuniformity and the variability of their dimensions and of their mechanical properties (even between individual plants in the same cultivation) as compared to synthetic reinforcing fibers (Bismarck *et al.*, 2005). A precondition for increased use of plant fibers in technically challenging applications is the availability of reproducible fiber mechanical and morphological properties. The major task to be solved, in order to boost the acceptance of plant fibers as a quality alternative to conventional reinforcing fibers is to develop fiber quality assurance protocols (John and Thomas, 2008; Nishino, 2004).

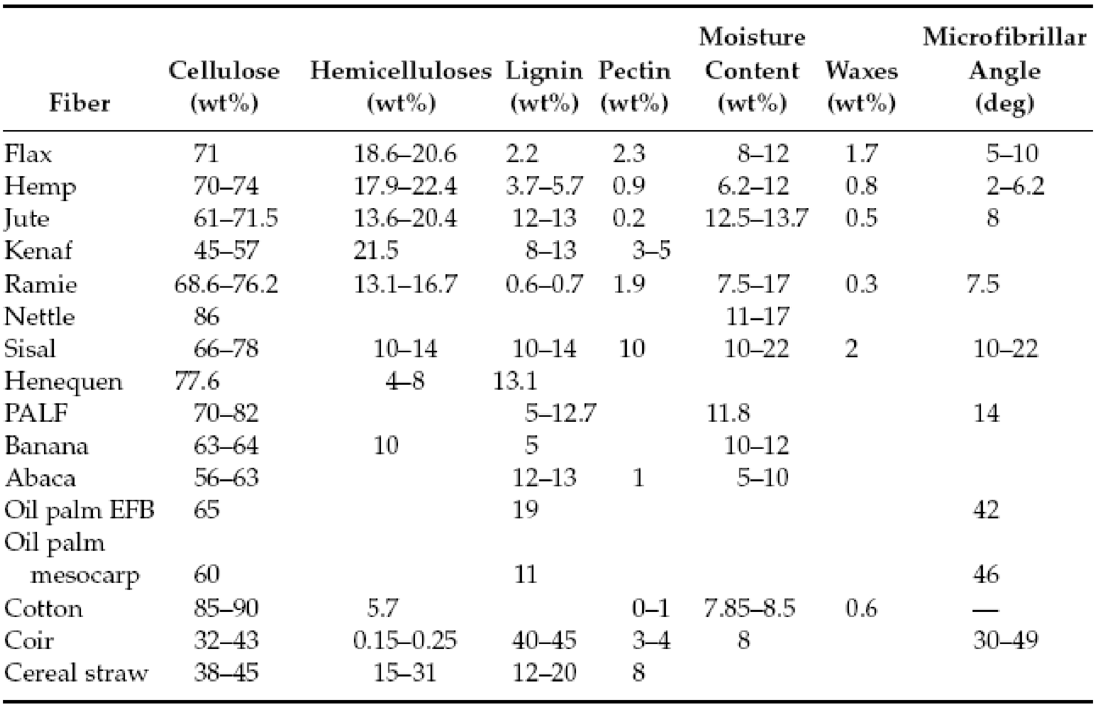
Plant fibers generally contains large amount of hydroxyl group, which makes it a polar and hydrophilic in nature. As we know, most of the plastics are hydrophobic in nature. Addition of hydrophilic plant fibers to hydrophobic plastic will result in composite with poor mechanical properties due to non-uniform fiber dispersion in the matrix and inferior fiber matrix interphase (Mehta *et al.*, 2004). This polar nature also results in high moisture sorption in plant fiber based composite leading to fiber swelling and voids in fiber matrix interphase. Moisture if not removed from plant fibers prior to compounding by drying would result in porous product. High moisture absorption could also cause deterioration in mechanical properties and loss in dimensional stability (Alvarez *et al.*, 2004; Baiardo *et al.*, 2004). These problems are generally solved by fiber surface treatment or matrix modifications (Alvarez *et al.*, 2004; Baiardo *et al.*, 2004; Masirek *et al.*, 2007).

Another major limitation for exploitation of plant fibers is limited thermal stability possessed by plant fibers. Plant fibers undergo degradation when processed beyond 200 °C; this further limits the choice of plastic materials to be used as matrix (Bismarck *et al.*, 2005; Glasser *et al.*, 1999). Plant fibers are also susceptible to rotting and posses low resistance to microbial attack. These problems are solved by adding anti fungal additives to the composites (John and Thomas, 2008; Verhey *et al.*, 2002).

2.3.2 Composition and structure of plant fibers

Plant fibers can be considered as naturally occurring composites consisting mainly of helically wound cellulose microfibrils embedded in amorphous lignin and hemicellulose matrix. The cellulose microfibrils are aligned along the length of the fiber, which render maximum tensile and flexural strengths, in addition to providing rigidity (John and Thomas, 2008; Bismarck *et al.*, 2005). Mechanical properties are mainly determined by the cellulose content, degree of polymerization and microfibrillar angle. The reinforcing efficiency of plant fiber is related to the nature of cellulose and its crystallinity. A high cellulose content and low microfibril angle are desirable properties of a fiber to be used as reinforcement in polymer composites. The main components of plant fibers are cellulose (α-cellulose), hemicellulose, lignin, pectins and waxes (John and Thomas, 2008; Bismarck *et al.*, 2005; Gaceva *et al.*, 2007). Table 2.2 shows chemical composition of few plant fibers.

