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# Recent advances in starch–clay nanocomposites

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**ABSTRACT**
Biological nanocomposites are a valuable addition to the existing nanocomposite materials and eventually can substitute petroleum-based composite materials in numerous applications due to their inherent advantages such as biodegradability, eco-friendliness, low cost, and easy availability to name a few. Recently, polymer–clay nanocomposites have achieved much more attention due to their enhanced properties such as size dispersion and significant enhancement in physicochemical and mechanical properties in comparison to the pure polymer systems. Among various biopolymers, starch is one of the most abundant natural polymers on the earth and is highly valuable due to its chemical and physical properties. Starch polymer has highly increased potential as an alternative to petroleum-based materials. However, starch cannot be used alone and starch–clay nanocomposite has emerged as a new potential green sustainable material. This article focuses on recent progress i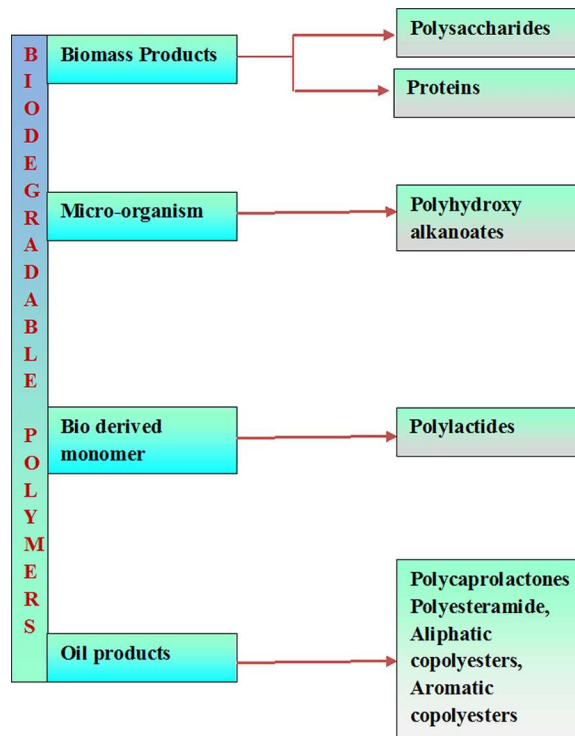n starch-based nanocomposites with particular emphasis on starch–clay nanocomposite preparation, properties, and applications.

## Introduction

Nowadays, most of the petrochemical polymers are highly hazardous to the environment and serious efforts are ongoing to reduce their use.[1–6] The synthesis of such polymers produces hazardous wastes that are not easily degradable, leads to environmental problems including production of high carbon dioxide,[1,7,8] whereas plants consist of many polymers that are easily degradable, renewable, and eco-friendly.[4,9,10] Different kinds of natural derived biopolymers are abundant and relatively inexpensive.[11–13] The research that has been extremely investigated in the recent years is the development of biodegradable materials including nanocomposites (Figure 1) from renewable sources. The natural derived nanocomposites of polymers provide significant improvements in mechanical and physical properties.[14–17] A composite can be defined as a material made up of two or more components.[18] Solid multiphase composites can be prepared through the combination of various materials in different structure, chemical and physical properties.[19] The unusual combination of component properties such as stiffness, permeability, electrical properties, and biodegradability leads to the formation of difficult structure of composite which cannot be separated by individual components. Single-phase composites are called as matrix and others are called as fillers which makes the dispread phase.[20–22] Due to the unique advantages like production, low weight, and ductility, polymeric composites have

**Figure 1.** Classification of biodegradable polymers.

become very familiar than metals and ceramics.[14,23] Polymeric composites can be formed by the combination of natural or synthetic inorganic fillers.[24] Inorganic fillers increase the properties of polymers and simply become very low cost. Polymeric composites used in a wide range of application in industry as well as research field because of their better mechanical, thermal, and fire retardancy-efficient properties.[25,26] The efficiency of polymer composites is further improved strongly by the fillers for mechanical, thermal, and electrical properties.[27] Platelet clays, carbon nanotubes, and nanofibers are commercially available and used as nanofillers for polymer composites due to its considerable attention of unique characteristics at low volume fractions.[28] As a result, low fillers and low density of polymers lead to the formation of nanocomposite in particular system.[29] Nanocomposite technology has a great importance in the preparation of synthetic and natural polymer-based nanocomposites.[30,31] Toyota has earlier reported on the improved properties of nylon-6 through the exfoliated clay.

