Chapter 2: Review of literature

2.1 Lignocellulosic fibers

Lignocellulosic fibers are an abundant renewable resource available throughout the world. These are natural fibers which can be extracted from various types of biomass and can be classified into following six major categories:

1. **Bast fibers** (jute, flax, hemp, ramie and kenaf),
2. **Leaf fibers** (abaca, sisal and pineapple),
3. **Seed fibers** (coir, cotton and kapok),
4. **Core fibers** (kenaf, hemp and jute),
5. **Grass and reed fibers** (wheat, corn and rice), and
6. Other types (wood and roots).

All the natural fibers consist majorly of cellulose, lignin and hemicelluloses and lower amounts of extractives, pectin and pigments. Natural fibers have a complicated chemical composition and cell structure (Satyanarayana et al., 1990). The lignocellulosic fibers are in the form of a complex composite material with lignin and hemicelluloses forming the matrix in which cellulosic microfibrils are embedded (Rong et al., 2001).

Cellulosic fibers from different plants and from different parts of the same plant have different properties that depend upon a number of factors like the fiber structure, cell dimension, and chemical composition and so on. Different cellulose types have different crystalline organizations impacting the mechanical properties hence the nature of cellulose present in the fiber determines its mechanical properties (Bledzki and Gassan, 1999).

Cellulosic fibers have interesting chemical bonding in which cellulose is linked to lignin and hemicelluloses by means of hydrogen bonds. Similarly chemical bonds exist between hemicelluloses and lignin also. Cellulose fibers consist of cellulose micro fibrils bound within the lignin – hemicellulose matrix. The cellular structure of lignocellulosic fiber is composed of cells containing both amorphous (disordered) and crystalline (highly ordered) regions interconnected through hemicelluloses and lignin fragments (Klemm et al., 2005).

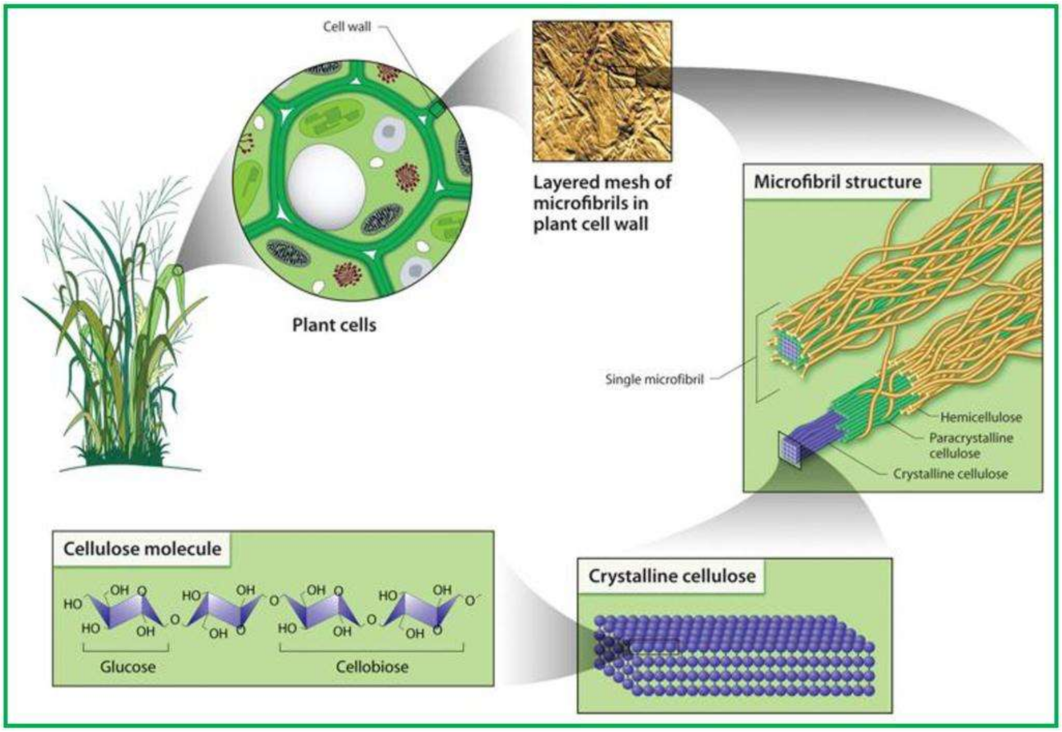

Fig. 2.1 Scheme of the cellulose cell wall and microfibrils organization (Siqueira et al., 2010)

Structure wise, a plain plant fiber is basically a single cell with length ranging from 1 to 50 mm and diameter around 10-50 µm. Plant fibers resemble microscopic tubes consisting of multiple cell walls formed from cellulose microfibrils of diameter 10-30 nm and are made up of 30-100 cellulose molecules. **Figure 2.1** shows the scheme of the cellulose cell wall and microfibrils organization (Chirayil et al., 2014). The structure of cellulosic fiber is shown in further detail in **Figure 2.2**. Cellulosic fiber is made of concentric cylindrical structures with lumen and a central channel in the centre, surrounded by cell walls which are also continuous and cylindrical. The lumen is for transportation of water and nutrients. The cell wall of each fiber is made up of three main layers viz. middle lamella, the thin primary wall, and the secondary wall in order from outer to inner layer. All these layers are composed of crystalline microfibrils embedded in amorphous regions of lignin, hemicelluloses and amorphous cellulose matrix. The secondary wall is further subdivided into external, middle and internal secondary walls denoted by S1, S2 and S3, respectively **(Figure 2.2)**. These layers are composed of crystalline microfibrils oriented at specific angles with respect to each layer, called the microfibrillar angle (Abdul Khalil et al., 2012; Pietak et al., 2007). The primary wall consists of disordered arrangement of cellulose fibrils (amorphous cellulose regions) embedded in a matrix of lignin, protein, pectin and hemicelluloses. Crystalline cellulose microfibrils arranged helically make up the secondary walls where the middle layer (S2) determines the fiber mechanical properties. This layer is composed of cellulose microfibrils arranged in a helical formation. The microfibrils, of diameter around 10 to 30 nm, are arranged in an amorphous region formed of lignin and hemicelluloses. The outer most layer of cell, the middle lamella, is predominantly composed of pectin acting as the cement between fibers (Abdul Khalil et al., 2012; Pietak et al., 2007).

Cellulose is the main part of cellulosic fibers. The chemical structure of cellulose is shown in **Figure 2.3**. Cellulose is a long chain polysaccharide formed by units of β-D glucose building blocks that bind together through the connections 1 and 4 carbons β (1→ 4) glycosidic linkages. (Thygesen et al., 2007)**.**

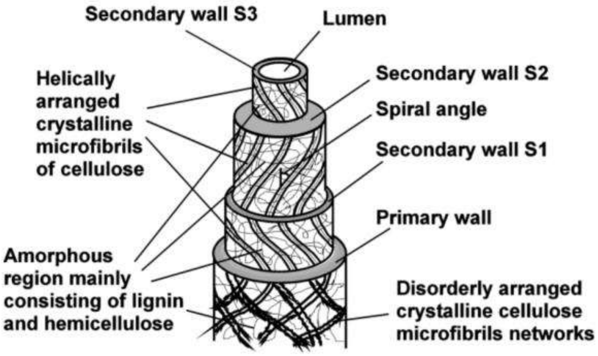

Fig. 2.2 Composition of cellulosic fiber (Rong et al., 2001)

Hemicelluloses are one complex group of carbohydrates as shown in **Figure 2.3** surrounding the cellulose fibers of plant cells with other carbohydrates (e.g. pectin). Hemicelluloses is considered to be the compatible agent between cellulose and lignin (Rong et al., 2001)**.** Mostly hemicelluloses consist of xylans (many five-carbon sugar molecules combined), uranium acid (i.e. sugar acid), and arabinose. Xylan is a polysaccharide of five carbon sugar pentose, D-xylose, linked by β (1→4). Hemicelluloses are highly hydrophilic and soluble in alkaline medium and hydrolyzed in presence of acids.

