

Cellulosic Biocomposites: Potential Materials for Future

A.H. Bhat, Y.K. Dasan, Imran Khan and Mohammad Jawaaid

Abstract Bionanocomposite is one of the remarkable achievements of nanotechnology in material science to replace conventional non-biodegradable petroleum based plastics for packaging applications. In general, bionanocomposites are made up of biodegradable polymers (biopolymers) and bio based reinforcing material in the size range of 10–100 nm in one or more dimensions. Bio based materials could provide a solution for petroleum shortage and waste management problems. One of the potential reinforcing agents is agro industrial based is cellulose. Such composites demonstrate improved properties as compared to the neat biopolymers due the large surface area and high aspect ratio of nanoparticles. This study has given a clear overview of nanocellulose based composites by describing their isolation, surface modification, composite preparation, properties, and applications. Furthermore, the obtained results for developed bionanocomposites materials shows that it can be a promising alternative for conventional packaging materials with improved properties.

Keywords Nanocellulose • Biocomposites • Bionanocomposite • Polymers

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M. Jawaaid et al. (eds.), *Green Biocomposites*,

Green Energy and Technology, DOI 10.1007/978-3-319-49382-4_4

1 Introduction

The increasing environmental and sustainability concern have played a major role in guiding to the exploitation of the next generation products, processes and materials (Abdelwahab et al. 2012). Bionanocomposite is one of the emerging group of materials comprise of biopolymer matrix reinforced with organic nanoparticle owning at least one dimension in the range of 10–100 nm (Bhat et al. 2011). Such composites demonstrate improved properties as compared to the neat biopolymers due the large surface area and high aspect ratio of nanoparticles. Moreover, the properties inherent by bionanocomposites, such as biodegradability provides solution for depletion of petroleum and disposal methods of persistent packaging materials (Darder et al. 2007).

Nanocrystalline celluloses are discerned as one of the promising reinforcing agents of bionanocomposite due to the interaction between the nano-sized components that form a percolated network connected by hydrogen bonding (Zhou et al. 2012). Nanocrystalline cellulose (NCC) is a fine, odorless, white, crystalline powder with rod shaped crystalline domain with 1–100 nm in diameter and 10–100 nm in length depending upon the resources of cellulose. Furthermore, it has a perfect crystalline structure with high aspect ratio and large surface area of 70 and ca. 150 m²/g respectively (Valentini et al. 2013; Haafiz et al. 2013). The major resources of cellulose are wood of forest, non-wood lignocellulose (cotton, hemp, ramie, kenaf etc.), and agricultural biowaste (corn cob, rice husk, sugarcane bagasse and oil palm biomass) (Ng et al. 2015; Espino et al. 2014). The utilization of agricultural biowaste is encouraged as it is renewable, abundant and cheap. Oil palm empty fruit bunch fiber (OPEFB) is one of the major industrial by product which has been incinerated at plantation areas without any profit (Shinoj et al. 2011; Khalil et al. 2013). However, OPEFB fiber is one of the potential sources of cellulose as the fibers are composed of 40–50% of cellulose, which is highest as compared to coir, bagasse, corn, and kenaf fiber. This agricultural biowaste presents unique characteristics including, good thermal properties, lower density and cost, and high specific strength (Lani et al. 2014). Generally, NCCs extracted from cellulosic fibers through acid hydrolysis process, which dissolves the amorphous region of fiber by retaining crystalline fractions. Sulphuric acid (H₂SO₄) hydrolysis is a well-known process to obtain stable colloidal suspension of NCCs due to the repulsion force induced by negatively charged sulfate ions on the crystals surface (Bondeson et al. 2006; Peng et al. 2011).

Biopolymers are an important ingredient in bionanocomposite preparation process. Among the biodegradable polymers, poly (lactic acid) (PLA) and poly (3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV) are of increasing commercial interest for packaging applications. PLA is a transparent and crystalline biopolymer which can be synthesized via ring opening polymerization through the lactide formation or by the condensation polymerization of the lactic acid. This biopolymer exhibits high mechanical strength, thermoplastic characteristics and biocompatibility. Moreover, thermal instability, low elongation at break, poor water vapor

barrier properties and brittleness are potential drawbacks for this polymer. Poly (3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV), also known as a bacterial polyester and it is a copolymer of hydroxybutyrate (HB) and hydroxyvalerate (HV). PHBV exhibits lower melting point with improved melting stability and higher flexibility as compared to the homopolymer, poly (3-hydroxybutyrate) (PHB). However, PHBV has mellow crystallization rate, high production cost and development of interlamellar secondary crystallization on storage. Therefore, the blend of these two biopolymers was proposed in order to combine the advantage of both polymer and to overcome their drawbacks. Several research studies show that the blend PLA-PHBV could improve crystallinity of PLA while improving the stiffness of PHBV (Arrieta et al. 2014; Bhardwaj et al. 2006; Ten et al. 2013).

The major challenge in the development of bionanocomposite is to increase the compatibility between NCC and biopolymer blend in order ameliorate the dispersion of nanocrystalline cellulose. Nanocrystalline cellulose reinforced composites exhibits poor dispersion of filler in the matrix due to the hydrophilic and hydrophobic nature respectively (Lindström and Aulin 2014). Therefore, surface modification process is an important step in order to improve surface functional groups and hydrophobic nature of NCC surface. On the contrary, solution casting and evaporation technique is one of the easiest methods of preparing bionanocomposite film with good dispersion and reinforcement results (Rebouillat and Pla 2013).

2 Natural Fibers as Fillers in Polymer Composites

Natural fibers symbolize a traditional class of renewable composite material which is known as biocomposites. It has gained tremendous attention among researchers due to its ecofriendly nature.

2.1 Source and Classification of Natural Fibers

Generally natural fibers are categorized according to their origin, which include plants, animal and/or minerals. Vegetable fibers which include cotton, jute, flax, ramie, sisal and hemp are generally referred as cellulosic fibers as cellulose is the primary structural component of all plants. Typically, natural animal fibers such as silk, wool, angora, mohair, and alpaca are composed of protein. Furthermore, mineral fibers are naturally occurring fibers or slightly modified fibers obtained from minerals. (Chandramohan and Marimuthu 2011). However, plant based natural fibers has received more attention due to their wide availability and renewability nature (Cristaldi et al. 2010). A broad classification of natural and synthetic fibers is represented schematically in Fig. 1.

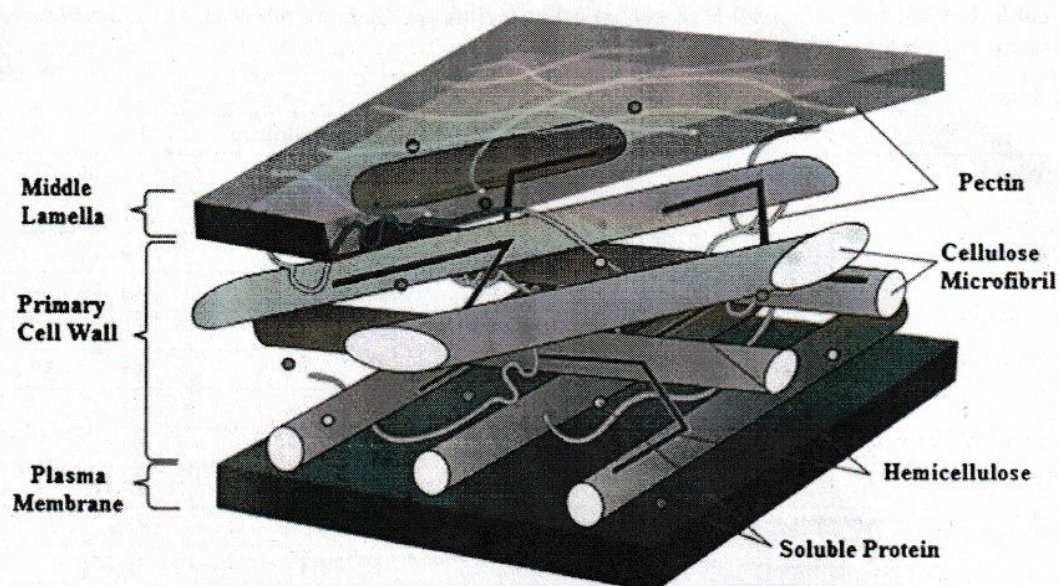


Fig. 1 A schematic diagram of plant cell wall structure (Sticklen 2008)

2.2 Chemical Compositions of Natural Fibers

The structure and chemical composition of a natural fiber depends on their climatic conditions, age and the degradation process. Natural fibers composed mainly of cellulose, hemicelluloses, lignin, and other extractives such as waxes, ashes, protein, starch and inorganic elements are shown in Fig. 1. The chemical components are distributed throughout the cell wall, which is composed of primary and secondary wall layers. The chemical composition varies from plant to plant, and within different parts of the same plant which is shown in Table 1 (Faruk et al. 2012).