Along with the properties of polymers, fillers' properties also have an important role in the morphology and properties of the resulting nanocomposite.[15,32] Clays is among one of the main groups of nanofillers being used due to its improved efficiency than that of conventional fillers.[33–35] There has been another development in the biodegradable materials, especially starch which is derived from higher plants that are lower in cost and biodegradable.[36,37] Furthermore, plasticizers with starches can be processed by conventional thermoplastic techniques. But still the mechanical characteristics of starch-based materials are more complex and are highly sensitive to temperature, humidity, and pH to name a few.[38,39] This limitation can be overcome by the addition of low amount of clay on starch and the main challenge in the proceedings of starch clay nanocomposites is to disperse clay into the starch matrix.[40,41] In the following section, we will be discussing different aspects of polymer/clay nanocomposites with particular emphasis on starch-based nanocomposites.[42–46]

## Polymer/clay nanocomposites

Polymer/clay nanocomposites achieved much more attention in the field of nanoresearch due to the interesting properties which cannot be attained by fillers with microsize.[43,47–50] The improved properties of clay makes pristine polymers of utmost importance in modern polymer industry.[51–54] About 30% of silicates contains minerals and the silicate structure is $SiO_4^-$ tetrahedron. Central silicon ion has positive charge surrounded by negatively charged oxygen. The silicon and oxygen bond is almost the same to the total bond energy of oxygen which leads to the bonding of another silicon ion, continuously linking with another to another silicon ion. Due to the different combinations of silicate tetrahedron, it forms a single units (nesosilicates), double units, namely, sorosilicates, chain units, namely, inosilicates, sheets (phyllosilicates), rings (cyclosilicates), and framed structure (tectosilicates). The phyllosilicates or layered or sheet silicates are the most used silicates for nanocomposites. Clays were considered to be an important mineral in the phyllosilicate or layered silicates with more percentage of water molecules in silicate layer. Most of the clays are chemically and structurally unique, but they have different quantities of water content which allows more replacement of cations.[55–57] Further, clay can be alienated into three primary groups: (a) The Kaolinite group, (b) the Smectite group, and (c) the Illite or the Mica–clay group. In polymer nanocomposite systems montmorillonite (MMT), hectorite, and saponite are most frequently used as the reinforcement. Among these, MMT is mostly used because of its well-controlled and chemical properties and more abundant/inexpensive.[58,59] Two properties of MMT play an important role in the preparation of polymer–clay nanocomposites. First of all, the ability of silicate to be dispersed in layers and second is their surface chemistry through ion-exchange reactions.[60] Most of the clays contain $Na^+$ and $K^+$ ions.[61–63] To obtain the biodegradable polymer, it must convert into organophillic one which makes interaction between the hydrophilic polymer such as poly(ethylene oxide)[64] or poly(vinyl alcohol) (PVA)[65] by the ion-exchange reactions. Sodium or potassium ions of MMT are dispersed in water uniformly and extend its swelling property by 30%. When alkyl ammonium/phosphonium salts are incorporated into the water dispersion, ions of the layer will exchange with the intergallery cations which leads to the insertion of alkyl ammonium/phosphonium between the layers.

### Types and methods of preparation of clay nanocomposites

Depending on the interaction between the studied polymer matrix and clay as reinforcement, three different polymer nanocomposites can be prepared: (a) Intercalated structure-based nanocomposites, (b) exfoliated structure-based nanocomposite sand, (c) flocculated structure-based nanocomposites.[66–68] Depending upon the starting materials and processing techniques, preparation of polymer/clay nanocomposites can be accomplished using three different techniques as given in the following.[69–71]

#### (a) In situ intercalative polymerization
In this method, polymerization is initiated by heating or irradiation or catalyst and the clay is swollen by the liquid monomer or a monomer solution under study.[72]

#### (b) Intercalation of polymer
It depends on the solvent system in which the clay particles are swellable as well as the polymer under study is also soluble.