Lignin is the strongly interlinked, amorphous and molecularly complex structure as shown in **Figure 2.3**, it is the binding agent between fiber cells and fibrils creating the cell wall. It is basically a three-dimensional and amorphous macromolecule composed of phenylpropane units. Lignin is mainly attributed for rigidity of the plant cell wall producing an impact and compression resistant structure. Lignin acts as a biological protection and a reinforcement agent to resist the gravity forces and the wind. By joining the fibers together lignin increases the compressive strength of natural fibers to form a rigid structure (Bjerre and Schmidt, 1997)

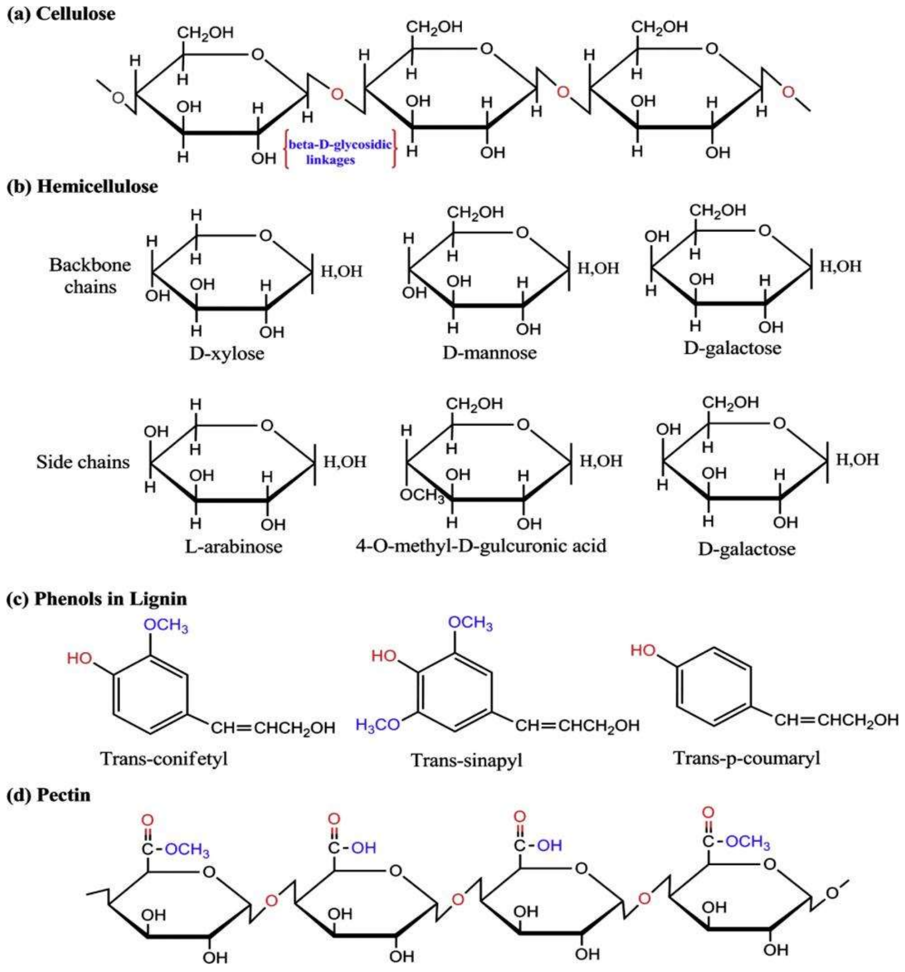

Fig. 2.3 Chemical Structure of major constituents in the fiber cell wall (Gurunathan et al., 2015)

2.2 Cellulose, Microcrystalline Cellulose and Nanocellulose

Cellulose is the most abundant renewable polymer on earth. Majority of cellulose is synthesized by plants while some aquatic organisms, amoebae, bacteria and fungi can also synthesize cellulose (Heux et al., 1999). Cellulose is a linear homopolymer of D-glucopyranose repeating units linked by α-1-4-glycosidic linkages. The D-glucopyranose monomer contains three hydroxyl groups which confer to it the ability to form hydrogen bonds. This hydrogen bonding directs the crystalline packing and thus governs the crystallinity of cellulose (John and Thomas, 2008). Cellulose micro fibrils are the elementary structural constituent of cellulose created during the biosynthesis.

These fibrils are long chains of poly- β-(1-4)-D-glucosyl residues aggregated to create long thread like bundle of molecules. Intermolecular hydrogen bonds are responsible for lateral stabilization of these threads (Andresen et al., 2006; Dufresne et al., 1997; Stenstad et al., 2008). Diameters of individual cellulose microfibrils range from 2 to 20 nm. Each microfibril can be thought of as a filament of cellulose crystals joined as per the micro fibril axis by amorphous domains (Azizi Samir et al., 2005). Siró and Plackett (2010) have reviewed the anomalies existing in the scientific literature on the categorization applied to cellulosic fibers. The expression **microfibril** commonly refers to the 2-10 nm cellulose fibers of high aspect ratio, which are formed during biosynthesis of cellulose in higher plants. However the micro fibril diameters may vary depending on their origin. **Nanofibrils** and **nanofibers** are synonyms used for micro fibril. Even though MFC nano elements of thickness 3-10 nm have been found, typically they are in the 20-40 nm range as bundles of cellulose microfibrils (Svagan et al., 2007). Acid hydrolysis causes transverse cleavage in the amorphous regions of cellulose microfibrils and sonication results in the formation of rod-like material with relatively low aspect ratio and is referred to as cellulose whiskers. Cellulose whiskers are also called **nanowhiskers** (Garcia de Rodriguez et al., 2006), **nanorods** (Dujardin et al., 2003), and rod like cellulose crystals (Iwamoto et al., 2009). Strong hydrogen bonding between the individual cellulose crystals causes aggregation (Levis and Deasy, 2001) leading to a cellulose structure called **microcrystalline cellulose** (MCC). MCC is available for commercial use and is basically utilized as a viscosity enhancer and as a binder in the pharmaceutical industry (Janardhnan and Sain, 2006).

