

# Starch-Based Nanocomposites: Types and Industrial Applications



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**Abstract** The extraordinary physicochemical and functional features offered by the starch material segregated from various sources of plants, such as rice, corn and wheat, are put into use for a large extent of applications. The physicochemical features of starch namely lipids content, a ratio of amylose to amylopectin, the size distribution of granule play a significant role to grasp the concept related to the mechanism on the functionality of starch in various systems. The starch-modified chemistry along with a large number of reactive sites carries the biologically active compounds as biocompatible carriers and are metabolized in the human body quickly and comfortably. The current chapter focusses on the different composites made up of starch along with polymers like polylactic acid, polycaprolactone, polyhydroxy alkaloid where the synthesis, chemistry and application part are greatly discussed. Further, the physicochemical stability of the nanocomposites relating the specific structure is compared in addition to their deployment in various industrial applications.

## 1 Introduction

In the present era, the everyday human life is entirely governed by the automated systems supported by the advanced materials with novel functionalities where a variety of synthesis approaches are adopted so as to form the human-made materials for the

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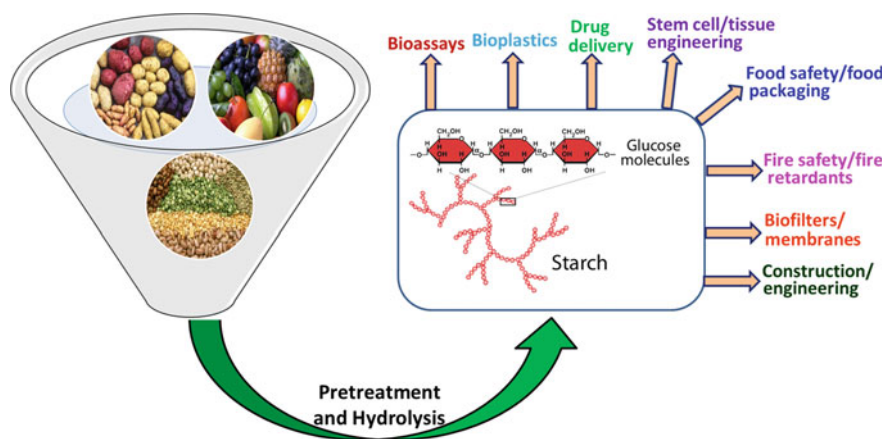
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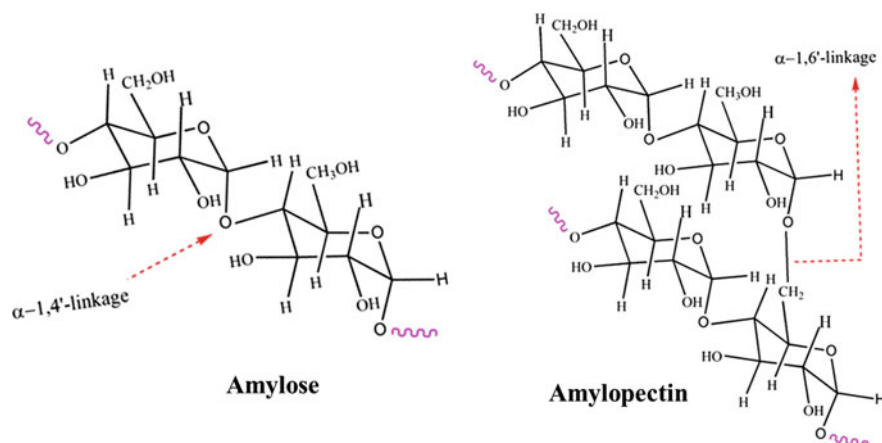
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betterment of life quality (Arfin and Athar 2018). In a similar way, the biomaterials from the renewable resources are the user-friendly substances and also considered to be the ideal ones for many different applications in several scientific fields like biotechnology, biomedicine, biofuels and bioenergy (Arfin et al. 2014; Arfin 2015). The naturally obtained materials are regarded as the sustainable ones with not much lessening to the efficiency and can be produced in high quantities with minimal reaction processes that can be employed in a variety of applications (Mohammad et al. 2015). Within the class of nature derived biomaterials, the starch-derived materials have attracted many advanced applications by taking advantage of the physiochemical and functional characteristics supported by the reactive oxygen containing groups. The products derived from starch-based materials have generated high level of interest in the design and formulation of green-based technology considering the raising threat posed by fossil-based product. Molecularly, the unique signature of starch as a heterogeneous material makes it the most essential and useful biocompatible material compared to all other polymers of natural origin (Arfin and Tarannum 2017). It occurs naturally and is the second extensive polysaccharide after cellulose. The various sources of starch are shown in Fig. 1.

Starch is available in the granules form and is composed by joining different glucose molecules through the glycosidic bonds (Mograrakar and Arfin 2017). The features of starch granules such as chemical composition, size and structure are dependent on the original state from where it is derived. Starch contains two macromolecules namely the amylopectin and the amylose. In the architecture of starch, the amylopectin and the amylose constitute the basic signature, structurally showing the amylose appearing as a linear structure of 1,4 linked glucose units, while the highly branched structure of short 1,4 chains linked by 1,6 bonds represents amylopectin (Nasserri and Mohammadi 2014). The structures of the respective macromolecules are represented in Fig. 2.



**Fig. 1** Different sources of starch, its extraction and applications into different sectors



**Fig. 2** Structures of amylose and amylopectin

As mentioned earlier, the structural architecture of the starch granules is directly influenced by the orientation in space of both the amylose and amylopectin units. The amylose molecules are oriented parallel between each unit and between adjacent chains held by hydrogen bonding. The orientation is also implicated in defining the chemistry of starch, influencing its water absorption capacity, degradation rate, gelatinization, etc (Mograkar and Arfin 2017; Nasserri and Mohammadi 2014).