Cellulose is the primary load bearing component of every plant cell wall. Polymerization of $\sim 30\text{--}36$ chains of $\beta\text{--}1, 4\text{-linked}$ glucose units form insoluble and rigid crystalline materials around the cell wall. Furthermore, hemicelluloses are plant polymers that make up of neutral and acidic polysaccharides such as xyloglucans, xylans, glucomannans and galactoglucomannans. Therefore, cellulose fibrils are coordinated with high molecular weight hemicelluloses molecules through hydrogen bond and engrafted in a matrix of pectin and lignins. Hemicelluloses act as clamp in between cellulose and, in some walls, with lignin (Scheller and Ulvskov 2010). Besides that, lignin act as a coupling agent and increase the strength of the cellulose-hemicellulose network (Stamboulis et al. 2001).

Table 1 Chemical composition of common lignocellulosic fibers (Faruk et al. 2012; Jawaid and Abdul Khalil 2011; Khalil et al. 2012)

Type of fiber	Composition (wt%)			
	Source	Cellulose	Hemicellulose	Lignin
Wood	Hardwood	31–64	25–40	14–34
	Softwood	30–60	20–30	21–37
Nonwood	Bagasse	32–55.2	16.8	19–25.3
	Coir	32–43.8	0.15–20	40–45
	Corn cobs	26.1	45.9	11.3
	Corn stalks	35	25	35
	Cotton	82.7	5.7	<2
	EFB	43–65	30	19
	Oil palm frond	56.03	27.51	20.48
	Flax	62–72	18.6–20.6	2–5
	Hemp	68–74.4	15–22.4	3.7–10
	Jute	59–71.5	13.6–20.4	11.8–13
	Kenaf	31–72	20.3–21.5	8–19
	Ramie	68.6–85	13–16.7	0.5–0.7
	Sisal	60–78	10–14.2	8–14
	Sunn	80	10	6
	Wheat straw	43.2	34.1	22
	Curua	70.7–73.6	9.9	7.5–11.1
	Abaca	56–63	20–25	7–13
	Alfa	45.4	38.5	14.9
	Bamboo	26–65	30	5–31
	Banana	63–67.6	10–19	5
	Coconut	36–43	0.15–0.25	41–45
	Soy hulls	56.4	12.5	18
	Rice husk	25–35	18–21	26–31
	Rice straw	59.1	18.4	5.3

3 Chemistry of Cellulose

Cellulose is a sustainable, abundant and naturally occurring biopolymer derived from biomass. Cellulose structure is organized into fibrils, which are surrounded by a matrix of lignin and hemicellulose (Rosa et al. 2010). It is a classic example of a renewable and biodegradable structural plant polymer which can be processed into fibrils (Haafiz et al. 2013). According to researchers, the estimated worldwide production of this biopolymer is more than 7.5×10^{10} tones each year. However, of this only about 6×10^9 tones are processed by paper, textile, material and chemical industries (Lavoine et al. 2012).

3.1 Structure and Properties of Cellulose

Cellulose, a high molecular weight carbohydrate polymer of β -1,4-linked anhydro-D glucose units is represented in Fig. 2 (Nguyen et al. 2013). This structure is secured by an intramolecular hydrogen bonds between the hydroxyl groups and oxygen of adjacent molecules. Cellulose molecular chains are biosynthesized and self-assembled into microfibrils in which crystalline regions alternate with amorphous regions (Haafiz et al. 2013). Cellulose microfibrils possesses diameter in the range of 10–30 nm and are made up of 30–100 cellulose molecules in extended chain confirmation and provide mechanical strength to the fiber (Kalia et al. 2011a, b, c). The hydrophilic nature of cellulose macromolecules is due to the three alcoholic hydroxyl (-OH) groups (Oksman et al. 2009). Therefore, unbonded hydroxyl group that mainly presents in amorphous region of cellulose plays the major role for their reactive nature during hydrolysis process whereas crystalline region of cellulose remain intact (Puri 1984).

The degree of crystallinity and degree of polymerization is very important in order to determine digestibility and mechanical properties (Gupta and Demirbas 2010). Furthermore, these two properties of cellulose may vary according to their source, age and pretreatments (Clarke 1996). Cellulose crystallinity is quantified based on the ratio of crystalline to amorphous cellulose and it is believed to play major role in the micro-accessibility of cellulose as well as in its effectiveness (Karimi 2015). X-ray analysis proves the existence of crystalline nature in cellulose with submicroscopic units, called crystallites or micelles, of varying length but of fixed breadth and thickness. Moreover, it shows the existence of smallest morphological units of ordered native cellulose on the surface of elementary fibrils, with diameter of about 3.5 nm. The average degree of polymerization (DP) of a cellulose is significantly related to their mechanical properties and also being used to access the degradation of cellulose by physical, chemical, or radiation damage.

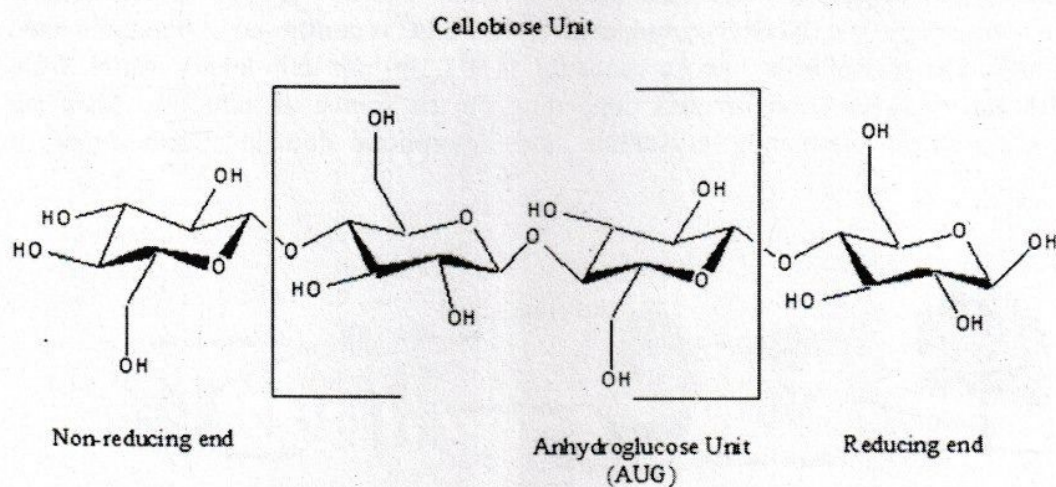


Fig. 2 The cellulose polymer chain structure

The DP of cellulose from primary cell wall is relatively low and heterogeneous (DP 2,000–6,000), while secondary cell wall cellulose is characterized by higher degree of polymerization and it is more homogeneous (DP 14,000) (Clarke 1996).

3.2 Nanocellulose and Their Characteristics

Nanocellulose, generally refers to the natural material that possess at least one dimension in the nanometer range which is extracted from native cellulose (Fig. 3) (Lin and Dufresne 2014; Khalil et al. 2014). There are three different types of nanocellulose which include nanocrystalline cellulose (NCC) or cellulose nanowhiskers (CNW), nanofibrillated cellulose (NFC), and bacterial cellulose (BC) which are categorized based on their dimension, function, preparation methods, and cellulosic source (Lin and Dufresne 2014; Brinchi et al. 2013). Nanocellulose has attracted great attention due to their unique characteristics such as sustainability, biodegradability, low density ($\sim 1.566 \text{ g/cm}^3$), abundant availability and low cost. Additionally, the nanoscale dimension of cellulose possess a very large surface to volume ratio, high modulus of elasticity ($\sim 150 \text{ GPa}$), high tensile strength, high stiffness, flexibility, electrical, good thermal and optical properties. Furthermore, the materials that are present in nanoscale range possess a different electronic, property, which successively affects its optical, catalytic, and other reactive properties (Silvério et al. 2013). The nanoscale dimensions and its capacity to form a strong entangles of nanoporous network have changed the emergence of new high value applications (Fig. 4).