#### (c) Melt intercalation
Due to the absence of organic solvent, this technique is more environmentally friendly and compatible with industry processes. In this method, solvent molecules are desorbed from the silicate layer to allow the incoming polymer chain during the polymerization process.

## Starch-based clay nanocomposites

Starch is a novel polysaccharide and is considered to be one of the most potential materials due to its readily availability, low cost, biodegradability, etc. Mostly, starches are isolated from grains such as wheat, corn, rice, potato, and tapioca to name a few. The main constituents of starch are amylase and amylopectin that are linked together with $\alpha$-d-(1–4) and/or $\alpha$-d-(1–6) linkages.[73] Figure 2 shows the structure of amylose and amylopectin. Amylase has been found to exhibit a linear structure, while amylopectin has a branched structure. Amylopectin forms the major part of the starch, while amylose is just between 15–20%. In general, the raw starch is not suitable for some applications such as paper industry due to the higher intermolecular hydrogen bonds among the chain. Furthermore, the melting temperature of starch is generally higher than its degradation temperature. To overcome these limitations, the structure of starch is modified or some plasticizers are added to decrease glass transition temperature.[74] The plasticizers are a low-molecular weight substance that increases the flexibility of film and processability when incorporated in the polymer matrix. This molecule also improves the mobility of polymer chain with significant decrease in hydrogen bonding between the polymer chains. Water is also frequently used as a solvent to destroy the granules of starch. At room temperature, although starch remains insoluble in aqueous medium, however at high temperature an irreversible swelling process, namely, gelatinization occurs which leads to degradation of amylase and amylopectin. However, the water content and plasticizer properties are strongly dependent on storage condition and this drawback can be solved using nonvolatile plasticizers such as glycerol. When the samples are stored at below glass transition temperature, the sample will undergo physical aging, poor water resistance, and variation in mechanical properties.[75] Although starch offers numerous advantages than synthetic materials, however it is still far of expectations due to its poor mechanical properties.[76] To overcome the disadvantage associated with the pristine starch, the addition of nanofillers in selected amount is a viable approach. The addition of definite amount of nanofillers can significantly improve the physico-chemical properties of starch as well the size can also influence the biological activities of starch-based materials.[77] In the following section, we have summarized the processing techniques used in the preparation of starch-based nanocomposites with special attention to starch/clay nanocomposites.

## *Processing and applications of starch-based nanocomposites*

Starch-based nanocomposites are generally processed using two different techniques, namely, solution casting and extrusion. The solution casting method is the most common and easiest method
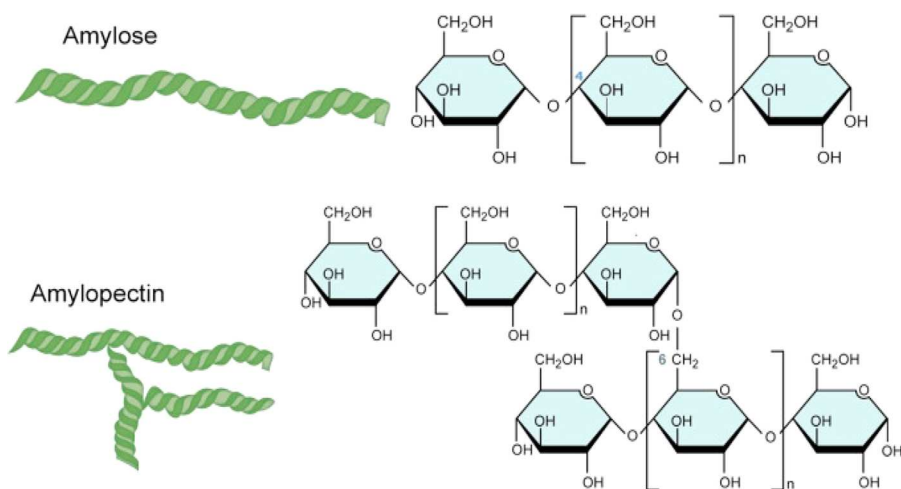


**Figure 2.** Structure of amylose and amylopectin units in starch. Reprinted with permission from Zia et al.[73] Copy right 2015 Elsevier.