As interesting as these properties entail starch in its natural form suffers from a number of limitations. Poor mechanical properties and high permeation are some of the few limitations of natural starch materials. However, process improvement following the doping of starch granules with filler materials or blending of the starch granules with other polymer-based materials to form starch-based nanocomposites has significantly ameliorated the aforementioned limitations. The chemistry was made possible owing to the interfacial molecular bridges between the starch matrix and the incorporated nanofiller (Ghanbarzadeh et al. 2011; Zuraida et al. 2012; Olsson et al. 2013; Gutiérrez et al. 2014; Famá et al. 2012).

### 1.1 Biodegradable Packaging Materials

Lorcks in 1997 proposed the properties and applications of plastics (Lörcks 1998). The biodegradable plastics stand out as a rare invention and substitute for the pollution creating plastics. Typically owed to its high biodegradability and less half-life, they can be disposed or degraded following environmental-friendly manner. Plastics are the polymers made up of monomers through chemical reactions. Condensation polymerization and polyaddition (chain and step reaction) are the necessary processes for plastic making.

- In poly-addition, the chemical reactions occur which forms polymers from monomers. For this process, energy and catalyst are mostly required. In some cases where the availability of insufficient catalyst/energy, the addition of monomers results in the loss of hydrogen movement that further restricts the separation of by-products.
- In case of poly-addition step reactions, the sufficient movement of hydrogen bonds results in the prevention of double bonded activities.
- Also, the poly-condensation reaction in which the actual plastic formation takes place and is a step reaction.

According to the properties and structure, they are classified into different classes. They may be thermoplastics, thermosets, polymer blends, elastomers and semi-conductor thermoplastics. This quest for biodegradable plastics leads to a number of engineering efforts that involved blending of either synthetic polymer or biopolymers with starch-based materials. Among many different applications, the important application of starch-based materials being the environmental safe biodegradable plastics production. In addition for being relatively cheap, spread widely in nature, the starch-based materials also possessed good oxygen barrier and biodegradability (Fabunmi et al. 2007). Starch has been used as a reinforcement/fillers polymer matrix, in the production of thermoplastic starch prepared following the plasticization of starch in the presence of plasticizers (e.g. glycerol), and it is also used in the production of synthetic polymer films like polylactic acid (PLA), polycaprolactone (PCL) and polyhydroxyalkanoate (PHA) (Avérous and Pollet 2012).

## 2 Biodegradable Starch-Based Nanocomposites

As mentioned earlier, the limitations associated with nature-based starch materials are readily overcome by converting the starch matrix into nanocomposites while retaining their active green chemistry. The search for biodegradable materials further reinforces the drive towards contextual application of starch-based materials reinforced with either natural or synthetic polymers specifically to meet the industrial demand for food packaging, surgery, pharmaceutical, biomedical applications (Bouyer et al. 2012). Of greater interest, cellulose, clays and number of synthetic materials are recently used as fillers in the development of biodegradable starch-based compounds (Thakur et al. 2012, 2014; Hassani and Nafchi 2014; Thakur and Thakur 2014). Preceding sections will cover development into the chemistry of starch-based nanocomposites.

### 2.1 Starch–Clay Nanocomposites

The formation of starch nanocomposites using various fillers has significantly improved the quality of starch-based materials. In comparison to the conventional

clays, the chart of nano-fillers to improve the efficiency of starch was found to rank the top (Mondragón et al. 2008). Avella et al. (2005) discovered that the starch–clay nanocomposite could be used for the food packaging purpose. The use of the nanoparticle in the different starch-based clays was applied to produce the starch-based film for packaging. Use of such materials for preparing films increases the properties of the packaging films and also tensile strength and modulus. The central aspect of this product is that it is the novel biodegradable material used especially for food packaging purpose.

Clay is a polymer composite of silicate consisting of a central positive charge silicon ion sandwiched by a negatively charged oxygen ion linking another silicon ion in a progressive manner. This arrangement can assume a different combination consisting of sheets arranged either in tetrahedral  $[\text{SiO}_4]_4$  or octahedral  $[\text{AlO}_3(\text{OH})_3]_6$  shape. Among these structural silicates, the clay composites consisting of two-dimensional layered silicates (montmorillonite) are widely used owing to its higher percentage of water molecules in the layer available for cation exchange processes (Huang et al. 2006; Ikeo et al. 2006). The cation exchange processes and the ease of intercalation make this clay types flexible and compatible with other polymer like starch. Park et al. (2002) introduced the preparation of hybrid composite of starch–clay. The process used for the preparation was melt intercalation. Natural and the starch–clays which are organically modified were only used for hybrid preparation. The storage modulus of this hybrid was higher in comparison with other composites.

The widely reported processing techniques used in the intercalation starch/clay are in situ intercalative polymerization, intercalation of polymer and melt intercalation (Schlemmer et al. 2010; Barzegar et al. 2014). In addition to the ion exchange processes, the polymerization processes that required the application of heat or passing of irradiation or use of a catalyst to facilitate the swollen up of the clay in the presence of a liquid monomer is called in situ intercalative polymerization. Conversely, in melt intercalation processes, the solvent molecules are reportedly desorbed from the silicate layer during the polymerization process allowing easy flow of the incoming polymer. This method is considered a greener approach and highly compatible with environmental best practices. In the intercalation of polymer, the polymer is dissolved in a suitable solvent in order to exfoliate (uniformly dispersed silicate layers in a continuous polymeric matrix) layered clays into a single platelet. This method is influenced by the choice of polymer/solvent pairs and is considered environmentally unfriendly owed to the use of unfriendly solvents (Cui et al. 2015).