Nanocellulose that is produced through mechanical processes is known as nanofibrillated cellulose (NFC), while nanocrystalline cellulose (NCC) is produced by acid hydrolysis which removes the amorphous segments and attain crystalline region of cellulose (Grossman et al. 2013). Nanofibrillated cellulose (NFC) was introduced by Turbak et al. in early 1980s as a cellulosic material, where high pressure homogenizer was used to produce cellulose from softwood with a diameter in nanometer scale (Nechyporchuk et al. 2015). NFC is composed of interconnected fibrils and microfibrils, whose diameter is 10–100 nm and length varies from 100 nm to several micrometers depending on the source of cellulose. They are comprised of alternating crystalline and amorphous domain. Furthermore, it

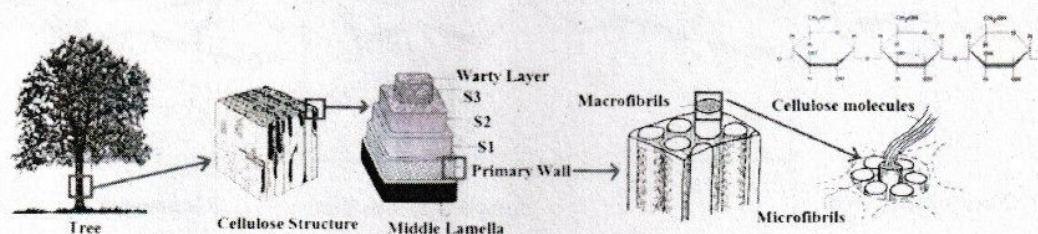


Fig. 3 Hierarchy of plant fiber

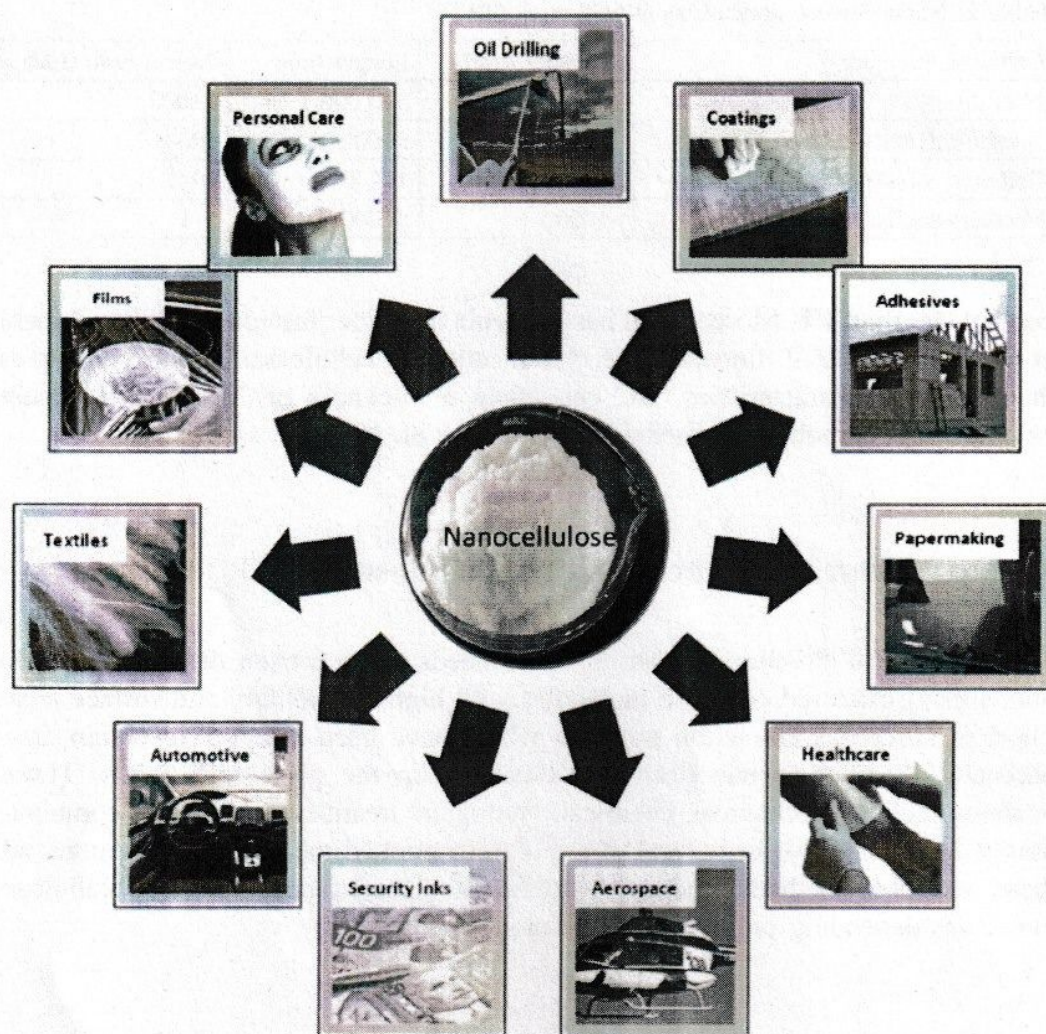


Fig. 4 Applications of nanocellulose

exhibits gel like properties in water with highly viscous dispersion at relatively low concentration i.e. 2% aqueous suspension (Besbes et al. 2011).

Nanocrystalline cellulose (NCC), also known as a cellulose nanowhiskers is a needle shaped cellulose particles with a diameter range of 2 to 20 nm and the length varies between 100 nm to several microns (Liu et al. 2011). Cellulose particles with rod like structure can be obtained through acid hydrolysis by removing amorphous region of cellulose chain. However, the degree of crystallinity, dimensional diversity and morphology depends on the source of cellulosic material and preparation conditions. These cellulose nanocrystals possess degree of crystallinity less than 400 and not more than 10% of the material has a particle size of less than 5 μm (Grossman et al. 2013).

Bacterial cellulose (BC) is an extracellular secretion of "vinegar bacteria" which is composed of cellulose nanofiber. Louis Pasteur in his study described them as "*a sort of moist skin, swollen, gelatinous and slippery...*" even though it has solid

Table 2 Nanocellulose dimensions (Khalil et al. 2012)

Cellulose structure	Diameter (nm)	Length (nm)	Aspect ratio (L/d)
Microfibril	2–10	>10,000	>1000
Microfibrillated cellulose (MFC)	10–40	>1000	100–150
Cellulose whiskers	2–20	100–600	10–100
Microcrystalline cellulose (MCC)	>1000	>1000	~ 1

content less than 1%. Moreover, it has no lignin and other foreign substance (Iguchi et al. 2000). Table 2 illustrates the classification of cellulosic fibers according to their physical characteristics. BC can attain a thickness of 25 mm under pure cultivation in carbohydrate media (Yamanaka et al. 1989).

4 Extraction of Nanocrystalline Cellulose (NCC)

The hierarchical structure of natural fibers needs to be broken down in order to obtain nanostructured cellulose molecules with high crystallinity and surface area. There is numerous extraction methods which have been reported to obtain nanodomain of cellulose nanofibrils by breaking up the glycosidic bonds. These methods include mechanical, chemical, Biological treatment, as well as combination of any of the two or several of the aforementioned methods. Furthermore, all these treatment methods lead to the different types of nanostructured cellulose molecules depending on their disintegration process.

4.1 Mechanical Treatment

Generally mechanical disintegration of cellulosic fiber produces nanofibrillated cellulose which is also called as a cellulose nanofiber. There are several mechanical approaches used to obtain cellulose nanofibers including, homogenizing, cryocrushing, microfluidization, grinding and high intensity ultrasonication (Khalil et al. 2014).

4.1.1 High Pressure Homogenizer

High pressure homogenization (HPH) (Fig. 5) is solely a mechanical process, where the fluid sample is forced to pass through the narrow gap of the homogenizing nozzle at high pressure (150–200 MPa). During the homogenization process the cellulosic fiber suspension is subjected to high pressure drop with shearing and impact force which leads to a high degree of fibrillation, resulting in the formation

of cellulose nanofibrills. High pressure homogenizing (HPH) treatment is an efficient way of refining cellulosic fiber, referable to its simplicity, efficiency, reproducibility, ease of scaling up in the industry and noncompulsory usage of organic solvent (Li et al. 2012; Wang et al. 2015). The application of HPH for isolation of cellulose nanofibrills was first introduced by Tubak et al. and Herrick et al., using Gaulin laboratory Homogenizer in year 1983 (Missoum et al. 2013). Since then, many researchers have used HPH to isolate cellulose nanofibrills from various raw materials. In the year 2007, Leitner et al., have used HPH to produce nanofibrillated cellulose from bleached sugar beet by 10–15 cycles at 30 MPa. Followed by Habibi et al. (2008) where nanofibrillated cellulose was isolated from bleached cellulose residue from the skin of prickly pear extract with a diameter of 2–5 nm by 15 passes through HPH at 50 MPa at a temperature below 95 °C, and Lee et al. (2009) has used HPH to produce nanofibrillated cellulose from microcrystalline cellulose (MCC) with a diameter range of 28–100 nm by 10 passes.

Even though, HPH is considered as efficient method in producing cellulose nanofibrills, insoluble properties of nanocellulose in water and most of the solvents causes clogging problems which leads to difficulty in obtaining uniformity (Lim et al. 2008). Therefore, it is necessary to reduce the size of cellulosic fibers prior to homogenization. Considering this, various pretreatment methods was employed prior to HPH process. Pretreatments such as refining and cryocrushing were applied for kenaf bast fibers which produces nanofiber with a diameter of 10–90 nm. While, kenaf core and stem was grinded prior to HPH process which produces nanofibrillated cellulose ranged from 20–25 to 15–80 nm. Zimmermann et al. introduced a milling pretreatment to obtain homogeneous cellulose fibrils bundles from wheat straw and wood fibers before using homogenizer with 150 MPa to produce nanofibrillated cellulose.