to prepare starch-based nanocomposites in aqueous medium. This method ensures the proper mixing of nanofillers with starch. In this method, both the mixing absorption and time are significant to ensure homogeneous dispersion of the fillers in the starch matrix. In general, starch powder, clay, and the plasticizer are dispersed in water and the mixture is then boiled for some requisite interval time. In the past, the solution casting method was used to prepare starch-based nanocomposites reinforced with tunicin whiskers using glycerol as a plasticizer. Different ratios of starch and glycerol were used to obtain composite films with a uniform dispersion and the complete mixture was subsequently gelatinized by an autoclave and degassed to prepare films.[78] The same method was also utilized by Mathew and Dufresne,[79] for the preparation of starch/tunicin whisker nanocomposites with sorbitol as plasticizers instead of glycerol. Additional treatments, namely, sonication, ultrasonication, and homogenization are also generally used for the dispersion of starch and fillers. The major limitation of the solution casting method is that the polymer needs to be soluble in the same solvent used for dispersion and swelling of the filler. The alternative technique used for casting method is tape casting process and is useful in the manufacturing of ceramics, plastics, papers, and paints. In a typical method of tape casting, suspension is kept in a reservoir with adjustable blade which is connected to micrometric screws. The suspension will cast like thin layer on tape due to the continuous mobility of blade. Extrusion is another important technique that is frequently used for the preparation of starch nanocomposites. Using the hydrophilic fillers, most of the difficulties encountered using starch nanocomposite processing can be overcome easily. The hydrophilic fillers are well suited with starch/glycerol and are able to group together in the matrix. Many researchers have proposed the synthesis of a dry starch/glycerol/nanofiller mixture in the absence of water.[80] On the other hand, some other researchers have indicated some issues and proposed the incorporation of hydrophilic fillers into water suspension by propelling the solution into an extrusion stage in which there is a molten polymer.[81] As an example, Hietala et al.[82] have reported their study on the preparation of cellulose nanofiber gels using starch, plasticizer, lubricant, and cellulose. All the components were mixed with more water content and then extruded the obtained dispersion in different concentrations of cellulose nanofiber. The water content in this work was removed by an extruder barrel equipped with two atmospheric vents and vacuum ventilation was proposed. As stated earlier, starch does not solubilize in water at room temperature and holds its granular structure and an increase in temperature significantly affects its structure. Although starch offers advantages in biomedical applications, its applications in packing and automotive industry application are limited and alone cannot satisfy most of the requirements as such. Hence, it is essential to incorporate some eco-friendly fillers to improve the existing properties of starch. Among different fillers, clay is most abundant, environment-friendly, and low-cost filler that is frequently used in many applications as fillers. Kaolin was also used in reinforcement to prepare the nanocomposites using thermoplastic starch (TPS).[83] The starch was obtained from corn that was plasticized using glycerin in a specific amount. The prepared nanocomposites were characterized for their mechanical properties analysis along with thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), and water sorption study. From scanning electron microscopy (SEM) study, it was established that strong bonding exsits between kaolin and the starch matrix. In addition to the enhanced mechanical properties, the use of clays resulted in an increase in the water resistance characteristics of TPS. Biodegradable TPS/clay hybrids were also prepared using melt intercalation technique.-[84] In this study, four types of MMT (three types of organically modified MMT with different ammonium cations and one pristine) were used. It was found that the unmodified MMT-based nanocomposites exhibit better properties than organically modified MMT. This behavior was attributed to the fact that the hydrophilicity of starch matches more with clay hydrophilicity which can be easily dispersed in the starch matrix in comparison to the organically modified MMT. As a result of the higher hydrophilicity of sodium ion-MMT compared to the organically modified MMT, 58% increment in the space basal was observed compared to less than 10% increase in the composites with sodium ion-MMT and organically modified MMT, respectively. Green nanocomposites from starch were also prepared using solvent casting method.[85] In this study, the dispersion of clay into starch was demonstrated in detail with dissimilar addition sequences of plasticizer. Wide-angle X-ray diffractometry study was