In order to overcome the poor water resistance, poor tensile strength and high brittleness of starch materials, a number of efforts in addition to the use of nanoclay as discussed earlier are reported (Zabihzadeh 2010; Jamshidian et al. 2010; Takegawa et al. 2010). Early study shows that the reinforcement of potato starch with 5% clay significant increases %E and tensile strength by >20 and 25%, respectively, and further shows a reduction in water vapour transmission rate by 35% (Park et al. 2003). Avella et al. (2005) and Pandey and Singh (2005) in a separate study reported increase in mechanical properties potato starch–clay

nanocomposite films and cornstarch–clay films, respectively. The cornstarch/clay nanocomposites following a study conducted by Huang et al (2006) reported about 450 and 20% increase in the tensile strength and strain, respectively, with the addition of 5% clay. In another study, reinforcement of Cará root starch/hectorite films with 30% clay level increases the tensile strength of the nanocomposites 70% and elongation at break (%*E*) decreased by 50% (Wilhelm et al. 2003). This observed improvement in both thermal stability and water absorbance capacity of the starch–clay composites makes it an attractive candidate for packaging materials (Chiou et al. 2007). Table 1 is a list of few process development made in engineering starch–clay nanocomposites.

Noble efforts were also made by using biopolymer extracted from cellulose, gelatin, chitosan and plant-based extracts to prepare starch-based nanocomposites. This quest for biodegradable polymers leads to the discovery that microorganism

**Table 1** Engineering starch–clay nanocomposites

Preparation/methods	Result	References
Green starch/clay nanocomposites were prepared by solution-induced intercalation method using starch, jute, glutaraldehyde, nanoclay and glycerol	In the study, the thermal stability and mechanical strength of the prepared composite were significantly improved with the addition of glutaraldehyde and nanoclay	Iman and Maji (2012)
Bio-nanocomposite films were prepared from potato starch by casting method using halloysite nanoclay as the reinforcing materials	The incorporation of halloysite nanoclay into the polymer matrix decreased the permeability of the material to gaseous molecules and improved the mechanical properties. Tensile strength increased from 7.33 to 9.82 MPa and elongation at break decreased from 68.0 to 44.0% with the filler addition	Hassani and Nafchi (2014)
The biodegradable trays of cassava starch and organically modified montmorillonite were prepared using a baking process	In the study, the stress at break of the samples was observed to be strongly affected on incorporation of the nanoclay	Matsuda et al. (2013)
In this study, biodegradable starch–clay nanocomposites were prepared by incorporating a dilute clay dispersion to a starch solution that was followed by co-precipitation in ethanol	Well-dispersed starch–clay nanocomposites were obtained	Chung et al. (2010)
In this study, a film blowing technique was used to prepare the starch–clay films using hydroxypropyl distarch phosphate and five different kinds of clays as materials	High tensile strength and improved barrier properties were observed in the prepared starch–clay film nanocomposites. Furthermore, a drop in glass transition temperature ( $T_g$ ) and better heat endurance were equally observed	Gao et al. (2012)

can synthesize biopolyesters from both natural and synthetic monomers. The biopolyesters synthesized through this process include but not limited to thermoplastic starch (TPS), polylactic acid (PLA), polycaprolactone (PCL), and polyhydroxyalkanoate (PHA) (Avérous and Pollet 2012).

## 2.2 Starch–Polylactic Acid (PLA) Composites

Muller et al. (2017) proposed in their recent work about the use of PLA-starch composite for making biodegradable food packaging plastics. The replacement of pollution creating plastics was done by using the plastic made from PLA and starch. Interestingly, PLA is nature-based materials derived from sugar stock, rice and corn by fermentation and chemical conversion of the sources to dextrose and then to lactic acid using poly-condensation processes (Rydz et al. 2015).

The suitable liquids for PLA in which it is soluble are acetonitrile, chloroform, benzene, ethyl acetate, acetone etc and is not soluble in ethanol, methanol and water. The biochemical aspects of this material being the biocompatibility, biodegradability, environmental friendly, renewable, and readily hydrolyzes to natural, nontoxic products on disposal. Most of food packaging industries require PLA for making biodegradable plastics. It has hydrophobic nature. Thus, before using PLA the drying of the pellets should be done at about 60–100 °C. This process modifies it physically (Lim et al. 2008). It has application in the tissue engineering field for wound healing (Armentano et al. 2013). It is resistant to elasticity, which enables it to be rigid plastic and brittle.

The properties of PLA and starch match each other. On the combination of both these materials, the product form will be more efficient and without creating any issue whatever it may be economical or pollution. As described PLA is hydrophobic whereas starch is hydrophilic, this makes the processing of the material difficult. The product obtained from PLA and starch is used in the food packaging industries. The films and packaging materials formed by the combination of PLA and starch are found to have enhanced properties as compared to the ones which are formed from the individual materials. By varying the ratios of starch and PLA, the blend can be made. It serves as the best alternative for reducing pollution caused due to plastics. The obtained plastic will have the properties of antioxidant and antimicrobial. The plastic or film has excellent flexibility and mechanical properties. However, the PLA material when applied alone, suffers from the required indices of efficient biodegradability which is a must so as to use in the industrial application due to its brittleness. Hence, the combination of PLA with other thermoplastic materials like polyethylene glycol (PEG) or dispersed nanoclay into the matrix found to significantly improved its biodegradability and associated marketability (Rydz et al. 2015).