4.1.2 Microfluidization

Microfluidizer (Fig. 6) is another instrument which is similar to HPH where the cellulose suspension is injected into the high pressure chamber fibrillation to produce cellulose nanofibrills (CNF). The fiber slurry is accelerated into the interaction

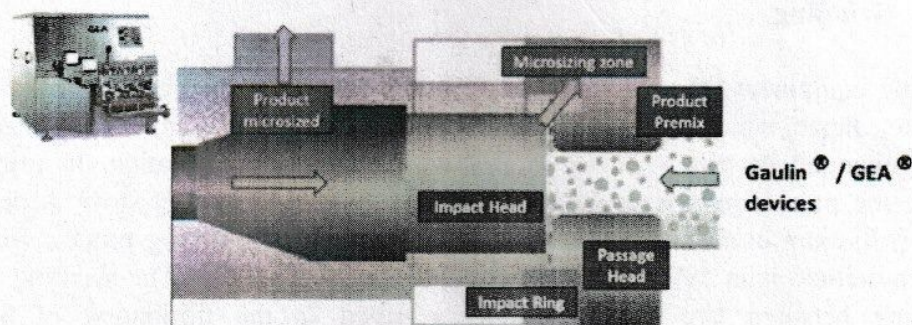


Fig. 5 High pressure homogenizer (HPH) (Missoum et al. 2013)

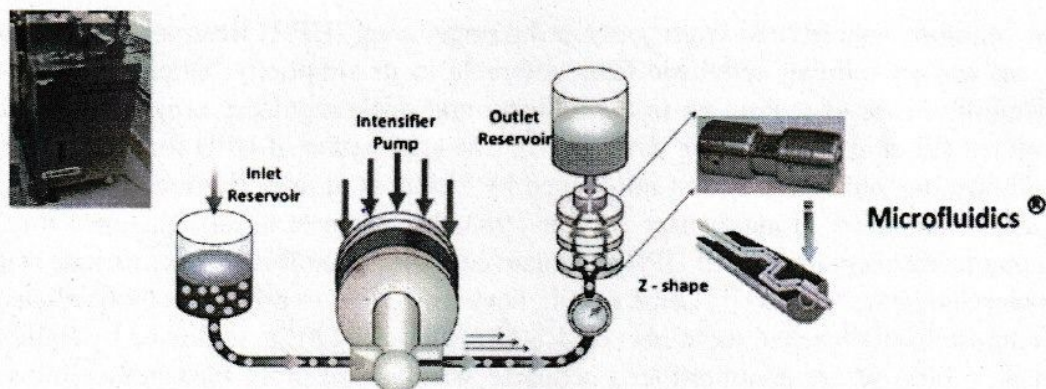


Fig. 6 Microfluidizer (Missoum et al. 2013)

chamber resulting from high pressure generated through pump intensifier. Once the pressurized product enters the interaction chamber, it passes through geometrically fixed micro channels, very high velocities are achieved. Apart from this, the degree of fibrillation is also determined by Z-chamber sizes (400–200–100 μm). There are several nanofibrillation works performed by using microfluidizer (Missoum et al. 2013).

Microfluidizer has been used in order to obtain nanofibrillated cellulose, where Charani et al. (2013) has obtained improved microfibrillated cellulose of kenaf unbleached pulp quality from higher pulp consistency of 5.5%, Jihua et al. (2014) have produced nanocellulose with smaller diameter ranged 5–12 nm and Bandera et al. (2014) has isolated of long and thin cellulose nanofiber from microcrystalline cellulose (Li et al. 2014). Furthermore, microfluidizer is used to improve the properties of reinforcement where Khan et al. (2014) improved the mechanical properties of CNC reinforced bionanocomposites by optimized microfluidization process (Khan et al. 2014). Microfluidizing procedure possess unique characteristics, such as efficient and rapid mixing which leads to rapid chemical reaction, homogeneous reaction environment, continuously varied reaction condition and also due to the precise time intervals for addition of reagent during reaction (de Moura et al. 2012).

4.1.3 Grinding

Grinding equipment (Fig. 7) was first proposed and developed by Masuko Sanyo Co., Ltd., Japan, which involves breakdown of the cell wall structure using shearing force generated by two grinding stones with countersense rotation. In grinding device, the pulp is passed between a static and rotating grinding stone at desired speed (Missoum et al. 2013). The first reported work of grinding process for fibrillation method is in 1998 by Taniguchi and Okamura (1998). The shearing force occurring between two ceramic stones resulted in the fibrillation of fibers. Furthermore, the fiber was treated sequentially by passing several times through the

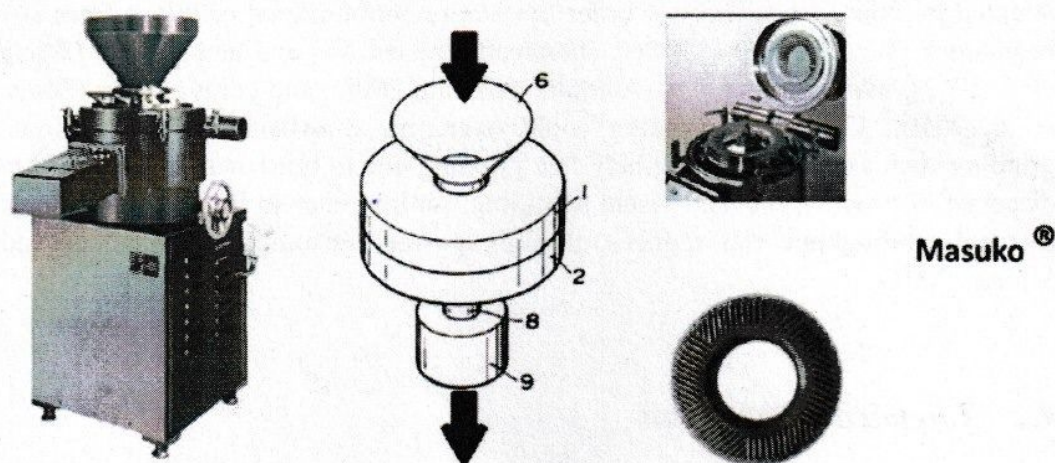


Fig. 7 Grinder (Missoum et al. 2013)

adjustable clearance between grinding stones until the desired quality was obtained (Iwamoto et al. 2007). Afterwards, many researchers have used grinding method in order to obtain nanofibrillated cellulose from various raw materials including, wood fibers (Abe et al. 2007), sludge fibers (Jonoobi et al. 2012), kenaf pulp (Jonoobi et al. 2010), bamboo pulp (Visakh et al. 2012), Agave tequilana and barley (Espino et al. 2014), and bleached Kraft pulp (Nair et al. 2014).

Apart from this, some researchers have combined this grinding process with mild chemical pretreatments, homogenization and ultrasonication processes in order to remove impurities such as lignin and pectin, also to improve their mechanical properties. Zhao et al. (2015) has prepared cellulose nanofibrills from coconut palm petiole powder by combining grinding/homogenization and grinding/ultrasonication with better tensile properties and transmittance (Zhao et al. 2015). On the other hand, Panthapulakkal and Sain (2013) and Karimi et al. (2014) have combined mild chemical pretreatments such as alkali pretreatment and bleaching prior to grinding process (Panthapulakkal and Sain 2013; Karimi et al. 2014). Grinding process has been used widely due to its simplicity, robustness with low cost and energy consumption. Furthermore, it doesn't have blocking problems like in homogenization process due to large fiber sizes (Josset et al. 2014).

4.1.4 Cryocrushing

Cryocrushing is a process where refined cellulose fiber is immersed in liquid nitrogen to free the water content in fibers and subsequently crushed by high impact grinding (Chakraborty et al. 2005). Microfibrils are generated from frozen fibers, in resultant of cell wall rupture due to exerted pressure of ice crystals generated by high impact forces. The resulting cryocrushed fibers might be dispersed uniformly into water suspension using disintegration before proceeding with the high pressure defibrillation process (Kalia et al. 2011a, b, c). Cryocrushing method has been

adopted by many researchers in order to obtain nanofibrillated cellulose from soy bean stock (Wang and Sain 2006), chemically treated flax and hemp fibers (Wang et al. 2007), wheat straw fibers (Alemdar and Sain 2008), and curava fibers (Souza et al. 2010). Cryogenic grinding could overcome drawbacks of conventional grinding such as produces extremely fine grinding due to brittleness, more uniform dispersal of product, reduced visual speckling, settling rates in liquid preparations, increases throughput and reduces grinding power consumption (Manohar and Sridhar 2001).