2.3 Methods of extraction of nanocellulose from microcrystalline cellulose

Broadly speaking nano-cellulose can be prepared by two methods: **mechanical and chemical**. Mechanical methods for preparing nanocellulose include **homogenization under high-pressure, micro-grinding, ultrasonication at high intensity, and PFI milling**. The high-energy consumption is the major drawback of physical methods (Spence et al., 2011). Chemical methods to prepare nanocellulose are **hydrolysis by acid and enzyme, and TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl] mediated oxidation**. Drawbacks of chemical methods are long duration, low-yield and harmful effect on the environment as the chemicals used are toxic and not easily recyclable (Tang et al., 2011). To diminish energy utilization, usually mechanical and chemical methods are combined; fibers are pretreated by chemical reagent followed by mechanical processing to prepare nanocellulose (Li et al., 2011).

First report of nanocellulose preparation dates back to 1947, where sulfuric acid and hydrochloric acid hydrolysis of wood fibers and cotton fibers was done to get nanocellulose (Nickerson and Habrle, 1947). Malainine et al. (2005) prepared cellulose microfibrils by means of homogenization under pressure in alkaline conditions. Abe et al. (2007) obtained nanocellulose fibers using a grinding treatment; while Cheng et al. (2009), utilized high intensity ultrasonication to prepare nanocellulose. Montanari et al. (2005) performed TEMPO-mediated oxidation followed by mechanical treatment of cotton linters to obtain surface carboxylated cellulose nanocrystals. Man et al. (2011) obtained cellulose nanocrystals using ionic liquid. Wang et al. (2014), prepared nanocellulose fibers from cellulose pulps by treating with 17.5 wt% NaOH followed by mechanical fibrillation. Shankar and Rhim (2016a) proposed a simplistic method to prepare nanocellulose from micro-crystalline cellulose using NaOH/urea dissolution followed by ultrasonication. Similar methods have been reported by (Adsul et al., 2012; Majdzadeh-Ardakani and Nazari, 2010).

The most commonly used method to prepare nanocellulose is acid hydrolysis. But the requirement of highly concentrated acid is a major drawback of this method (Man et al., 2011). Concentrated acid is not only corrosive to the reaction container; the acidic liquid waste generated is hard to recycle thereby causing serious pollution to the environment. Further, controlling the reaction and the degree of hydrolysis is difficult resulting in reduced yields usually less than 50%. While the TEMPO mediated oxidation treatment is toxic to environment, the enzymatic treatment is time consuming and highly expensive.

A facile approach for preparing nanocellulose fibers is therefore needed and to this effect, the alkali – urea method gives a hope. The chilled alkali - urea solution is used to dissolve microcrystalline cellulose followed by regeneration with excess water and subsequent ultra sonication treatment is done to further break the fiber bundles and destroy the amorphous regions. Cai and Zhang (2005) used chilled sodium hydroxide-urea aqueous solution with weight ratio of NaOH: urea: H_2O as 7:12:81, to dissolve cellulose while Adsul et al., (2012) and Majdzadeh-Ardakani and Nazari (2010) utilized similar alkali – urea dissolution – regeneration of cellulose followed by ultrasonication for preparation of nanocellulose. Compared with usual pretreatment reagents, like concentrated sulfuric acid, ionic liquid, and TEMPO, NaOH/urea pretreatment is economical and relatively less harmful to environment. The probable mechanism of the breakdown of microcrystalline cellulose to nanocellulose by NaOH- urea aqueous mixture is that sodium hydroxide hydrates and disturbs the inter and intra molecular hydrogen bonds in cellulose, while the amino groups of urea easily form hydrogen bonds with hydroxyl groups in cellulose. The combined action of NaOH and urea avert binding between cellulose molecules and weaken the macrostructure of cellulose molecules (Cai and Zhang, 2005; Yan and Gao, 2008). Compared to the NaOH solution alone, the presence of urea could further enhance the effect of pretreatment due to its synergy with NaOH and lead to better swelling of the cellulose (Wang et al., 2016).

2.4 Pretreatments/ Surface Modifications of Lignocellulosic Fibers

There have been numerous attempts to improve upon the compatibility between fiber and matrix using chemical modifications of the fiber. Such chemical modifications can be brought upon by chemical treatments with alkali (sodium hydroxide, potassium hydroxide), **acetyl, silane, benzyl, acryl, permanganate, peroxide, isocyanate, titanate, zirconate** and acrylonitrile treatments and use of **maleated** anhydride grafted coupling agent (Faruk et al., 2014; Singh et al., 1996). With maleated anhydride grafted coupling agent and alkali, acetyl, silane treatments being conventionally used and due to their effect on environment, enzyme treatment is slowly being favored upon due to its environmental friendliness (Faruk et al., 2014).

Alkali treatment

Alkali treatment removes hemicelluloses, lignin and pectin, and exposes cellulose. It also increases surface roughness and surface area to offer better interfacial interaction. Alkali action can modify cellulose structure, mild treatments enhance cellulose crystallinity while harsher treatments convert crystalline cellulose to amorphous material (Beckermann and Pickering, 2008; Kabir et al., 2012a). Alkali treatment has been reported to improve fiber strength also (Beckermann and Pickering, 2008; Bera et al., 2010). Improvements in properties such as tensile strengths, Young's modulus and impact strength have been reported in many studies along with improvement in fracture toughness and flexural properties of composites as well as thermal stability and long term moisture resistance. The moisture resistance is reported to improve due to the reduced moisture uptake observed with alkali treated natural fibers (Bera et al., 2010; Goda et al., 2006; Gomes et al., 2007; Islam et al., 2010; Kabir et al., 2012b; Nor Azowa Ibrahim et al., 2010).

Acetylation treatment

Acetylation treatment causes esterification by reaction of acetyl groups with hydroxyl groups on the fibers and increases hydrophobicity (Hill et al., 1998). Acetylation has been reported to improve interfacial bonding, mechanical properties as well as thermal stability and microbe resistance in natural fiber composites (Bledzki et al., 2008; Khalil et al., 2001; Tserki et al., 2005). Over-treatment has been reported to be detrimental to mechanical properties. It has been reported that degradation of cellulose and cracking of fibers occurs due to the catalysts used as a result acetylation lowers the mechanical properties (Bledzki et al., 2008). Commonly acetylation treatment is preceded by the alkaline treatment.

Silane treatment

Silanes are versatile reagents that are used for the treatment of fibers. Silanes are advantageous when composites of natural fiber with hydrophobic polymers are to be made as they have different functional groups at either ends and while one end can join covalently with hydrophilic groups of the fiber, the other end can bond with hydrophobic groups in the matrix joining them. In silane treatment of natural fibers, alkoxy groups of silane is hydrolyzed with water to form silanol (Si–OH) groups which then react with hydroxyl groups on the fiber surface as shown in **Fig. 2.4** to form hydrogen or covalent bonds (Rachini et al., 2012; Xie et al., 2010). The most commonly used silanes are amino, methacryl, glycidoxy and alkyl silanes. Silanes increase the hydrophobicity of natural fibers and strength of NFCs. Significant improvements are seen when silane and the matrix form covalent bonds (Pickering et al., 2003; Rachini et al., 2012).