Sheth et al. (1997) proved about the use of PLA and PEG for making the plastic whereby varying the concentrations of both materials, and the composite can be prepared. Depending on the concentrations, the mixture becomes partial miscible and miscible. If PLA is more than 50% of a mixture, then PEG crystallinity

increases, and if PEG is more than 30%, then the weight loss occurs and it will be mainly due to PEG as it gets dissolved. Also, the tensile strength decreases if PEG is high in concentration. Ayana et al. (2014) prepared the composite from thermoplastic starch (TPS), PLA and dispersed nanoclay. Potato starch was in situ gelatinized. The thermo-mechanical properties and tensile strength of the composite were increased by the use of PLA and clay. The synthesis of novel material was done in the environmental fever, so that it can be used as a packaging material also.

In another study, solvent casting methods using *N,N*-dimethylacetamide was used to prepare uniformly dispersed cellulose nanofibrils using bleached wood pulp/PLA with PEG to improve the interfacial bonding/adhesion between the matrix and the fibre. In the study, the tensile strength increases by 28.2% and similar increases in the percentage elongation by 25% following the addition of PEG to the blend (Qu et al. 2010). One-step extrusion process was used to prepare binary and ternary TPS/PLA-PCL nanocomposites. The result from the study shows that at 36% plasticizer (glycerol), a transition temperature for the TPS/PLA-PCL nanocomposites was recorded at  $-57^{\circ}\text{C}$ . It was further observed that varying up the TPS concentration in the blend has a direct impact towards increasing the strain at break (Sarazin et al. 2008).

### 2.3 Cellulose Fibre

Cellulose in addition to its natural responsibility as shielding material in maintaining the rigidity of plant also presents remarkable properties for various applications. Cellulose-based fibres derived from nature are widely used to reinforce polymer composites due to its compatibility with many polymer matrixes. Essentially, the chemistry between the cellulose nanofibre and the polymer matrix enables excellent dispersion of the reinforcement species within the matrix. The molecular structure and interfacial similarity of the cellulose material further favours effective chemistry among many different matrix species (Rydz et al. 2015). This organic polymer is widely spread in nature and consisting of *D*-anhydroglucopyranose units linked together with  $\beta$ -(1-4) glycosidic bonds (Thakur et al. 2010, 2012). Despite being nature derived, is a poor material to dissolve in aqueous media. However, further modification following simple esterification or etherification of the hydroxyl groups was reported to confer a solubility characteristic in water (Mischnick and Momcilovic 2010).

Wan et al. (2009) used a biodegradable reinforcement in the form of bacterial cellulose nanofibres. They discussed the entire phenomenon occurring during the formation of nanocomposite. The method used was solution impregnation. The comparison was made between the nanocomposite of cellulose and starch and the unreinforced starch. Sorption diffusion process was used for the kinetic analysis, and then the different parameters were determined. The study of tensile strength and microbial attacks was performed. The use of bacterial cellulose in making of nanocomposites increases the strength and ability to resist the attack of microbes.



This can have broad application in the protection of the environment. In another study, Khan et al. (2010) improved the properties of cellulose by synthesizing a water-soluble methylcellulose (MC)-based biodegradable nanocomposite films. In the study, simple mechanical processes involving stirring and sonication in the presence of plasticizer (glycerol), vegetable oil and Tween 80 were followed under room temperature. The outcome of the study revealed that the addition of CN enhanced the mechanical and barrier properties of MC-based films. Similarly, a decrease in water vapour permeability was observed indicating the moisture barrier properties of MC-based films. Zhou et al. (2009) follow a low energy pathway to synthesis cellulose-based nanocomposite from bacterial cellulose nanofibrils coated with hydroxyethyl cellulose (HEC). The experiment was conducted by press drying of the water suspension of the cellulose nanofibres. The characterization revealed a material with encouraging tensile strength and optical transparency.

The potential of hydroxypropyl methylcellulose (HPMC)/cellulose whiskers nanocomposite films as suitable material for packaging applications was investigated and reported. The addition of cellulose nanowhiskers was observed to have a direct relationship with increase in tensile strength, Young's modulus and the water barrier properties of the composite films (Sáinz et al. 2010, 2011). Furthermore, carboxymethyl cellulose (CMC) is another water-soluble derivative of cellulose often combines with carbon nanotubes (CNTs) as fillers to reinforce polymer nanocomposites. The CNTs in the presence of plasticizer (glycerine) were reported to have improved the strength and stiffness of the CMC polymer nanocomposite (Choi and Simonsen 2006).

## 2.4 Starch-Polyhydroxy Alkaloid (PHA) Composites

Molyneux (1993) gave their review on the isolation, characterization and application of PHA. It is the class of phytochemicals. It is a newly discovered class, and therefore, the analysis and detection are ongoing. Polyhydroxy is the compounds which have the active inhibitory property of glycosidase. The activities depend on the stereochemistry and the hydroxyl groups. For the processing of glycoproteins in organisms, PHA is needed so that the biological mechanisms get regulated. It is proved that glycoproteins are indirectly the enhancer of the immune response (Molyneux 1993). The source of PHA is ground plant material. It can be extracted by using ethanol or methanol or water by just varying the proportion of solvent. Since few compounds isolated at each time, chemical determination is limited. Mass spectroscopy, UV-Vis spectroscopy, nuclear magnetic resonance spectroscopy and X-ray crystallography are the characterization technique for PHA.