performed to study the extent of dispersion of the fillers in the synthesized nanocomposites. Different characterization techniques, namely, Fourier-transform infrared spectroscopy (FTIR), water absorption studies, mechanical properties, and thermal stability were performed to completely analyze the material properties. It was concluded from this study that incorporation of starch/plasticizer (glycerol)/clay exhibit an imperative impact on the overall properties of the resulting nanocomposites. Starch plasticization without clay leads to the formation of huge composition with low mobility and decreased diffusion of starch into clay matrix. Thermoplastic starch–clay nanocomposites were prepared using starch that was procured from potato.[86] The potato starch was reinforced with four different types of clays, namely, natural sodium montmorillonite, natural hectorite, a hectorite modified with 2-methyl, 2-hydrogenated tallow quaternary ammonium chloride, and kaolinite. These nanocomposites were prepared by melt processing technique. Different characterization techniques were used to study the intercalation behavior and it was observed in the TEM images that the untreated hectorite nanocomposites were partially exfoliated. On the other hand, the treated hectorite nanocomposites exhibited the exfoliated and intercalated structures. Rheology study of the starch–clay nanocomposites was also performed.[87] In this work, the MMT clay was used to reinforce different types of starch (i.e., starch from wheat, potato, corn, and waxy corn) and it was found that the nanocomposites with hydrophilic MMT exhibit good mechanical properties due to its greater intercalation in the gelatinized starch. It was observed that the nanocomposites procured from wheat/corn starches demonstrated almost the same elastic modulus values on gelatinization. On the other hand, for both the potato and waxy corn starch samples with an increase in temperatures, the elastic modulus was found to decrease. Melt intercalation was used to prepare the starch/silicate polycaprolactone blend nanocomposites that was followed by compression molding.[88] Different mechanical properties of the nanocomposites were investigated in detail. The interaction between dissimilar components of the starch nanocomposites was thoroughly investigated using SEM, dynamic mechanical analysis, X-ray diffraction (XRD), and tensile strength testing. It was demonstrated using XRD analysis that the polymeric chains and clays were strongly intercalated. Similarly, the effect of glycerol content on the structure and properties of starch/clay nanocomposites was also studied in detail.[89] In this work, melt extrusion processing was used to prepare the nanocomposites using corn starch and MMT nanoclay. The prepared nanocomposites were thoroughly characterized for their structure and property analysis by transmission electron microscopy (TEM), XRD, TGA, and barrier/mechanical properties measurement. The plasticized nanocomposite films of starch–clay were found to exhibit higher glass transition temperature (54.74°C), lower water vapor permeability (0.58 g mm/kPa h m$^2$), and advanced tensile strength of 26.64 MPa. As a conventional plasticizer, the influence of glycerol content was first investigated. With the glycerol concentration up to 5 wt%, the nanocomposites can be prepared by twin-screw extruder. However, the degree of clay exfoliation was found to decrease with further increase in glycerol content (20%) as the higher glycerol content increases the spacing between starch and glycerol that subsequently decreases the attractive force of starch and clay. From this study, it was demonstrated that the performance of nanocomposite films is significantly affected by the strong polar–polar interactions among plasticizer, clay surface, and starch. Clay was incorporated into starch to form new nanocomposites with enhanced properties.[90] In this study, the polymer matrix was starch that was procured from potato starch, while the mixtures of glycerol and a urea/ethanolamine were used as plasticizers. Polymer nanocomposites were prepared using the neat starch as well as 20 wt% plasticized starch with 6 wt% organically modified montmorillonite nanoclay as well as the pristine MMT. The MMT nanoclay was modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium. Although there was no notable enhancement in the thermal stability of the matrices after the addition of nanoclay, there was an enhancement in the dispersion of MMT-Na$^+$ as compared to MMT-OH. These results were supported by the TEM and XRD results. Water sorption and oxygen permeability studied were also performed and it was found that the oxygen permeability was higher for the plasticized films compared to the pristine films. The effect of processing conditions as well as of citric acid on the performance of starch-based nanocomposites was also studied.[91] In this work, a facile two-step melt