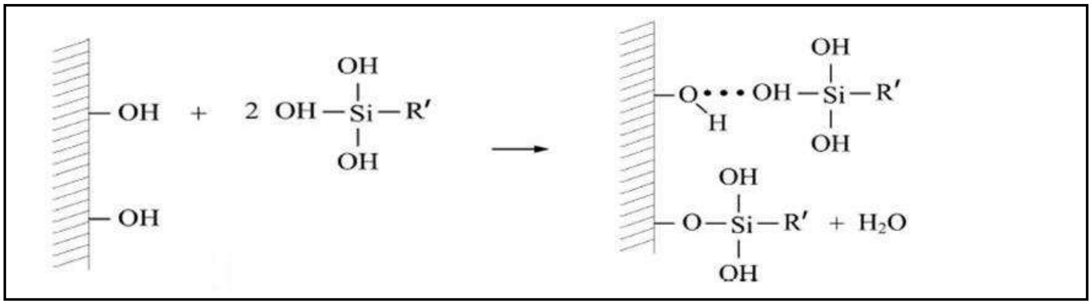

Fig. 2.4 Reaction of silane coupling agent with natural fiber

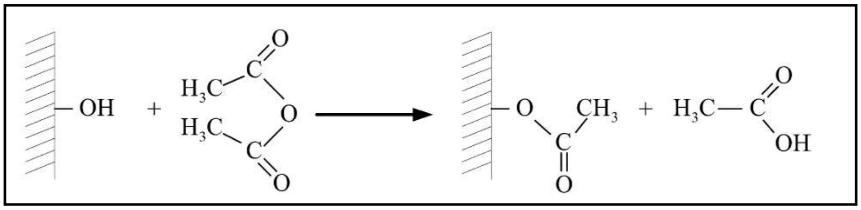

Fig. 2.5 Reaction of acetic anhydride with natural fiber

Maleic anhydride grafting

Maleic anhydride (MA) grafted polymers have been widely used as linking agents to improve composite properties. Scientific literature about maleic anhydride grafting shows that MAPP, a maleic anhydride grafted polypropylene, is the most commonly used graft polymer. MAPP improves the composite properties by reacting with hydroxyl group on fiber surface by covalent or hydrogen bonding **(Figure 2.5)** while the polymer attached to the maleic anhydride provides compatibility with the matrix, usually PP. Franco-Marquès et al. (2011) found that maleic anhydride grafting to PP improved mechanical strength of PP matrix composites. Maleic anhydride grafting can be regarded as the best among other surface treatments to improve matrix-fiber interactions as shown by Bera et al. (2010) who found MAPP to give two times higher composite strength compared to silane treatment. Kazayawoko et al. (1999) explained that MAPP could improve mechanical strength of composites due to its ability for better dispersion and wetting of the fiber. The MA grafted PLA has shown improvements in mechanical properties and thermal stability of the PLA matrix – natural fiber composite (Avella et al., 2008; Kang et al., 2014; Yu et al., 2014).

2.5 Nanoclay / Montmorillonite clay

Montmorillonite clays ($(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$) are aluminium and magnesium silicates stacked in form of nano scale platelets of thickness 1 nm and diameter 100–500 nm. Their aspect ratio ranges from 50–1,000. The MMT shares oxygen between Al and Si with many –OH groups at the edges.

The MMT unit includes an alumina octahedron crystal lattice embedded between two silica tetrahedron crystals (Arora and Padua, 2010; Rhim and Ng, 2007; Sapalidis et al., 2011), as shown in **Figure 2.6**. MMT is easily available and found in abundance in nature and its high aspect ratio makes it very versatile and potent nano filler. Further, the presence of hydrated potassium or sodium ions imparts hydrophilic nature to MMT making it compatible with hydrophilic polymers such as PVA, PEO and natural biopolymers like protein and starch (Rhim and Ng, 2007; Sapalidis et al., 2011). MMTs clays can be dispersed into polymeric matrix in three dispersion states viz., tactoid, intercalated and exfoliated as shown in **Figure 2.7**. **Tactoid** dispersion results when the montmorillonite nanoclay is poorly dispersed within polymer matrices resulting in conventional microcomposites instead of nanocomposites.

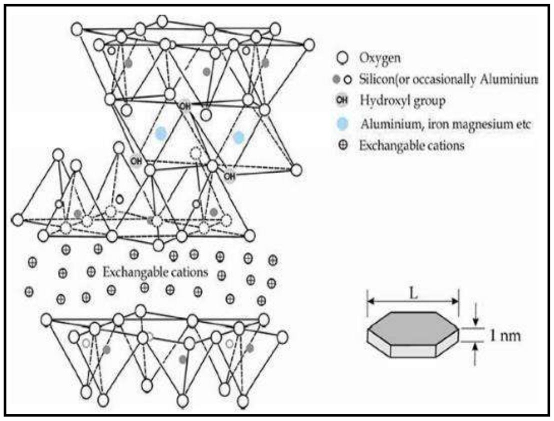

Fig. 2.6 Structure of Montmorillonite (Sapalidis et al., 2011)

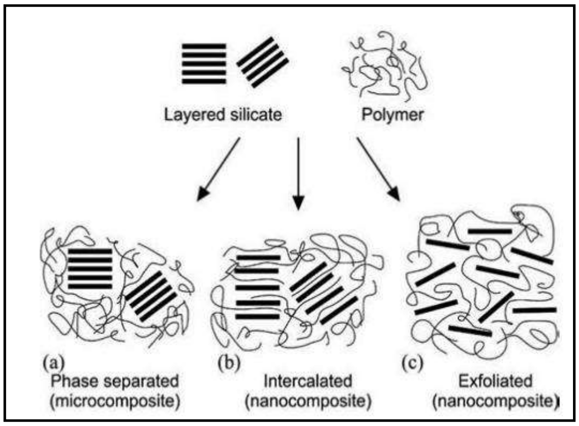

Fig. 2.7 Dispersion states of MMT (Azeredo, 2009)

Intercalation is said to have occurred when polymer chains disperse between the layers of clay thus broadening the d-spacing and forming stacks of layered structures.

Exfoliation is the best dispersion state as it provides the best results in formed nanocomposites. In exfoliation the clay layers are diffused homogeneously within polymer matrices and d-spacing increases as compared to intercalated tactoids (Arora and Padua, 2010; Avérous and Halley, 2009; Ray et al., 2006; Rhim and Ng, 2007; Rhim et al., 2013).

2.6 PVA composite films reinforced with lignocellulosic fibers:

Polyvinyl alcohol is an excellent film forming polymer with high gas barrier properties and water solubility. It is also biodegradable which has made PVA a material of choice for biodegradable composite films. PVA has been successfully incorporated with polymers like starch, chitosan and xylan etc to improve properties and/or to reduce costs. Lignocellulosic fibers are by product of various agricultural activities like growing and harvesting crops and fruits etc. A number of such lignocellulosic fibers have been utilized for the preparation of biodegradable composite materials with PVA with the objective of providing strength to the composite, utilizing waste from agricultural residue and to make PVA composites more economical. Starch is also fairly economical agricultural commodity which has been used in conjunction with PVA to form PVA-Starch composites. **Table 2.1** lists the properties of different composite films prepared using PVA and lignocellulosic fibers; and PVA-starch and lignocellulosic fibers.

Asgher et al. (2017) prepared bacterial lignolytic enzyme mixture and treated wheat straw with the lignolytic enzymes which enhanced the cellulose and reduced the lignin content. The delignified wheat straw was further modified by bacteria which deposited bacterial cellulose fibers over the delignified wheat straw. Modified straw-PVA composites were prepared using compression moulding. The bacteria modified wheat straw showed best results of tensile strength. Glycerol addition improved the tensile strength further. However the water uptake rate was very high in case of bacteria modified wheat straw – PVA composite.