In the class of starch-based biodegradable polymers, PHA has the highest degradation rate of about 100% and thus stands out as a remarkable eco-friendly biosynthetic polymer of the century. The microorganisms synthesize this material intracellularly by means of a carbon-based chemical approach and can be stored as an energy reservoir (granules) (Jendrossek and Handrick 2002; Shan et al. 2011).

The storage granules in the bacteria following anaerobic respiration converts the stored granule into a hydroxyl acid homopolymer, derivatives of PHA called or poly(3-hydroxybutyrate) (PHB). The PHB and its copolymers consisting of few units of hydroxyvalerate (HV), and significant amount of hydroxybutyrate (HB) units (PHBV) is the product of the anaerobic degradation of the granules (El-Hadi et al. 2002; Lenz and Marchessault 2005).

Study revealed that the amount of HV units in PHBV significantly improved the mechanical and physical properties compared to its homopolymer (PHB) (Choi and Park 2004). Similarly, the HV units provide a platform for the properties to be modified to suits specific objectives (Hu et al. 2004; Shang et al. 2011; Ferreira et al. 2002). Thus, this unique disposition allowed modification such as the addition of plasticizer, formation of blends with other biopolymers such as PCL, poly(lactides), starch and cellulose (El-Hadi et al. 2002; Ferreira et al. 2002).

Reis et al. (2008) studied the characteristics of the composite film formed by the combination of PHB-HV (polyhydroxybutyrate-hydroxyvalerate) maize starch prepared by means of a casting method. The use of maize makes the blend more economical as compared to the original PHB-HV blend. As the concentration of starch varies, the properties vary including the parameters like Young's modulus and tensile strength. In a separate study, similar solution casting methods were used to PHB/HV and organo-modified mica composites. The preparation was achieved by dispersing the modified clay in chloroform to produce a material with intercalated structures (Garcia and Lagaron 2010; D'Amico et al. 2012). Other study also reported the preparation of organo-modified clay/PHB, PHB/HV and PHB/PCL (Bordes et al. 2008; Botana et al. 2010; Bruzard and Bourmaud 2007).

## 2.5 Starch–Polycaprolactone (PCL) Composites

Polycaprolactone (PCL) is a highly versatile nature-based polyester with low melting point and viscosity derived essentially from oil-producing plants. There are supporting materials widely recruited to reinforce the mechanical properties of polymer like collagen or gelatin to form PCL/collagen or PCL/gelatin nanofibrous, a material suitable for tissue engineering purposes (Sohier et al. 2014; Choi et al. 2008). The beauty of PCL-based material is their simple method of preparation, using simple conventional melt blending technologies to synthesize same. The PCL material can be blended with other biopolymers for improving the fundamental properties to suit the specific objectives that range from food packaging to biomedical applications (Ludueña et al. 2011).

Lo et al. (2010) studied the morphology and properties of the composites made from PCL-starch and PCL-pine composite in the presence of silane as coupling agent. The formed composites were observed to be non-toxic and highly biodegradable, thus showing good prospect in the design of food packaging materials. The mechanical properties of layered silicate/starch PCL blend nanocomposites were investigated by Pérez et al. (2007). In the study, melt intercalation method followed

by compression moulding was used to prepare the nanocomposites. The characterization using various instruments shows a strong intercalated silicate or starch PCL blend nanocomposites. In another study, the efficacy of modified PCL-based nanocomposites was investigated using melt intercalation on a twin-screw extruder. The study shows that the modification processes improve the stability and chemical compatibility of the PCL with the clay, leading to the formation of a dispersed material with strong mechanical stability (Ludueña et al. 2011). In the melt intercalation processes, it was observed that shear forces are responsible for further breaking down of the PCL/clay to nanoform. The same author further reported that the exfoliation of the PCL/layered is facilitated by the chemical compatibility between the PCL matrix and clay layers (Homminga et al. 2005). Processing technique such as the melt intercalation methods is reported by a number of researchers to produce largely an exfoliated and well-intercalated material (Pantoustier et al. 2002; Gain et al. 2005). Similar intercalation/exfoliation structure was reported by solvent casting (Wu et al. 2000), by swelling effect under ultrasonic agitation (Ludueña et al. 2011). Other process improvement in the synthesis of PCL-based nanocomposites was also reported (Chang et al. 2009; DeKesel et al. 1997; Pérez et al. 2008).

Fibre-based PCL nanocomposites were also synthesized and reported. Azimi et al. (2014) synthesize different forms of fibre-based PCL nanocomposites, and according to their content, they were used in the different areas of biomedical field. The choice of using PCL in the preparation being aliphatic polyester was highly biodegradable. Furthermore, the fibre was selected because it is environmentally friendly and biocompatible. The study reported that the formed PCL fibres are a good candidate for tissue engineering and drug delivery applications.

## ***2.6 Starch-Polyethylene Terephthalate (PET) Composites***

Siracusa and co-workers have given the review on the use of PET as a biodegradable polymer (Siracusa et al. 2008). They have presented the complete review on the use of plastics. It is not possible to replace the plastic, but to a certain extent it is possible. The consumption of plastics is more than about 200 million, and hence, it is the critical issue. The substitute for the petrochemical-based plastics is an important point of the discussion.

The United States-based chemist E.I. du Pont developed the polymer PET when he was trying to make textile fibres. It is a thermoplastic polymer, and the main components or monomers required for the synthesis of PET are ethylene glycol and terephthalic acid. The esterification process converts two monomers mainly into alcohol and an organic acid with ester and water. But PET is a polymer; hence, it can also be called as “polyester”, where it is resistant to moisture and so it can be used for the packaging-related applications in food, textile and agriculture industry. It can also be used for preparing fibre for clothes as it does not have colour, clearly transparent and semi-crystalline in nature. In order to increase the strength and other associated properties, it can be used by combining with the other materials like

CNTS and glass. It is straightforward to use PET for everyday applications as compared to many other synthetic fibres where the PET is considered to be cheap, non-breakable unlike glass, and the most interesting thing with this material being its recycling property. It is a lightweight material but very strong. Since it is lightweighted, less amount of compound is required and transport also becomes easy with less consumption of fuel. It can be easily used in food packaging industries because it has the property which does not affect food and water when gets in contact with it (Xie et al. 2015).