4.2 Chemical Treatments

4.2.1 Alkali Pretreatment

Alkaline pretreatment is employed to break down the lignin structure, hence improving the susceptibility of the remaining polysaccharides (cellulose and hemicelluloses) for other treatment (Sun and Cheng 2002). Generally, NaOH, KOH, $\text{Ca}(\text{OH})_2$, hydrazine and ammonium hydroxide are used as a pretreatment agents for alkaline hydrolysis (30, 31). Alkaline hydrolysis is usually conducted under mild condition (below 140 °C) as compared to other pretreatment technologies. During the pretreatment, intermolecular ester bond, which cross links Xylan (hemicelluloses) and lignin are saponified subsequently to increase their porosity (Sun and Cheng 2002). Furthermore, nucleophilic acyl group in the presence of alkaline salt substitutes the cleavage of this ester linkage to form a carboxylic salt and an alcohol (Pedersen and Meyer 2010). Moreover, ferulic acid and p-coumaric acid are produced when two types of aryl ether bonds split during the alkaline hydrolysis. Besides that, alkalis are good swelling agent, increases internal surface area and also decreases the degree of polymerization and crystallinity of cellulose. However, the removal of hemicelluloses component from lignocellulosic material with diluted acid treatment is required before alkali pretreatment in order to avoid over degradation of cellulose to sugar. It is because, lignin act as a protective layer for cellulose during solubilization of hemicelluloses, thus increases the cellulose yield for nanocellulose synthesis. However, it needs further separation process in order to dissolve strong poly-ring bonds C-O-C, C-C of the lignin matrix while maintaining the recovery rate of nanocellulose production (Sánchez et al. 2011).

4.2.2 Acid Hydrolysis

Controlled acid hydrolysis is one of the most common methods in dissolving amorphous domains of cellulose fiber and hence longitudinal cutting of the microfibrils. The resulting particles are generally named as a cellulose nanocrystal (CNC). Acid concentration, reaction time, and reaction temperature are some of the

most important parameters for controlling the acid hydrolysis process. If the temperature of acid treatment is low (25–30 °C) then hydrolysis process needs long time too. On the other hand, if the hydrolysis temperature is higher than 60 °C darkening of cellulose particles takes place due to hydration and carbonization. Therefore, the optimal temperature of the acid treatment is in the range of 45–55 °C. Furthermore, the low acid to cellulose ratio of below 5 wt% leads to wide distribution in particle size. Therefore, homogenous acid treatment is performed at acid to cellulose ratio of more than or equal to 20 wt% (Ioelovich 2012). The nanocrystalline cellulose that is formed through the acid treatment is of colloidal dimensions and forms an aqueous suspension when stabilized. The critical concentration of colloidal suspension, which is the lowest concentration where the whiskers self-organizes, depends on particle size, acid treatment, preparation condition, aspect ratio, and ionic strength (Börjesson and Westman 2015). Hydronium ions that are present in acid breaks down the rigid structure of cellulosic fibers by attacking the glycosidic bonds, which release individual crystallites (Dufresne 2013). There are various types of acids used for lignocellulosic fiber hydrolysis which includes Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Hydrobromic acid (HBr), Phosphoric acid (H_3PO_4), and Nitric acid (HNO_3). However, H_2SO_4 is the most common acid used for this purpose. This is because, it produces CNC particles grafted with the sulfate ester group. The presence of these negatively charged groups makes the CNC particles as negative electrostatic repulsion force to promote uniform dispersion in water. Furthermore, H_2SO_4 gave the highest crystallinity index followed by H_3PO_4 . The mixture of acetic and nitric acid solution and hydrochloric acid contributes to the lowest crystallinity index due to higher tendency to promote the breakage of the hydrogen bonds in crystalline region of cellulose. Moreover, both the mixed acetic and nitric acid solution and, hydrochloric acid have better capability to swell cellulose, thus facilitates the breakage of intra- and inter molecular hydrogen bonds in the crystalline region of cellulose (Börjesson and Westman 2015).

The usage of concentrated acid for nanocellulose preparation requires extreme care in handling and processing and therefore it is expensive. However, the recovery and reuse of concentrated acid makes it more economical and environmental friendly (Harmsen et al. 2010). Besides that, many researches has been reported on the usage of diluted acid hydrolysis as it is more cost effective and less hazardous (Li et al. 2010; Moe et al. 2012).

4.2.3 Oxidizing Agent

Delignification process can also be catalyzed by oxidizing agent such as organic peroxide (H_2O_2 , $\text{C}_2\text{H}_4\text{O}_3$), ozone, oxygen, or air (Abdel-Halim and Deyab 2011). Generally, oxidation agents are used to enhance the effects of alkaline pretreatments. Furthermore, this treatment oxidizes the aromatic ring of lignin and a part of hemicellulose polymer to carboxylic acids compounds. Therefore, oxidative delignification is one of the promising pretreatment for extraction of cellulose as it

is more aggressive on lignin and partially on hemicellulose, while it retains cellulose from getting decomposed (Miron and Ben-Ghedalia 1982).

Hydrogen peroxide is an effective method for delignification of lignocellulosic biomass. However, it is strongly pH dependent with an optimum pH of 11.5–11.6 pKa for the dissociation reaction of H_2O_2 . Studies have shown that hydrolysis of Hydrogen peroxide under alkaline condition solubilize the lignin to form lower molecular weight, water soluble oxidation products which is hydroxyl radical (OH). Furthermore, the removal of lignin leads to the exposure of cellulose in the end product. According to some researchers, 50% of lignin and most of the hemicelluloses has been removed during hydrolysis reaction using 2% H_2O_2 at 30 °C (Chaturvedi and Verma 2013; Fang et al. 1999). On the other hand, ozonolysis treatment attracts aromatic rings structure of lignin to solubilize it. Furthermore, it has several advantages over other pretreatments methods such as effective removal of lignin without affecting cellulose and hemicelluloses, it does not produce toxic residue, and can conduct the reaction at an ambient temperature and pressure. However, the process is expensive as the amount of ozone needed for it is high. Many researchers have used ozone as a pretreating agent for lignin removal in wheat straw, bagasse, green hay, peanut, pine, cotton straw, and poplar sawdust. Wet oxidation is oxidative pretreatment that operates with water and Oxygen or air at elevated temperature and pressure. During the wet oxidation, organic polymers oxidized into low molecular weight carboxylic acids, or even to CO_2 and H_2O . Some researchers have used wet oxidation method to recover cellulose and obtain high yield from wheat straw, corn stoves and spruce (Alvira et al. 2010; Palonen et al. 2004).

4.2.4 Organosolv

Organosolv pretreatment is a process to degrade and solubilize lignin fragments from lignocellulosic material by using organic solvent or mixture of solvents in combination with water. Organic solvents such as ethanol, methanol, acetone and ethylene glycol act as a dissolving agent for lignin under heating condition as high as 200 °C. However, the heating temperatures may vary according to the type of biomass and use of catalyst (organic and inorganic acids). During the organosolve pretreatment, OH-ions from alcohol solvent hydrolyses the internal bonds in lignin and glycosidic bonds in hemicellulose (Lee et al. 2014).

Sun and Chen (2008) and Panagiotopoulos et al. (2012) employed organosolve pretreatment, to degrade lignin and hemicellulose from wheat straw and poplar wood pulp respectively with 98% of cellulose retention (Sun and Chen 2008; Panagiotopoulos et al. 2013). Furthermore, Ichwan and Son (2011) utilized various combinations of solvent mixtures in order to extract cellulose from oil palm pulp. The analysis of yield shows that ethanol-water mixture pulping resulted in higher crystallinity of cellulose pulp as compared to ethylene glycol-water and acetic acid-water mixture. Besides that, alcohol based organosolv pretreatments was used in order to improve enzymatic digestibility of Japanese cypress by

Hideno et al. (2013). The major disadvantage of using solvent and catalyst based treatments is that they are expensive. Since, pretreated fibers need an extensive washing with organic solvent to avoid precipitation of dissolved lignin which involves the usage of large amount of solvent. However, the recovery of the solvent through distillation process could reduce the operational cost (Lee et al. 2014).

4.2.5 Ionic Liquids

Ionic liquids are recognized as “green solvents” to replace harmful organic solvents as it is recyclable and environmental friendly. Ionic liquids are organic salts composed of anions and cations. The ionic liquids chemistry makes it highly capable of dissolving wide varieties of biomass types. Ionic liquids are known to possess properties such as high dissolution capacity for lignin, low melting point, good thermal stability, non-volatile, non-toxic, chemically stable, and low cost. Moreover, it possesses widely tunable properties such as polarity, solvent power and hydrophobicity. Ionic liquids that are worth to cite are, 1-alkyl-3-methylimidazolium [mim]⁺; 1-alkyl-2,3-dimethylimidazolium [mmim]⁺; 1-allyl-3-methylimidazolium [Amim]⁺; 1-allyl-2,3-dimethylimidazolium [Ammim]⁺; 1-butyl-3-methylpyridinium [C₄mPy]⁺; and tetrabutylphosphonium [Bu₄P]⁺ with = number of carbons in the alkyl chain (Tadesse and Luque 2011; Zavrel et al. 2009). There are several studies that have been conducted on the efficacy of ionic liquids in considering the fact that isolation of nanocellulose from lignocellulosic biomass is a complicated process. Researchers have suggested that alteration of ionic liquids properties plays a major role in solubilization of lignin and hemicelluloses. For instance, 1-ethyl-3-methylimidazolium acetate [Eminm] Ac has high tendency to degrade lignin as compared to cellulose. Apart from being selective toward lignin, an ionic liquid reduces the crystallinity of cellulose to amorphous nature. Since ionic liquids tend to disrupt the hydrogen bonds that exist in cellulose by forming another hydrogen bond between anions of ionic liquids with cellulose, it reduces the compactness of cellulose and therefore the crystallinity decreases (Yinghuai et al. 2013; Moniruzzaman et al. 2013).