Mittal et al. (2016) prepared PVA-starch composite films with barley husk and palmitic acid graft copolymerized barley husk. The films were cross linked with urea-formaldehyde and plasticized with glycerol. Addition of starch to PVA films reduced the tensile strength and elongation at break-point while cross linking helped in increasing the tensile strength and reducing elongation at break-point. They reported increase in %elongation and tensile strength with reinforcement of barley husk and graft copolymerized barley husk, the observed increase was greater in case of the latter. Water uptake and water vapour permeability increased with addition of natural barley husk while it decreased upon cross linking. Similarly the graft copolymerized barley husk reinforced composite films showed comparatively lower values of water uptake and water vapour permeability.

Meng et al. (2018) prepared PVA-carrageenan composite films plasticized with polyols derived from liquefied banana pseudo-stem. They studied the effect of novel plasticizer on thermal, mechanical and hydrophobic properties of carrageenan – PVA composite films. The polyol addition progressively reduced tensile strength and increased % elongation. However incorporation of inorganic ions like calcium and potassium ions improved the tensile strength as well as % elongation. Swelling in water also got reduced after plasticization with liquefied banana pseudo-stem derived polyol. Shi et al. (2017) used spirulina, PVA and glycerol to cast composite films. Tensile strength and water resistance increased while % elongation decreased with increasing PVA concentration.

Ali et al. (2015) studied the physico-mechanical properties of lignocellulosic kenaf fiber reinforced polyvinyl alcohol (PVA) biocomposite films. Kenaf fibers were chemically treated with either chromium sulphate alone or with chromium sulphate followed by sodium bicarbonate. The PVA composite films having treated fibers showed higher tensile strength compared to composite films having untreated fiber. The chromium sulfate-sodium carbonate treated kenaf fiber showed better mechanical properties and lower moisture uptake than chromium sulfate treated kenaf fiber.

Kalambettu et al. (2015) prepared PVA-pineapple leaf fiber composite films and evaluated their water uptake behavior. The films with higher fiber content showed lower water uptake exhibited higher tensile strength. A soil burial test was performed to investigate the biodegradability. The composite films were buried in soil in laboratory and were taken out after a fixed period to measure biodegradability, the samples were thoroughly washed with water to remove all PVA and the degradation of leaf fibers in terms of weight loss was measured. This method might estimate the degradation of fibers but that of PVA could not be determined.

Shen et al. (2015) prepared composite films of PVA and sugar beet pulp. The water vapour permeability and tensile strength increased with increase in sugar beet pulp content but %elongation at breakpoint decreased. Sorbitol was found to be a better plasticizer than glycerol for SBP-PVA composite films.

Solikhin et al. (2018) studied the properties of PVA-chitosan films reinforced with lignocellulosic nanofibers (LCNF). The films made with 0.5% LCNFs had the highest tensile strength which decreased with increased loading. PVA/chitosan polymer blends with 0.5% LCNFs resulted in regular and smooth external surfaces and enhanced tensile strength of the films.

Sutka et al. (2015) prepared electro-spun fibrous mats of PVA and lignocellulosic nanowhiskers (LCNWs) from hemp shives prepared via ball milling, ultrasonication and steam explosion. They reported an increase in the tensile strength with addition of LCNWs up to 10 wt%.

2.7 PVA-starch composite films reinforced with lignocellulosic fibers:

Priya et al. (2014) investigated the effect of citric acid as plasticizer and glutaraldehyde as cross linker on the properties of *Grewia optiva* fiber reinforced composite films. Best values of TS and EB were displayed by films having 20 wt% citric acid, 0.2 wt% glutaraldehyde, and 20 wt% fibers. The films also exhibited antibacterial activity against gram positive and gram negative bacteria.

Singha et al. (2015) prepared PVA-starch composite films reinforced with delignified and MMA grafted delignified *Grewia optiwa* fibers. The films were also plasticized with citric acid and cross linked with glutaraldehyde. The composite films exhibited maximum tensile strength and % elongation at 20 wt % for ungrafted fiber and at 15 wt% for MMA grafted fiber. The increase in tensile strength in case of ungrafted fiber was due to the better adhesion between fiber and polymers while in case of grafted polymer composite films it was due to the rough surface created by the grafting of MMA which led to better adhesion between matrix and fiber.

Guimarães et al. (2015a) studied thermal, mechanical and structural properties of PVA-modified cassava starch (MCS) films. The films showed best mechanical properties at the PVA: starch ratio of 20: 80. Higher proportions of MCS made the composites opaque, rigid and brittle while also being thermally stable and water vapour resistant. Higher amount of PVA (60 and 80 %) resulted in flexible, ductile, less thermally stable, transparent and water soluble composites. The group also prepared bamboo nanofibrils through mechanical defibrillation of refined bamboo pulp after treatment with alkali and bleaching. The best values for tensile strength, %elongation and water vapour permeability were exhibited by films having 6.5% bamboo nanofibrils reinforcement. The improved distribution of nanofibers led to compact structure and efficient packing (Guimarães et al., 2015b).

Das et al. (2011) prepared jute nanofibrils by acid hydrolysis of jute fibers. They reinforced starch-PVA composite films with jute nanofibrils and reported improvement in tensile strength at 15wt% loading. The water uptake rate was reported to be lower with 15 wt% jute nanofibrils reinforcement. The availability of lesser number of free hydrogen bonds due to interaction with nanofibrils to interact with water molecules was responsible for the lowering of the water uptake.

Table 2.1: Properties of PVA and PVA - starch composite films reinforced with lingo-cellulosic fibers

Polymer matrix	Reinforcement	Additives	TS MPa	EB %	WVP g.m/m^2.s.Pa	Remarks	Reference
PVA	Bacteria modified wheat straw	Glycerol	64.73	6.73	-	High water uptake rate due to impregnation with bacterial cellulose	(Asgher et al., 2017)
PVA - Starch	Barley Husk (Graft copolymerized)	Urea Formaldehyde	18.54	48.37	1.64E-10		(Mittal et al., 2016)
PVA	carrageenan	KCl, liquified wood flour derived polyols as plasticizer	44.3	648.25	-	High water uptake rate.	(Meng et al., 2018)
PVA - Starch	Spirulina	Glycerol	32.5	11.6	-		(Shi et al., 2017)
PVA	Alkali treated Kenaf fiber		13.8	80	-		(Ali et al., 2015)
PVA	Pineapple leaf fiber		25.6	68.9	-		(Kalambettu et al., 2015)
PVA	Sugar beet pulp		53.84	12.45	1.61		(Shen et al., 2015)
PVA - Chitosan	Oil palm empty fruit bunch LCNF		32.15	-	-		(Solikhin et al., 2018)
PVA - Starch	MMA grafted Grewia optiva fiber	Citric acid, glycerol	45.62	264.64	-		(Singha et al., 2015b)

PVA - Starch	Grewia optiva fiber	Citric acid, Glutaraldehyde	38.53	182.1	-		(Priya et al., 2014)
PVA - Starch		Glycerol	26.4	183	1.39E-11		(Guimarães et al., 2015a)
PVA	Lignocellulosic nanowhiskers from hemp		8.81	9.35	-	PVA LCNW electro spun mat	(Sutka et al., 2015)
PVA - Starch	Bamboo nanofibrils	Glycerol	32.6	280	1.09E-11		(Guimarães et al., 2015b)
PVA	Bacterial cellulose nanocrystals	Glycerol, Boric acid	72.84	293.43	-		(Rouhi et al., 2017)
PVA	Nanocellulose		63.5	183.7	-		(Frone et al., 2011a)
PVA – Starch	Jute nanofibrils	Glycerol	46.8	-	-		(Das et al., 2011)

2.8 Nanocellulose reinforced PVA composite films:

Various authors have investigated nanocellulose incorporation in PVA composite films to improve upon the composite's properties. **Table 2.2** lists the properties of different composite films prepared using PVA or other polymer and nanocellulose.