extrusion for intercalation of starch in clay galleries was reported. The nanocomposites were prepared using the glycerol-modified MMT/pristine MMT (PMMT) and TPS. In a typical method, the first step involved the blending of PMMT/glycerol mixture with emulsifying machine (high speed). Subsequently, the modified MMT was also mixed with TPS at different compositions for intercalation and excellent tensile strength analysis. From the TEM and XRD study, it was demonstrated that glycerol facilitates the d-spacing as well as leads to the destruction of MMT structure. Figure 3 shows the TEM micrographs of the studied nanocomposites. Furthermore, the citric acid was found to enhance the TPS plasticization as well as increase in the mechanical properties of the nanocomposites. Biodegradable starch–clay nanocomposites were prepared by incorporating a dilute clay dispersion to a starch solution that was followed by coprecipitation in ethanol.[92] This process leads to nanocomposites with well-dispersed starch–clay. Figure 4(a) depicts the synthesis of starch–clay nanocomposites. One of the significant advantages of this technique was that the intercalation of the plasticizer (glycerol) in clay was minimized in this work that is generally required during hot pressing. It was also found that the starch crystalline structure was not significantly influenced [Figure 4(b)]. However, the enhanced dispersion between MMT/polymer matrix increases the interaction between starch molecules/clays and resulted in higher mechanical properties as a result of the stress transfer to the reinforcement phase. The chitosan-modified clay and corn starch nanocomposites prepared at pH of 4.9 showed improvement in modulus and strength. The increase in modulus/strength of the nanocomposites was 65 and 30%, respectively, for the nanocomposite containing 5 wt% clay in comparison to the pristine starch material. Subsequent increase in clay content resulted in weakening the properties as a result of poorer dispersion of clay and low polymer crystallinity.
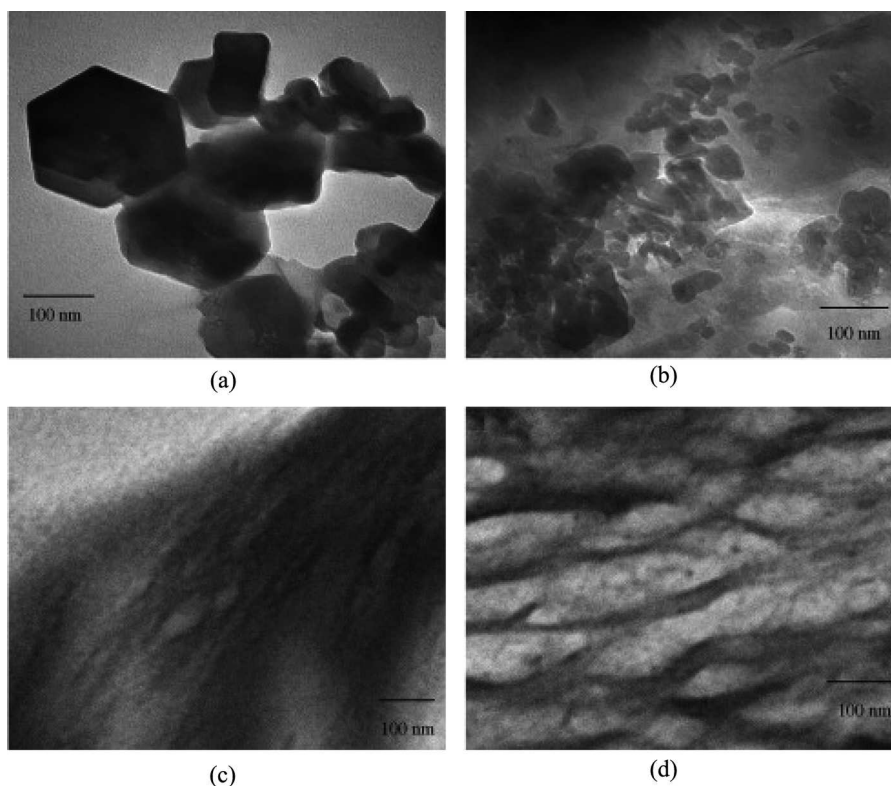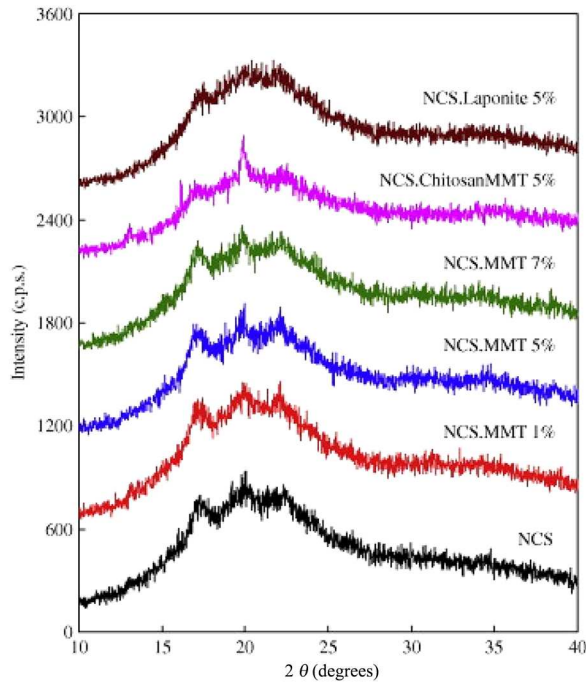