4.3 Biological Treatments

Enzymatic pretreatment of lignocellulosic fiber is an attractive approach for delignification process. Biological pretreatment is known to be cost effective, low energy requirement, environmental friendly, higher yields, higher selectivity and can be conducted at mild condition as compared to chemical treatment. Microorganisms such as brown-, white-, and soft-rot fungi and bacteria are used in biological pretreatment to degrade lignin and hemicelluloses from lignocellulosic material. Besides that an enzyme that has been extracted from microbes can be used for biological treatment. Brown rot and soft rot fungi mainly attacks cellulose while

a white rot attacks both the cellulose and lignin. However, enzymatic hydrolysis has its own disadvantages as compared to other pretreatments such as longer pre-treatment time, and expensive because of the enzymes used (Narayanaswamy et al. 2013).

5 Bionanocomposites

The emerging field in the frontier between material science and nanotechnology has created new generation of hybrid nanostructure materials. Bionanocomposites can be regarded as the new emerging group of nanostructured hybrid materials. Bionanocomposites is defined as a mixture of naturally occurring polymer (biopolymer) and inorganic or organic filler materials that has at least one dimension on the nanometer scale. This new class of composites exhibits significant improvements in mechanical, barrier, and thermal properties, and dimensional stability. Furthermore, it also offers benefits like transparency, low density, better surface properties, good flow properties and recyclability. Figure 8 illustrates the set of composite materials that are classified according to the constituents which determines the structure, properties, functionalities and applications. In order to produce fully renewable and biodegradable nanocomposites, both the polymer matrix and the nano reinforcement have to be derived from renewable resources (Haafiz et al. 2013).

Biopolymer or biodegradable polymer can be disposed by degradation process as a result of the action of microorganism such as bacteria, fungi, or algae with low

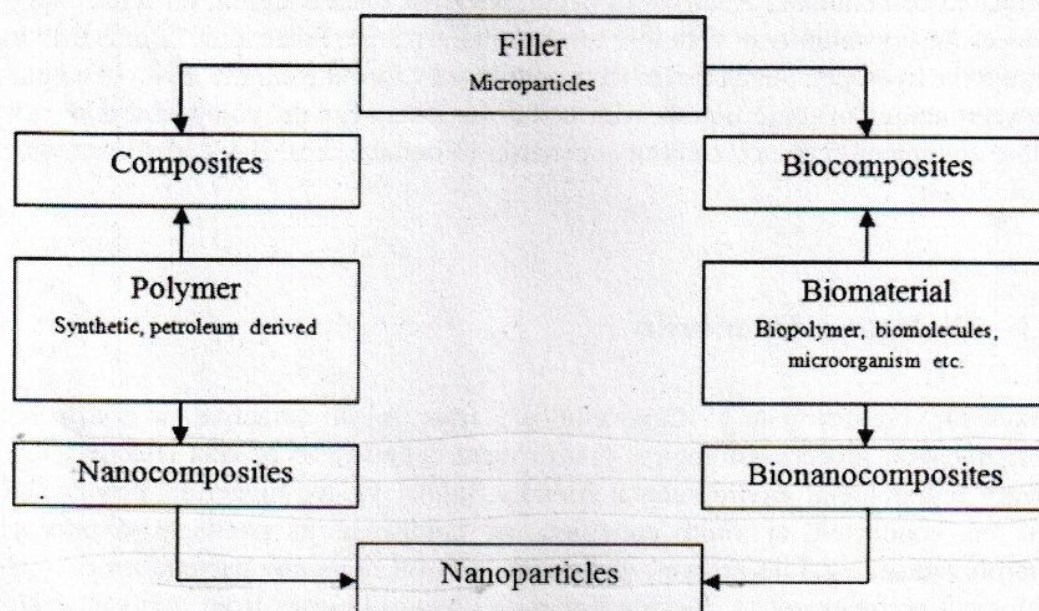


Fig. 8 Main types of composite materials and their constituents (Shchipunov 2012)

environmental impact. The degradation process produces carbon dioxide under aerobic condition or methane under anaerobic condition, in addition to hummus. The properties need to be tuned in order to obtain suitable and competitive materials for vast range of applications. On the other hand, nanocellulose based bionanocomposites combine the advantage of both the guest nanomaterial and the nanocellulose substrate and often exhibit synergetic properties. Nanocellulose is an ideal platform to house a range of guest nanomaterials due to its high specific surface area (Wei et al. 2014).

Various techniques are available for bionanocomposite fabrications. These methods are divided into three types based on the starting materials and processing conditions (Mittal 2015):

- (a) Solution casting method—the nanofillers dispersed in the polymer solution for better dispersion. Subsequently the solvents removed by fast evaporation.
- (b) Melt extrusion technique—blend of nanofiller and polymer matrix prepared in the molten state preferably in single/twin screw extruder.
- (c) In situ polymerization—nanofillers first dispersed in monomers followed by polymerization using solution method in the presence of small amount of catalyst.

5.1 Biopolymers

To comply with the term of green composite, many studies have been conducted to produce 100% eco sustainable biocomposites. These biocomposites are made up of biodegradable polymers and filler materials. Generally, biodegradable polymers can be classified according to their origin, such as polymers that are synthesized from agro based monomers (e.g. poly lactic-acid), agropolymers (e.g. starch and lignin), microbial derived (e.g. polyhydroxyalkanoates) and conventional monomers (e.g. synthetic polyesters). The classification of biopolymers based on their production routes are shown in Fig. 9. The physical, chemical and mechanical properties of biopolymers tabulated in Table 3.

Elaboration of multiphase materials such as blends and composites are most common methods applied in the polymer industry to get tough material. In general, biodegradable polymers are classified according to their origins. The three major categories of biopolymers are (Mittal 2015):

- (a) Synthetic polymers, particularly aliphatic polyesters, such as poly (lactic acid) (PLA), poly(butylene succinate) (PBS), poly(ϵ -caprolactone) (PCL), and poly (*p*-dioxanone) (PPDO).
- (b) Polyesters produced by microorganisms, which are various types of poly(hydroxyalkanoate)s, including poly(3-hydroxybutyrate) (P3HB) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).

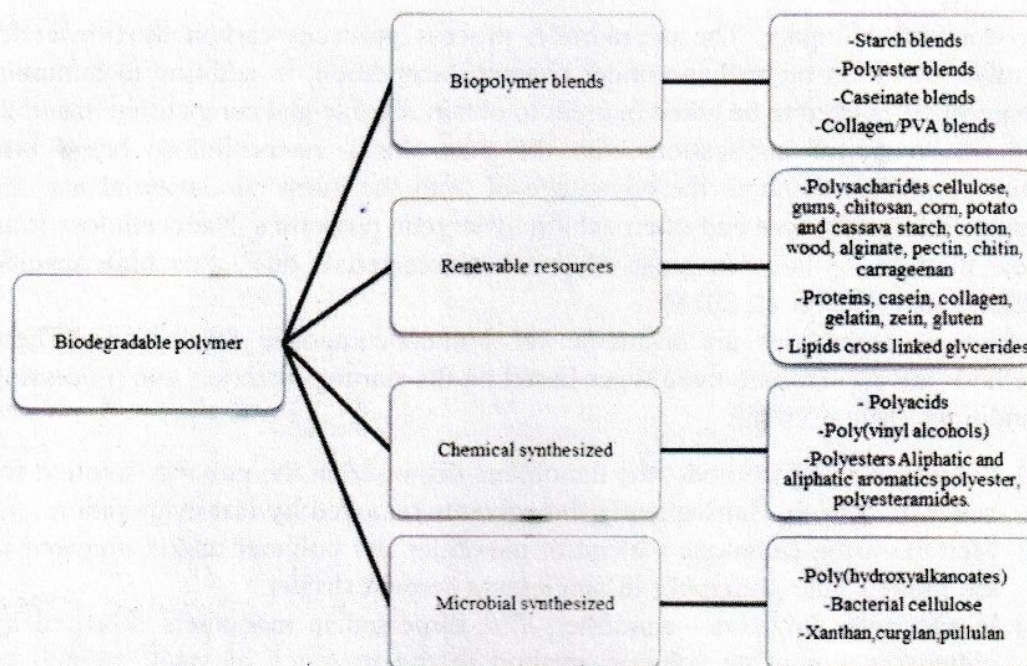


Fig. 9 Classifications of biopolymers and their nomenclature (Satyanarayana et al. 2009)