Asad et al. (2018) prepared TEMPO-oxidized nanocellulose (TONC) from oil palm empty-fruit-bunches (OPEFB) pulp using TEMPO mediated oxidation by NaOCl and NaBr in water at 25 °C and at 10 pH. TONC PVA Nanocomposite films were prepared by solution casting using 0.5 to 6% (w/w) TONC loading with highest tensile strength (122% increase) and modulus (291%) at 4% (w/w) TONC content. The elongation at breakpoint decreased by about 42.7%.

Rouhi et al. (2017) investigated the effects of bacterial cellulose nanocrystals (BCNC) (as reinforcement), glycerol (plasticizer) and boric acid (cross-linker) on the mechanical properties of PVA films using response surface methodology (RSM). The models showed the maximum UTS of 72.84MPa and %elongation of 293.43% could be achieved at 13.89% glycerol concentration, 5.00% BCNC concentration and a boric acid content of1.96%. They confirmed the formation of intra and intermolecular hydrogen and ether cross linkages by FTIR analysis in boric acid cross linked films.

Frone et al. (2011) reported noteworthy improvement in tensile and thermal properties of PVA films when reinforced with cellulose nanofibers. The cellulose nanofibers were obtained from microcrystalline cellulose (MCC) by ultrasonication and used at 1 to 5 wt % loading in polyvinyl alcohol films. They attributed the enhancement of mechanical properties of PVA-cellulose nanofiber composites to the interfacial adhesion at the fiber/matrix interface through hydrogen bonding between the OH groups of cellulose fibers and the PVA matrix. Also, mechanical properties were better in case of smaller size fibers compared to when large size fibers were used, attributed to higher surface area and the larger probability of hydrogen bonding in the case of smaller size fibers.

Li et al. (2013) prepared nanocellulose fibrils (NCFs) from bleached hard Kraft pulp (BHKP) using high-intensity ultrasonication and investigated effect of their reinforcement in PVA films. NCFs had higher crystallinity and thermal stability than BHKP due to removal of hemicelluloses. PVA composites with 4 wt% NCFs content showed best mechanical properties, with tensile strength and Young’s modulus 1.86 and 1.63 times better than plain PVA.

Shankar and Rhim (2016b) prepared nanocellulose from micro crystalline cellulose using NaOH/urea treatment. The prepared nanocellulose was used as reinforcement in agar films. The addition of nanocellulose up to 3 wt% increased the tensile strength up to 52.8 MPa from 46.7 MPa. The % elongation of films also increased marginally at higher concentration of nanocellulose. The WVP of films reduced with increasing nanocellulose concentration and best results were obtained at 3 wt%.

Ching et al. (2015) prepared PVA nanocomposites by solution casting reinforced with nanosilica and nanocellulose derived from oil palm empty fruit bunches. Nanosilica reinforcement improved thermal stability of PVA/nanocellulose composites by reducing the mobility of matrix molecules. The PVA composites with 3 wt% nanocellulose and 0.5 wt% nanosilica showed best thermo-mechanical properties while retaining good optical properties due to effective dispersion and polymer-filler interaction.

Li et al. (2014) studied the thermal stability and mechanical properties of PVA composites reinforced with filamentous nanocellulose fibrils (NCFs) from chemical-thermo mechanical pulps (CTMP) obtained using ultrasonication. The NCFs had diameters ranging from 50 to 120 nm and showed higher crystallinity (72.9%) compared to CTMP (61.5%). The best thermal stability, light transmittance, and mechanical properties were achieved at 6 wt% NCF content. Tensile strength and young's modulus was improved by 2.8 and 2.4 times respectively compared to plain PVA. The composites also exhibited a visible light transmittance of 73.7%.

Zhou et al. (2012) isolated nanocellulose from microcrystalline cellulose using three methods viz., acid hydrolysis (AH), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation (TMO) and ultrasonication (US). Nanocellulose isolated by TMO was higher in yield (37%) and had high aspect ratio. Nanocellulose isolated by AH treatment had higher crystallinity index (88.1%) and better size dispersion. Both the AH-derived and TMO-derived nanocellulose was dispersed homogeneously in the PVA matrices. Elongation at break was higher for AH/PVA films (51.59% at 6 wt% nanocellulose loading) compared to TMO/PVA. The TMO/PVA films showed increments of 21.5% and 10.2% in tensile modulus and strength at 6 wt% nanocellulose loading.

Jasmani and Adnan (2017) incorporated NCC isolated from acacia wood pulp via acid hydrolysis in PVA films. 2wt % loading of NCC into the PVA film improved tensile strength by 30% while maximum value of the tensile strength was obtained at 10 wt% loading of NCC. The results indicate reinforcement potential of acacia derived NCC.

Z. Wang et al. (2018) obtained cellulose nano-fibrils from TEMPO mediated oxidation of microfibrils obtained after alkali treatment of steam exploded rice straw fibers. Rice straw CNF and CMF reinforced polyvinyl alcohol (PVA) composite films were prepared by solution casting method. The authors reported CNFs/PVA composite films to be having uniform fiber dispersion, better mechanical properties and transparency but weaker water resistance compared to the rice straw CMFs/PVA composite films. More polar groups in rice straw CNFs compared to CMFs were cited as the reason for this.

Table 2.2: Behavior of PVA composite films reinforced with nanocellulose

Matrix Polymer	**Other Polymer**	**Additives used (w/w % of polymers)**	**TS (MPa)**	**EB (%)**	**WVP g.m/s.m^2.Pa**	**WST (%)**	**Preparation Method**	**Application**	**Reference**
PVA 10 wt%	-	BHKP NCF 4 wt%	34.7	-	-	-	Solvent casting	Packaging	(Li et al., 2013)
PVA	Nanocellulose		29.3	121.5	-				(Cabuk et al., 2017)
Agar 2 wt%		Glycerol 30 wt% Nanocellulose 3 wt%	52.8	15.8	0.97 E-9	-	Solvent casting	Packaging	(Shankar & Rhim, 2016)
PVA 10 wt%		Nanosilica 0.5 wt% Nanocellulose 3 Wt%	37.5	198.5	-	-	Solvent casting	Packaging	(Ching et al., 2015)
Pectin 5 wt%		Glycerol 30 wt% Nanocellulose 5 wt%	13.7	29.4	9.06 E-11	28.76	Solvent casting	Packaging	(Chaichi et al., 2017)
Cassava starch 72.5 wt%		Glycerol 25 wt% Rice husk cellulose nanofibrils 2.5 wt%	18	15	1.8 E-10	-	Blow film extrusion	Packaging	(Nascimento et al., 2016)
PVA 10		NCF 6 wt%	58.7	-	-	-	Solvent	Packaging	(Li et al.,

wt%							casting		2014)
PVA 10 wt%		TEMPO oxidized OPEFB nanocellulose	136	4.25	-	-	Solvent casting	Packaging	(Asad et al., 2018)
PVA 10 wt%		TEMPO oxidized nanocellulose	120	35	-	-	Solvent casting	Packaging	(Zhou et al., 2012)
PVA 10 wt%		Acacia mangium nanocellulose 10 wt%	29.3	103.4	-	-	Solvent casting	Packaging	(Jasmani & Adnan, 2017)
PVA 10 wt%		Rice straw NFC 3 wt%	59.8	117.6	-	108.4	Solvent casting	Packaging	(Z. Wang et al., 2018)