## 2.7 Starch–Gelatin Nanocomposites

Gelatin is a soluble protein-based biopolymer consisting of  $\alpha$ -amino acids linked by peptide bonds (Guillen et al. 2011). They form the basic component in the design of drug capsules and in food industry as additive used in preserving the composition of food active ingredient. The biochemical properties of gelatin such as its high hydrophilicity were exploited in the design of nanofibrous systems with the ability to affect cell–tissue regeneration or engineering (Lee et al. 2012; Jafari et al. 2011; Zhuang et al. 2010).

The property of gelatin was made better by blending it with compatible materials such as PCL, polyaniline (PAN)–CNTs to form engineered nanofibrous scaffolds. Li et al. (2013a) introduced the use of gelatine starch octenyl succinic anhydride (OSA) to enhance the stability and properties of orange oil in water emulsion. The cornstarch was modified by using OSA before blending it with gelatine. This OSA starch absorbs the interface of oil and water and acts as a stabilizer. Another cited example is blending of PCL with gelatin to form gelatin/PCL-blended nanofibres. The blending was reported significantly to enhance the proliferation of tissue cells (Gupta et al. 2009). Other study by Li et al. shows a significant enhancement in the myocardial proliferation following the blending of gelatin with PAN (Li et al. 2006). Also, some similar end results in terms of tissue-cell proliferation and engineering were obtained following the blending of gelatin with chitosan to obtain chitosan/gelatin hybrid nanofibers (Jafari et al. 2011; Dhandayuthapani et al. 2011; Qian et al. 2011).

In addition to biomedical applications as discussed above, George and Siddaramaiah (2012) in a separate study observed that blending of gelatin to CNTs results in the formation of percolated networks of CNTs within the gelatin matrix. The obtained gelatin/CNT matrix was observed to have significantly improved mechanical properties of the films, thus providing adequate properties for the design of packaging materials.

## 2.8 Chitosan-Based Films

Structurally, the unique signature of chitosan lies on the solution sensitivity of the positive charged  $\text{NH}_2$  groups in its molecular chains (Poverenov et al. 2014).

This structural characteristic increases the advantages of chitosan as a matrix material and nanoenforcement in composite formation (Rydz et al. 2015; Yu et al. 2014). These cationic properties increase the adsorption capacity of the polymer, its biocompatibility and biodegradability (Yu et al. 2014; Shawky et al. 2012; Nitayaphat and Jintakosol 2014; Popuri et al. 2014).

Chitosan is a product of de-acetylated chitin made up of about greater than 5000 units of glucosamine and readily found in nature in whole body of fungi, sea animals like crabs, insects and shrimp shells. The chitosan from the crustacean is extracted by the de-acetylation of the parent chitin while enzymatic extraction is used to extract same from fungi (Arfin and Mohammad 2016). The de-acylated chitosan consists of  $\beta$ -1,4 linkage of D-glucosamine and N-acetyl-D-glucosamine (Mohammad et al. 2015) and possesses excellent properties with the wide range of application, as excipient in drug formulation and reinforcement materials in the design of non-toxic biodegradable packaging.

As highlighted above, chitosan-based films related to its physiochemistry play a key role in the formulation of biodegradable packaging materials with properties that could increase the shelf life of food (Wang et al. 2018). Aider (2010) in an effort to develop a biodegradable material for packaging purposes introduced the application of chitosan bio-based films as a substitute for fossil-based packaging material. This effort attracted considerable interest owing to the rising cases of food spoilage relating to food storage and security. The most common method of preserving food using chitosan-based materials is in vacuum packaging where pure chitosan film is used in the vacuum preparation (Saiz et al. 2013). Studies further show that chitosan within nanorange compared to microparticle has a better chemistry in forming packaging materials. Similarly, reinforcement or blending chitosan with other polymer fillers or plasticizers was reported to have improved the mechanical properties and chain mobility of the composites (Gol et al. 2013; Garza et al. 2015; Vimaladevi et al. 2015).

An excellent chitosan/gelatin composite based on emulsion of oil in water was prepared and reported by Rui et al. (2017). The reaction between the polymers was favoured by hydrogen bonding (Rui et al. 2017) leading to the formation of biocompatible film and micro-carriers used for animal cell culture on a large scale (Taravel and Domard 1993). Other effort reported also involved in the union of chitin and starch. In a study, Chang et al. (2010a, b) generated the starch from glycerol plasticized potato using casting/evaporation method to make the starch-chitin nanoparticles. The formed nanoparticles when tested are found to improve the tensile strength, water vapour bearing, and increased glass transition temperature, i.e. all the characteristic features are mostly required to check the suitability for a material to be good or not towards packaging-related applications. Both acetylated chitin and de-acetylated chitin were blended to produce chitin/chitosan nanofibres as material for tissue engineering and other biomedical applications (Jayakumar et al. 2010).