Table 3 Properties of biodegradable polymers

	PLA Dow– Cargill (nature works)	PHBV Monsanto (Biopol D400G) HV = 7 mol%	PCL Solway (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (eatar, bio 14,766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (°C)	152	153	65	112	114	110–115
Glass transition (°C)	58	5	–61	–29	–45	–30
Crystallinity (%)	0–1	51	67	33	41	20–35
Modulus (MPa) (NFT 51-035)	2050	900	190	262	249	52
Elongation at break (%) (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break (MPa) (NFT 51-035)	–	–	14	17	19	9
Biodegradation (%)	100	100	100	100	90	100
Water permeability WVTR at 25 °C (g/m ² /day)	172	21	177	680	330	550
Surface tension (g) in mN/m	50	–	51	559	56	53

(continued)

Table 3 (continued)

	PLA Dow– Cargill (nature works)	PHBV Monsanto (Biopol D400G) HV = 7 mol%	PCL Solway (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (easter, bio 14,766)
gd (Dispersive component)	37	–	41	37	43	43
gp (Polar component)	13	–	11	22	14	11

*Poly lactic acid (PLA); Poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV); Polycaprolactone (PCL); Polyesteramide (PEA); Aliphatic copolyester (PBSA); and Aromatic copolyester (PBAT) at break results (Zhao et al. 2013)

- (c) Polymers originating from natural sources, including starch, cellulose, chitosan, chitin, lignin, and proteins.

Nanoparticles with at least one dimension in the nanometer range (1–100 nm) are generally used for nanocomposite fabrication in order to improve their mechanical properties. These nanosized fillers are classified according to their aspect ratio and geometry (Siqueira et al. 2010; Avérous and Pollet 2012; Han 2005):

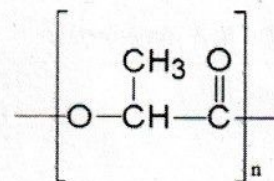
- Isodimensional nanoparticles/spherical—silica, metal and metal oxide nanoparticles
- Nanoparticles with two dimensions in nanometer range/acicular—carbon nanotubes and cellulose nanowhiskers.
- Nanoparticles with one dimension in nanometer range/layered—layered silicate clays or layered crystals

In particular, poly (lactic acid) (PLA) and poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) biopolymers have high significant potential to be used in packaging industry due to their biodegradability, sustainability and biocompatibility. Furthermore, they have comparable mechanical and thermal properties to those of some conventional polymers (Abdelwahab et al. 2012).

5.1.1 Poly(Lactic–Acid) (PLA)

Poly(lactic–acid) (PLA) is a thermoplastic aliphatic polyester, which is highly versatile, biodegradable and biocompatible polymer. Figure 10 shows the chemical structure of PLA. PLA is derived from renewable and biodegradable plant resources such as starch and sugar. Lactic acid is a monomeric building block of PLA which exists in two optical isomers, L- and D-lactic acid due to their chiral nature. The L-isomer rotates clockwise on the plane of polarized light while the D-isomer rotates counterclockwise. The main fraction of PLA derived from renewable resources is made up of L-isomers, which is a biological metabolite Lasprilla et al. 2012). On the

Fig. 10 Chemical structure of PLA



other hand, D-lactic acid isomers can be produced by microorganisms or by racemization. Lactic acid is mainly found in fermented milk products and also can be commercially manufactured by bacterial fermentation process using various source of carbohydrates. PLA can be synthesized by two main synthetic methods which includes, ring opening polymerization, and direct polycondensation (including solution and melt polycondensation) of lactic acid monomers (Ahmed and Varshney 2011; Martin and Averous 2001).

Great interest is given for the application of PLA in packaging industry due to their good optical, physical, mechanical and barrier properties as compared to synthetic polymers. The permeability coefficient of CO₂, O₂, N₂, and H₂O for poly lactic acid (PLA) polymer is lower as compared to polystyrene (PS). Furthermore it has comparable barrier properties as polyethylene terephthalate (PET) against organic permeates (e.g. ethyl acetate and limonene). Oriented PLA has better mechanical performance than oriented PS, but comparable to PET. PLA possesses higher tensile and flexural moduli as compared to PS, polypropylene (PP) and high density polyethylene (HDPE) (Lim et al. 2008). PLA is a promising thermoplastic polymer with unique characteristic to replace conventional polymers like PET, PS and PC for packaging, electronic and automotive applications. The application of PLA and their blends has been tabulated in Table 4. However, neat PLA is a brittle polymer with fracture strain is about 5%, which leads to poor impact and tear resistance. PLA exhibits poor heat stability with low level of heat deflection temperature (HDT) (Zhang et al. 2011, 2012). Furthermore, it is relatively hydrophobic and chemically inert with no reactive side chain group. These drawbacks of PLA have been a major bottleneck for its large scale commercial applications (Rasal et al. 2010).

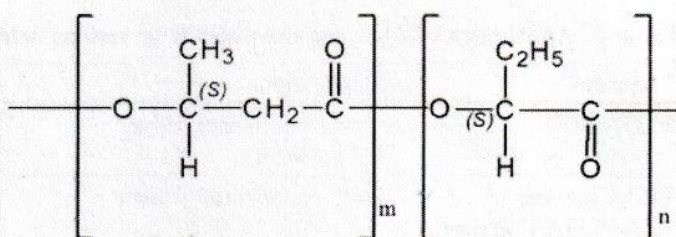
5.1.2 Polyhydroxyalkanoates (PHA)

Bacterial polyhydroxyalkanoates is another family of biopolymer that is produced as intracellular energy and carbon storage materials by various microorganisms. Poly-3-hydroxybutyrate (PHB) is the most common member of PHA family which belongs to the short chain length PHA (scl-PHA) with its monomers made up of 4–5 carbon atoms. Medium chain length of PHA (mcl-PHA) is made up of 6–12 carbon atoms, such as poly (hydroxyoctanoate-co-hydroxydecanoate) or P (HO-co-HD). Copolyesters such as 3-hydroxybutyrate (HB) and 3-Hydroxyhexanoate (HHx) which are the scl and mcl monomers respectively possesses dramatic improvement in their mechanical properties as compared to PHB (Smith 2005).

Table 4 Application of PLA and their blends in various fields (Babu et al. 2013)

Polymer	Applications	References
PLGA/PGA	Ovine pulmonary valve replacement	Williams et al. (1999); Sodian et al. (2000); Cheng et al. (2009)
PLA/Chitosan PLA/PLGA/Chitosan PLA	Drug carrier/drug release	Jeevita and Kanchana (2013); Jayanth and Vinod (2012); Nagarwal et al. (2010); Chandy et al. (2000); Valatin et al. (2003)
PLGA and copolymers	Degradable sutures	Rajev (2000)
PLA/HA composites	Porous scaffolds for cellulae applications	Jung-Ju et al. (2012)
PLA-CaP and PLGA-CaP	Bone fixation devices, plates, pins, screws, and wires, orthopedic applications	Huan et al. (2012)
PDLLA	Coating on metal implants	Schmidmaier et al. (2001)
PLA/PLGA	Use of cell based gene therapy for cardiovascular diseases, muscle tissues, bone and cartilage regeneration, and other treatments of cardiovascular and neurological conditions	Coutu et al. (2009); Kellomakiet al. (2000); Papenburg et al. (2009)
PLA and PLA blends	Packaging films, commodity containers, electrical appliances, mobile phone housings, floor mats, and automotive spare parts	Rafael et al. (2010)
PLA	Textile applications	Gupta et al. (2007); Avinc and Akbar (2009)

Poly (3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) biopolymer is a copolymer made up of hydroxybutyrate (HB) and hydroxyvalerate (HV) monomer units. Poly (3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) (Fig. 11) is one of the PHA family members with attractive characteristics such as excellent biodegradability, biocompatibility, and some properties similar to those of polypropylene (Zhang et al. 2012). It is a brittle polymer with elongation at break less than 15%, and had modulus and fracture stress value of 1.2 GPa and 25 MPa respectively (Bugnicourt et al. 2014). Furthermore, PHBV possesses high melting temperature (T_m), up to 170 °C for the homopolymer (Gunaratne and Shanks 2005). PHBV demonstrates excellent barrier properties, thus it can be used in packaging industry to replace aluminum as the inner lining of packaging cardboard (Pilla 2011). The thermal and mechanical properties of PHBV can be altered by varying the percentage of hydroxyvalerate (HV) content. The glass transition temperature, impact and tensile strength, melting point and crystallinity decreases as the HV content increases (Ghanbarzadeh and Almasi 2013). However, its brittleness, low impact strength and

Fig. 11 Chemical structure of PHBV**Table 5** Application of PHA and their blends in various fields (Babu et al. 2013)

Polymer	Applications	References
P(3HB), P (3HB-co-3HHX) and blends	Scaffolds, nerve regeneration, soft tissue, artificial esophagus, drug delivery, skin regeneration, food additive.	Yang et al. (2002); Chen and Qiong (2005); Bayram and Denbas (2008); Tang et al. (2008); Clarinval and Helux (2005)
mcl-PHA/scl-PHA	Cardiac tissue engineering, drug delivery, cosmetics, drug molecules	Sodian et al. (2000); Wang et al. (2003); de Roo et al. (2002); Zhao et al. (2003); Ruth et al. (2007)
P(4HB) and P (3HO)	Heart valve scaffold, food additive	Clarinval and Halleux (2005); Valappil et al. (2006)
P93HB-co-4HB), P(3HB-co-3HV)	Drug delivery, Scaffolds, artificial heart valves, patches to repair gastrointestinal tracts, sutures	Turesin et al. (2001); Williams et al. (1999); Chen et al. (2008); Freier et al. (2002); Kunze et al. (2006); Volova et al. (2003)
PHB, Mirel P103	Commodity applications, shampoo and cosmetic bottles, cups and food containers	Philip et al. 2007; Amass et al. 1998; Walle et al. (2001)

high production cost limits the broad range application of PHBV (Ha and Cho 2002) (Table 5).