Table 2.2 Chemical composition, moisture content and microfibrillar angle of plant fibers (Bismarck *et al.*, 2005)



Fiber	Cellulose (wt%)	Hemicelluloses (wt%)	Lignin (wt%)	Pectin (wt%)	Moisture Content (wt%)	Waxes (wt%)	Microfibrillar Angle (deg)
Flax	71	18.6–20.6	2.2	2.3	8–12	1.7	5–10
Hemp	70–74	17.9–22.4	3.7–5.7	0.9	6.2–12	0.8	2–6.2
Jute	61–71.5	13.6–20.4	12–13	0.2	12.5–13.7	0.5	8
Kenaf	45–57	21.5	8–13	3–5			
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9	7.5–17	0.3	7.5
Nettle	86				11–17		
Sisal	66–78	10–14	10–14	10	10–22	2	10–22
Henequen	77.6	4–8	13.1				
PALF	70–82		5–12.7		11.8		14
Banana	63–64	10	5		10–12		
Abaca	56–63		12–13	1	5–10		
Oil palm EFB	65		19				42
Oil palm mesocarp	60		11				46
Cotton	85–90	5.7		0–1	7.85–8.5	0.6	—
Coir	32–43	0.15–0.25	40–45	3–4	8		30–49
Cereal straw	38–45	15–31	12–20	8			

Cellulose is a natural linear crystalline polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1,4-β-D-glycosidic linkages at C_1 and C_4 position. The degree of polymerization (DP) is around 10,000. Structure and configuration of cellulose are displayed in Figure 2.9. Each repeating unit contains three hydroxyl groups. Two of these hydroxyl groups form intermolecular bonds, while the third one forms intramolecular hydrogen bonds. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose (Hon, 1994; Bismarck *et al.*, 2005). Solid cellulose forms a microcrystalline structure with regions of high order (crystalline regions) and regions of low order (amorphous regions). Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents (Li *et al.*, 2007; John and Thomas, 2008; Bismarck *et al.*, 2005).

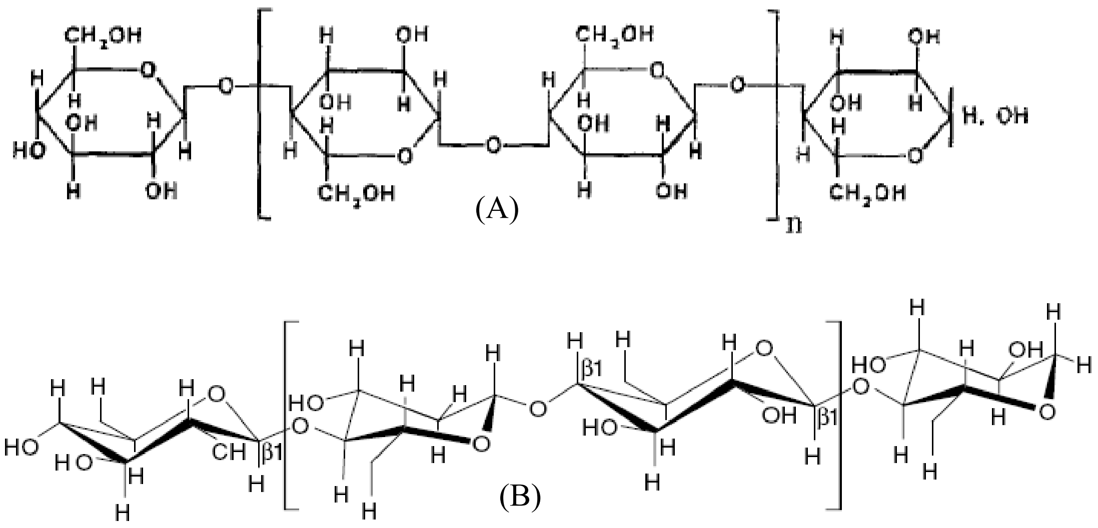


Figure 2.9 (A) Cellulose molecules (Hon, 1994) and (B) its configuration (Bismarck *et al.*, 2005)

Hemicellulose is not a form of cellulose and the name is a misnomer. They comprise a group of polysaccharides composed of a combination of 5- and 6-carbon ring sugars. Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units such as xylose, mannose and galactose whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its non crystalline nature, whereas cellulose is a linear polymer. Thirdly, the degree of polymerization of native cellulose is 10–100 times higher than that of hemicellulose. The degree of polymerization (DP) of hemicellulose is around 50–300. Hence, molecular weight of hemicellulose is significantly lower than cellulose (Li *et al.*, 2007; John and Thomas, 2008; Bismarck *et al.*, 2005). Hemicelluloses form the supportive matrix for cellulose microfibrils, presumably by hydrogen bonding. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is hygroscopic, partly soluble in water, soluble in alkali and easily hydrolyzed in acids (John and Thomas, 2008).

The exact chemical nature of the principal component of plant fiber, the lignin, still remains obscure. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents (Mohanty *et al.*, 2002). They are totally insoluble in most solvents and cannot be broken down to monomeric units. Lignin is generally amorphous and hydrophobic in nature. It is the compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight. Hydroxyl, methoxyl and carbonyl groups have been identified. Lignin has been found to contain five hydroxyl and five methoxyl groups per building unit. It is believed that the structural units of lignin molecule are derivatives of 4-hydroxy-3-methoxy phenylpropane (John and