An interesting effort was presented by Jantanasakulwong et al. (2016), introduced the blending of thermoplastic starch (TPS) with chitosan and rubber. In the study, the thermoplastic plastic was prepared by using plasticizer (glycerol), cassava starch and chitosan. Due to the  $\text{NH}_2$  group, the reaction of chitosan with any

other group becomes easy and fast. In a study, the blend leads to increase mechanical strength and tensile strength forming a low weight composite. Lopez et al. (2014) in a separate experiment used chitin, chitosan and thermoplastic cornstarch to formulate a biodegradable film by thermo-compression method. The modifications were done in the film by the addition of chitosan. Increase in crystallinity was obtained. The obtained film was of very efficient quality, i.e. with a smooth surface and homogeneous nature. There were no cracks or pores in the film. The combination of chitin and chitosan increases the elastic modulus and strength.

The chemistry exerted between chitosan and cellulose leads to the formation of a composite film that exhibited improved water vapour barrier property and reduced bacterial adhesion on the packaging material (Xiao et al. 2013; Bansal et al. 2016; Li et al. 2013a, b; Sundaram et al. 2016). A cited example shows and increases in shelf life of cheese and wheat bread preserved using a packaging material made from chitosan/carboxymethyl cellulose film (Sundaram et al. 2016). Similar chemistry was also exploited to develop different chitosan/cellulose films (Gol et al. 2013; Noshirvani et al. 2017; Chen et al. 2016; Liu et al. 2013). Table 2 is a summary of selected events on efforts made in using chitosan-based composite in food industries and other related applications.

**Table 2** Different types of starch–chitosan-based composites

Preparation/methods	Result	References
The study reported on the reinforcing effect of chitin whiskers (ChW) in PVA matrix	The result shows that the tensile strength and the mechanical properties of the polymer increase to 1880 MPa and 535 toughness (68 J/g) at 5 wt% ChW loading. Furthermore, tensile modulus was observed to reach its peak value of 50 GPa at 30 wt% ChW loading	Uddin et al. (2012)
The study covered the preparation of bio-based nanocomposite films using cellulose whiskers as the reinforcing phase and chitosan as the matrix	The results showed that the whisker content enhances the mechanical properties of the composites. The tensile strength of the composite films in the dry state increased from 85 to 120 MPa with increasing filler content from 0 to 20 wt%	Li et al. (2009)
In this study, chitosan was used to reinforced nanocrystalline cellulose and reported the mechanical and barrier properties nanocomposite film	The nanocomposites showed a 25% increase in tensile strength and a 87% increase in tensile modulus at this CNC content reported an optimum content of 5 wt% of CNC in chitosan matrix	Khan et al. (2012)
In this study, a packaging material was fabricated using glycerol plasticized starch matrix films reinforced with chitosan nanoparticles by physical crosslinking	The nanocomposites show a good degree of dispersion, an increase in tensile strength and storage modulus	Chang et al. (2010a, b)

(continued)

**Table 2** (continued)

Preparation/methods	Result	References
The researchers prepared bio-based plastics for packaging using eugenol-loaded chitosan nanoparticles by extrusion method. The base materials used in the study consist of mixture of cassava, rice and waxy rice flours	The incorporation of the base materials with eugenol introduced some changes in the physicochemical properties of the composites. The elongation at break behaved as the matrix. The incorporation of these nanoparticles caused a reduction of WVP, indicating that this property was enhanced by the incorporation of the nanofillers	Woranucha and Yoksana (2013)
The study reported on porous CNTs/chitosan composite with lamellar structure prepared by ice templating	The incorporation of chitosan leads to a well-defined microchannel porous structure that is biodegradable and biocompatible with promising adsorption properties	Wu and Yan (2013)
The study reported on novel chitosan/PVA thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes	The formed nanocomposites effectively remove Cu(II) from water. Thus, the composite systems could offer exclusive properties as a composite in the removal of heavy metal ions and treatment of wastewater	Salehi et al. (2012)
The study talked about the synthesis of multi-walled CNTs/chitosan polymer composite modified glassy carbon electrode for sensitive simultaneous determination of levodopa and morphine	The CNTs-filled chitosan demonstrated a modulated release of dexamethasone	Babaei and Babazadeh (2011)
The researchers prepared polymeric composites containing chitosan/ CNTs for improved blood biocompatibility and bone tissue engineering	The study shows that the manipulation of CNTs/chitosan composites leads to the formation of scaffold with promising properties for cell–tissue engineering applications	Sahithi et al. (2010)
In this study, chitosan/alginate was developed via layer-by-layer electrostatic deposition edible coating on fresh-cut melon model	The obtained film showed excellent gas-exchange performance and water vapour permeability property. The chitosan/alginate film displayed great potential for food packaging	Da Silva et al. (2013)
The researchers incorporated photoactive of chlorophyll, essential oil and carvacrol in chitosan/ cyclodextrin films to prepare a bioactive food packaging material	The incorporation of the cyclodextrin increased the tensile strength of chitosan film and also enhanced the antimicrobial activities of the film	Sun et al. (2014), Higuera et al. (2014)

(continued)