5.1.3 Polymer Blend

Blending of PLA/PHBV is a practical and economical way to develop new materials with unique properties such as mechanical, thermal, and dynamic mechanical properties. It has been reported by Ma et al. that the blending of PLA/PHBV and an increase in the PHBV content reduces the storage modulus of PLA in the glassy state (Mofokeng and Luyt 2015). The PLA/PHBV blend with 25/75 composition respectively has phase separated particles acting as sites for heterogeneous cell nucleation resulting in high cell density and small cell size. Besides that, another study reported that 15 wt% of PHBV in PLA/PHBV blend is an ideal composition to fully take advantage of the immiscible particle heterogeneous cell nucleation phenomenon due to the maximized interfacial area to volume ratio (Guan and Naguib 2014). According to Zhao and co-workers study the PLA/PHBV mixture

ratio of 70/30 wt% was found to be more ductile than the PLA/PHB mixture ratio of 85/25. Besides that, the standard deviation for the elongation to break of PLA/PHBV (70/30) specimens was higher than the other specimens tested for the strain.

6 Application of Bionanocomposites

Cellulose nanoparticles present the potential for diverse applications, and their use in nanocomposites has been extensively studied. By embedding biofibers with renewable resource-based biopolymers such as cellulosic plastics; starch plastics; polyhydroxyalkanoates; polylactides, the so-called green biocomposites could soon be the future. Applications of nanocellulose are mainly considered to be in paper and packaging products, although construction, automotive, furniture, electronics, pharmacy, and cosmetics are also being considered (Fig. 12). For companies

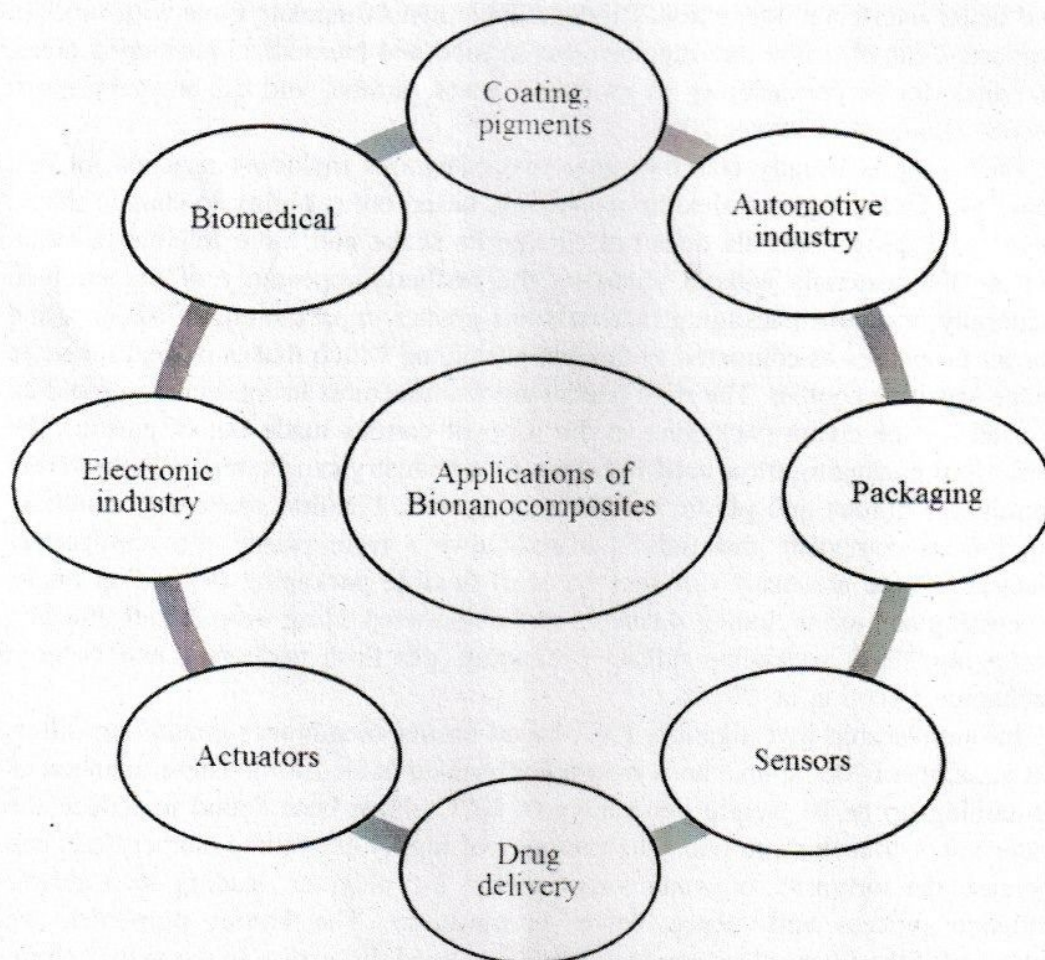


Fig. 12 Applications of bionanocomposites in various fields

producing electroacoustic devices, nanocellulose is used as a membrane for high quality sound. Additionally, nanocellulose is applied in membrane for combustible cells (hydrogen); additives for high quality electronic paper (e-paper); ultrafiltrating membranes (water purification); membranes used to retrieve mineral and oils, and nowadays, nanocellulose has been greatly discussed and researched a huge variety of applications. The high strength and stiffness as well as the small dimensions of nanocellulose may well impart useful properties to composite materials reinforced with these fibers, which could subsequently be used in wide range of applications (Kalia et al. 2011a, b, c).

6.1 *Bionanocomposites for Packaging Applications*

One future area of application wherein NCC-containing polymer nanocomposites can make an impact is in the field of biodegradable packaging materials. The incorporation of NCC can significantly improve the mechanical performance, thermal stability, and barrier and optical properties due to its improved crystallinity and better interfacial interaction. Biodegradable nanocomposite films with superior properties can also find their applications in food and biomedical packaging areas, in which lower permeability to moisture, gases, aroma, and oil are very much needed (Lange and Wyser 2003).

Packaging is usually classified into two categories including rigid packaging, semirigid packaging, and flexible packaging, based on its ability to change shape. Rigid packaging materials does not change its shape and more reliable in transporting the materials without changing the aesthetic appearance of the product. Generally, the rigid packaging materials has greater impact strength, stiffness and barrier properties as compared to flexible packaging which makes it ideal for more shape sensitive content. The rigid packaging manufactures using injection molding is used for ice cream packaging in the form of cartons made out of plastic. The semi-rigid packaging trays used in frozen food industry can be manufactures from aluminum, fibrous and plastic composite materials. Flexible packaging manufactured from composite materials is almost always from plastic film composites material. There are many different types of flexible packaging depending on its processing and use including shrink wrap, bubble wrap, cling wrap, breathable film packaging, retort packaging, blister packaging, gas flush packaging and vacuum packaging (Alavi et al. 2014).

In one research investigation, PVA-based barrier membranes containing different amounts of NCCs have been reported (Paralikar et al. 2008). These membranes containing up to 10 weight percentage of NCCs have been found to reduce the water vapor transmission rate. The presence of highly crystalline nanocrystals can increase the tortuosity of water vapor within the polymer, leading to a slower diffusion process and, hence, lower permeability. The barrier properties are enhanced if the filler is less permeable and has good dispersion in the matrix along with a high aspect ratio (George and Sabapathi 2015). This improved barrier

properties in bionanocomposites is explained on the basis of increased path length due to the presence of cellulose nanofillers which attributes to the increase in tortuosity induced by the presence of the nanofibers (Reddy et al. 2013). NCC also often pressed into thin transparent films referred to as nanopapers and has been identified as potential packaging material (Salas et al. 2014).

However, many scientific and technological challenges have to be addressed in several areas, such as optimizing suitable processing technologies for reducing the production cost, establishing the compatibility between products and packaging materials, and meeting several packaging legislations before achieving a truly biodegradable packaging material that satisfies both industry requirements and consumer expectations (George and Sabapathi 2015).

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