2.9 Nanoclay reinforced PVA composite films:

The ions present in unmodified MMT for e.g., Na+, promotes the interaction between water- soluble polymer matrix like PVA and MMT due to ion–dipole interactions between water molecules and MMT. The PVA/MMT nanocomposites have therefore been investigated thoroughly due to their exceptional properties and diverse applications (Dean et al., 2008). PVA/MMT nanocomposites with varying MMT contents of 5, 10, and 20 wt% were prepared and their morphology was studied by (Sapalidis et al., 2011). The TEM results indicated that exfoliation dispersion occurred at MMT addition of 20 wt%. (Li et al., 2015) reported that with increasing MMT loading the intercalated structures became more apparent in place of exfoliated structures for PVA/MMT nanocomposites. The MMT incorporation also interfered with crystallization of PVA due to the high affinity between PVA and MMT. Interestingly, Young's modulus of nanocomposites was reported to increase linearly with increase in d-spacing values as a result of larger numbers of polymer chains diffusing between clay platelets, which correspond to proper intercalation and effective filler dispersion (Chiou et al., 2005; Majdzadeh-Ardakani et al., 2010). The effect of MMT on properties of nanocomposites as indicated by the d-spacing values is greater at higher nanoclay loading than at lower loading (Majdzadeh-Ardakani and Nazari, 2010) when PVA/ starch/MMT nanocomposites were prepared with nanoclay loadings of 0, 4, and 8 wt%. They showed that mechanical properties were enhanced by increasing the MMT content above 4 wt%. **Table 2.3** lists the properties of PVA composites incorporated with nanoclay.

Noori et al. (2015) prepared poly (vinyl alcohol) (PVA)/chitosan (CS)/montmorillonite (MMT) nanocomposite hydro gels by freezing-thawing method, as a biocompatible wound dressing. The X-ray diffraction analysis showed exfoliated morphology of the nanocomposite hydrogels. Use of 3 wt. % of nanoclay enhanced the tensile modulus of nanocomposite hydro gel by nearly 35% compared to the neat hydro gel counterpart. The authors found the MMT reinforced hydro gels to be a good candidate for wound dressing application.

Wang et al. (2018) prepared starch/polyvinyl alcohol (PVA)/clay nanocomposite films with high mechanical and barrier properties by extrusion blowing. The X-ray diffraction and transmission electron microscopy results demonstrated that the starch/PVA/clay nanocomposite films exhibited intercalated structures and the extent of intercalation increased with increasing PVA content. The FTIR spectra showed that the molecular interactions were enhanced in the starch/PVA/clay films with higher PVA content. Dynamic mechanical analysis revealed partial miscibility between the starch and PVA in the films and the compatibility was improved when the PVA content was 50%. The maximum tensile strength and elongation at the break point for films were 30.18 MPa and 224.40%, respectively. The oxygen permeability of the starch/PVA/clay film with 50% PVA dramatically decreased by about 210 times compared with that of the starch/clay film. A continuous phase inversion mechanism was proposed to explain the improvement in performance of the starch/PVA/clay nanocomposite films. The results indicated that starch/PVA/clay nanocomposite film is a promising material for high barrier food packaging.

Abdullah and Dong (2018) used poly (vinyl) alcohol (PVA)/starch (ST) in the weight ratio of 80/20 to prepare films using solution casting method with 30 wt% glycerol (GL) as the plasticizer. Halloysite nanotubes (HNTs) were used as filler at loadings of 0.25, 0.5, 1, 3 and 5 wt% to enhance mechanical and thermal properties of resulting PVA/ST/HNT nanocomposites. The tensile strength of nanocomposites was found to be improved by 20 and 3.4%, respectively, for nano-composites made with 0.25 and 0.5 wt% HNTs compared to those of PVA/ST/GL blends. However, beyond the HNT loading of 0.5 wt% strength decreased due to HNT agglomeration, as exhibited by the scanning electron microscope (SEM) photo-micrographs. The X-ray diffraction (XRD) analysis indicated slightly intercalated nanocomposite structures formed at low HNT loadings of 0.25–1 wt%.

Polyvinyl alcohols-based nanocomposite films with four types of montmorillonite (MMT) nanoclay, including 18-amino stearic acid (I.24TL), methyl, bis hydroxyethyl, octadecyl ammonium (I.34TCN), di-methyl, di-hydrogenated tallow ammonium/siloxane (I.44PSS) organically modified MMT and a natural MMT (Na+-MMT) were fabricated by a solution-intercalation, film-casting method by Liu et al. (2014). Transmittance, WS, SR, WVUR, and WVP of the nanocomposite films were significantly reduced compared to a pure polyvinyl alcohols film. The WVP decreased by 11.8-20.7%, and WS, SR and WVUR decreased by 19.9-41.8%, 9.1-26.4%, and 4.8-12.8%, respectively. The extent of changes was dependent on nanoclay type. X-ray diffraction patterns revealed intercalation formed in nanocomposite films. Among all the tested nanoclays, Na+-MMT showed more impact on physical properties of polyvinyl alcohols films, and the polyvinyl alcohols film compounded with quaternary ammonium group displayed remarkable antimicrobial activity against Gram-positive bacteria.

Slavutsky et al. (2012) observed improvements in the functional properties of corn starch based films by incorporating nanoclay (Montmorillonite). Nanoclay was incorporated in the polymer matrix using dry clay or using clay dispersed in water and the films were formed by casting. Depending on film preparation method used, intercalated or exfoliated nanocomposite films were obtained. Water vapor solubility and permeability decreased with increasing montmorillonite content and were affected by the dispersion method. Water diffusion was dependent only on the nanoclay content due to the increase in tortuosity of the diffusion path, caused by the nano particles. The results showed that incorporation of 5% of montmorillonite using an adequate dispersion method, improved the water resistance and barrier properties of corn starch based films. Nano particles reduced the deterioration in the properties of these hydrophilic films by increase in the moisture content.