**Table 2** (continued)

Preparation/methods	Result	References
Caseinate, with excellent thermoplastic and film-forming properties, was combined with chitosan to prepare chitosan/caseinate film, through ionic interaction to form a coating material for paper packaging	Improvement like water vapour permeability	Khwaldia et al. (2014)
In the study, controlled release of nisin from HPMC, sodium caseinate, PLA and chitosan was investigated for active packaging applications	The material was observed to be favourably used in extending the shelf life of packaged foods	Iman and Maji (2012)
Combination of nisin and $\epsilon$ -polylysine with chitosan coating inhibits the white blush of fresh-cut carrots	When the chitosan/ $\epsilon$ -polylysine/ nisin film was applied to fresh-cut carrots, the carrots showed the inhibited respiration rate, the declined ascorbic acid, the decreased growth of microorganism and the suppressed synthesis of white blush and lignin	Song et al. (2017)
The extent of Maillard reaction on antioxidant properties was investigated using chitosan–glucose conjugates	The chitosan/glucose films, with enhanced antioxidant property, were observed to effectively delayed the declines of total soluble solids, decreased decay and weight loss, suppressed respiration rate and ensured better berry texture and higher sensory scores of food	Kosaraju et al. (2010)
The antimicrobial activity of lysozyme–chitosan was investigating and its effects in prolonging the shelf life of chicken eggs during storage	Lysozyme–chitosan films were reported to enhance the freshness of the egg during storage, improve shell strength and maintain the internal quality	Yuceer and Caner (2014)
A film-based gelatin reinforce with chitosan was reported to demonstrate improved properties for the fabrication of fish packaging	Films based on chitosan/gelatin were reported to show improved properties, like mechanical properties and barrier properties, against water vapour and light	Hosseini et al. (2016), Kowalczyk et al. (2015)
The mechanical/antimicrobial properties of PVA reinforced chitosan and chitosan/PVA/clay nanocomposites were investigated for its application in food packaging	The PVA was observed to contribute to the plasticization and improves the water and oxygen barrier properties of the obtained films, affirming its suitability as food packaging material	Wang et al. (2018), Giannakas et al. (2016)
The study reported the synthesis and characterization of nanoamphiphilic chitosan dispersed PLA–bionanocomposite films for packaging application	The formed films demonstrated improved thermal, mechanical and gas barrier properties	Pal and Katiyar (2016)

(continued)



**Table 2** (continued)

Preparation/methods	Result	References
The study reported on the antimicrobial properties of composite films derived from PLA/starch/chitosan blended matrix	The increase in the tensile and thermal properties of the nanocomposite film further verified the promising use of the obtained material in packaging food	Bie et al. (2013)
The application of chitosan-g-salicylic acid towards arresting postharvest losses was investigated.	The formed nanocomposites were reported to alleviate the chilling injury and were able to preserve the quality of cucumber	Zhang et al. (2015)
The study reported on the effect of chitosan/nanosilica coating on the physicochemical characteristics of longan fruit under ambient temperature	The chitosan/nanosilica films were observed to lower the decay of food by preventing the membrane structure from peroxidation, thus preserving the quality and elongating the storage shelf life	Shi et al. (2013)
The study investigated the barrier properties of nanosilicon carbide/chitosan nanocomposites for food packaging application	In the study, the nanosilicon carbide incorporated chitosan nanocomposite films was reported to substantially decrease the oxygen barrier properties and enhances the thermal stability and strengthen the chemical resistance of the film	Pradhan et al. (2015)
The molecular dynamics simulations of hydration effects on solvation, diffusivity and permeability properties were investigated on chitosan/chitin films	The film-forming ability of the chitin blended with chitosan was reported to introduce special properties on the films such as lower oxygen permeability. The chitosan/silver nanoparticle bionanocomposite films on the other hand were also reported to have improved the mechanical and barrier properties of the obtained films	McDonnell et al. (2016)

## 2.9 Starch–Propolis-Based Composites

Propolis is a natural resinous blend extracted from plants buds, honey, wax and vanilla naturally utilized as anti-predator and sealant in maintaining beehives (Hashemi 2016). The material composition of raw propolis consists mainly of 50% resins, 30% waxes, 10% essential oils, 5% pollen and 5% of various organic compounds (Park et al. 2002; Burdock 1998; Pietta et al. 2002; Huang et al. 2014). The antioxidant, antimicrobial and antifungal activities of propolis are recently utilized by food industries as a preservative in food packing material in addition to other uses, especially in pharmaceutical (Wagh 2013).

The assessment of propolis as a suitable material for food packaging was also reported by da Silva et al. (2013). The purpose of the study was to prepare a powdered form of propolis with a good antioxidant property, storage stability and dispensability in both aqueous and alcohol medium. The antimicrobial properties of propolis were used as a bio-additive in coatings to control fruit quality losses. For this purpose, chitosan containing propolis-ethanolic extract was used as the coating material. The results showed a reduced deterioration index and infection diameter of the fungus *Colletotrichum gloeosporioides*, as compared to the control papayas, thus elongating the shelf life of the fruit by two days (Barrera et al. 2015). In a similar development, a patent filed by Mizuno (1989), further confirmed the active role played by propolis as a preservative in food packing material. Tosi et al. (Tosi et al. 2007) used the bactericidal and bacteriostatic properties of propolis by agar diffusion and plate culture methods. By relating the zone of cellular growth inhibition with the propolis extracts concentration, a linear inhibition response was obtained, thus confirming the suitability of propolis as component for food preservation.

Other study showed the effectiveness of blending propolis with biopolymers. Chitosan film containing beeswax was prepared as a coating material to prolong the shelf life of strawberries on storage following layer-by-layer coating method. In the study, the composite was observed to modify the respiration rates, slowed down the metabolism of the fruit and at the same time preserved the physical architecture and taste of strawberries (Velickova et al. 2013). In another study, chitosan film containing propolis extract high in polyphenols was developed. In another study, chitosan film containing propolis extract high in polyphenols, were developed, where the characteristics of the resultant films reported for high tensile strength, elongation at break, and antioxidant activity due to the increased addition of propolis to the chitosan polymer. The blending of chitosan with the propolis further reduces the water vapour/oxygen permeability index, thus improving the potentials of employing the chitosan-based propolis films as active materials for the food packaging (Siripatrawan and Vitchayakitti 2016).

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