Spoljaric et al. (2013) prepared nanocomposites of poly (vinyl alcohol) (PVA), nanofibrillated cellulose (NFC), and montmorillonite (MMT) clay via solvent casting. Scanning electron microscopy revealed effective NFC and MMT clay dispersion throughout the nanocomposites, while X-ray diffraction highlighted the effectiveness of PAA to encourage clay dispersion. The clay provided a barrier against the diffusion of water and oxygen (molecules) through the nanocomposite films. Permeability and adsorption were further reduced by cross linking, while oxygen barrier properties were remarkably enhanced at elevated values of relative humidity. Thermal stability of the PVA segment was strengthened by the presence of MMT clay and cross links. The clay interacted with PVA and NFC within the films thereby improving the mechanical properties and the glass transition temperature.

Majdzadeh-Ardakani and Nazari (2010) used melt extrusion method to prepare thermoplastic starch/poly (vinyl alcohol) (PVOH)/clay nanocomposites, exhibiting the intercalated and exfoliated structures. The effects of clay cation, water, PVOH and clay contents on clay intercalation and mechanical properties of nanocomposites were investigated. The experiments were carried out according to the Taguchi experimental design method. Montmorillonite (MMT) with three types of cation or modifier (Na+, alkyl ammonium ion, and citric acid) was examined. The prepared nanocomposites with modified montmorillonite indicated improvement in the properties in comparison to pristine MMT. It was also observed that increases in tensile strength and modulus would be attained for nanocomposite samples with 10%, 5% and 4% (by weight) of water, PVOH and clay loading, respectively. The clay intercalation was examined by X- ray diffraction (XRD) patterns.. The WXRD revealed that citric acid modification had increased gallery spacing in CMMT and improved tensile properties as it allowed for incorporation of PVA chains.

Table 2.3: Properties of PVA composite films reinforced with nanoclay

Matrix Polymer	**Other Polymer**	**Additives used (w/w % of polymers)**	**TS (MPa)**	**EB (%)**	**WVP g.m/s.m^2.Pa**	**WST (%)**	**Preparation Method**	**Application**	**Reference**
PVA 10 wt%	C: 2 wt%	Nanoclay 3 wt%	26.9	156.9	-	-	Solution casting	Wound dressing	(Noori et al., 2015)
PVA 50 wt%	Starch 50 wt%	G: 40 wt% Nanoclay 10 wt%	32.8	206.7	1.92 E-10	-	Blow film extrusion	Packaging	(W. Wang et al., 2018)
PVA 80 wt%	Starch 20 wt%	G 30 wt% HNT 5 wt%	-	-	-	69%	Solvent casting	Food packaging	(Abdullah & Dong, 2019)
PVA		Na-MMT	53.2	111.5	2.36E-10	258.69 %	Solvent casting	Food packaging	(Liu et al., 2014)
Starch 20 wt%		MMT 5 wt% G: 30 wt%	-	-	2.5E-10	14.27 %	Solvent casting	Food packaging	(Slavutsky et al., 2012)
PVA 5 wt%		NFC 5 wt% MMT	-	-	9.06E-11	584%	Solvent casting	Food packaging	(Spoljaric et al., 2013)

PVA 10 wt%	Starch 10 wt %	Citric acid modified MMT 4 wt%	55.3	13.11	-	-	Extrusion. Hot pressing	Packaging	(Majdzadeh-Ardakani et al., 2010)

2.10 Banana pseudo stem fibers as biomass for composite materials

A summary of the available reported information on the methods used for preparation and pretreatment of fibers, polymer – fiber ratio used and the corresponding values of tensile strength and elongation at the break-point for the resulting composites is given in **Table 2.4**.

A survey of available literature on the use of banana pseudo stem fibers for composite preparation showed that banana pseudo stem fibers have rarely been studied for composite preparation with PVA. There are numerous reports on the preparation of composite with epoxy, polyester and polypropylene and HDPE. The fibers have been pretreated using alkali, silane and maleic anhydride, the alkali has been the common choice. The composites have been prepared using cold or hot pressing techniques.

Table 2.4: Properties of polymer composites reinforced with banana fibers

Composite	Treatment	Preparation process	Fiber/resin ratio	TS (MPa or kN/mi)	Water absorbance (%)	EB (%)	Reference
Banana-epoxy	Mercerization with 5% NaOH for 72 h	Cold press for 12 h	–	58–62	–	–	(Bhoopathi et al., 2017)]
Banana-epoxy	–	Cold press of 25 kg for 24 h)	50:50	17.92	1.24	–	(Boopalan et al., 2013)
Banana-epoxy	–	Cold press	16:84h	16.12	21	–	(Venkateshwaran et al., 2011)
Banana-high-density polyethylene	Alkaline pulping, electrical rotary autoclaving	hot press at 130° C for 5 min	40:60	5.2i	–	1.4	(Ibrahim et al., 2010)
Banana-HDPE-nylon	–	Injection moulding at 190° C	38.8:61.2	31.6	1.5	–	(Liu et al., 2009)
Banana-polyester	–	Hot press	0.4:0.6	–	–	6	(Idicula et al., 2005b)
Banana-polyester	–	Hot press	0.4:0.6	57	–	–	(Idicula et al., 2005a)
Banana-polyester	–	Cold press of 1 MPa for 24 h	0.4:0.6	57	–	6	(Idicula et al., 2010)

Banana-polyester	Silane, 0.5% or 1% NaOH/ acetylation with glacial acetic acid	Cold press	40:60	57	27e	–	(Pothan et al., 1997)
Banana-polyester	-	Cold press	0.374:0.626i	60.9	–	–	(Murali Mohan Rao et al., 2010)
Banana-polyester	4% NaOH for 4 h	hot press of 5 MPa at 120□ C for 30 min	40:60	–	5.9	–	(Kumari et al., 2018)
Banana-polystyrene	Esterification with maleic anhydride in xylene	Hot press	40:60	–	10	–	(Naik and Mishra, 2006)
Banana-polyurethane	10 wt% NaOH for 4 h	Cold press	15:85c	10.12	–	–	(Merlini et al., 2011)
Banana-LDPE	10 wt% NaOH	Hot press	20:80c	10 Pa	2	25	(Ogunsile and Oladeji, 2016)
Banana-polypropylene	2% NaOH at 120□ C	Injection moulding	30:70	42.5	–	2.7	(Paul et al., 2007)

Objectives

From the review of the available literature and the relevant experimental information summarized in Table 2.1 - 2.4, it is seen that efforts have been made to reinforce PVA films with chitin, starch, etc. but scanty information is available on the use of lingo-cellulosic fibers for re-enforcing the films. Some workers have tried to use palm oil fruit bunch fibres, *Grewia optiva*, pineapple leaf fibers, etc. but in spite of its availability in abundant quantity no effort has been made to use banana pseudo-stem fibers for making composite bio-degradable films. Some information on the use of chitosan, nano-clay, nano-cellulose, and starch in making composite films with PVA are available but no effort has been made to prepare PVA films reinforced with lingo-cellulosic fibers *and* nanoclay/ nanocellulose. In view of this the present work has been planned with following specific objectives:

- To preparation composite films with poly vinyl alcohol (PVA) and banana pseudo stem fibres,
- To study the effect of acid- and alkali-treatment of banana fibre on the behavior of films prepared using these fibres,
- To evaluate the effect of nano-cellulose reinforcement on composite films prepared with PVA and banana pseudo stem fibre,
- To evaluate the effect of nano-clay (Na-montmorillonite) and modified nano-clay (citric acid modified) reinforcement on PVA-banana pseudo-stem fiber composite films.