**Figure 3.** The TEM photographs of PMMT, GMMT, TPS/PMMT, and TPS/GMMT. (a) PMMT, (b) GMMT, (c) TPS/PMMT4, (d) TPS/GMMT4. Reprinted with permission from Wang et al.[91] Copy right 2009 Elsevier. *Note*: TEM, transmission electron microscopy; PMMT, pristine montmorillonite; GMMT, glycerol-modified montmorillonite; TPS, thermoplastic starch.
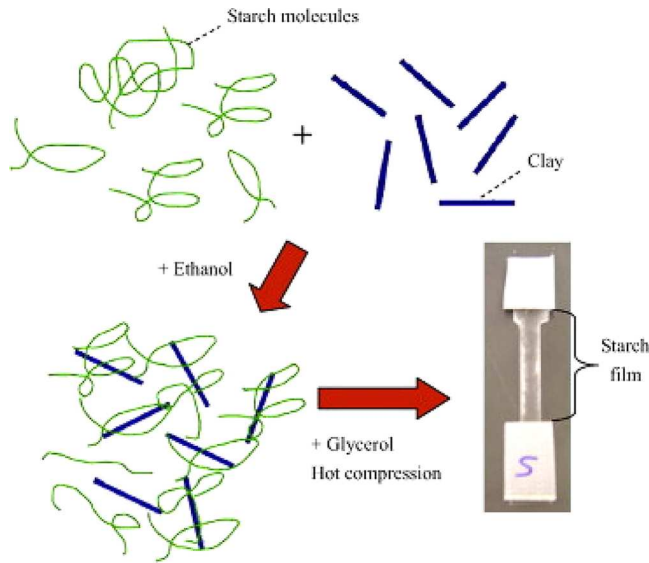
**Figure 4.** (a) Schematic representation of the synthesis of well-dispersed starch–clay nanocomposites. (b) XRD patterns for starch and various starch–clay nanocomposites containing different amounts of clay. Reprinted with permission from Chung et al.[92] Copy right 2010 Elsevier. *Note*: XRD, X-ray diffraction.

The same research groups have also reported their studies on the starch-layered double-hydroxide (LDH) nanocomposite.[93] In this work, nanocomposites were prepared by a new technique in which LDH was directly synthesized in the dispersion of starch. An acid modification technique was also used to reduce the molecular weight/pasting viscosity of the starch that significantly facilitated the LDH crystallites' dispersion in the starch nanocomposites. The nanocomposites prepared using the

acid-modified corn starch (AMS) were also investigated for their mechanical properties. It was found that the crystalline structure of starch was not much affected by the LDH, its high concentration improved the separation in starch but not AMS. Both the nanocomposites showed no change in transparency/moisture sensitivity; however, there was a significant increase in the modulus of nano-composites. Solution casting method was used to prepare the starch/clay nanocomposites in which the effects of clay cation, starch source, glycerol content as well as the mode of mixing on intercalation of clay was studied.[94] In addition, the mechanical properties of the nanocomposites were also studied using a Taguchi experimental design approach. Citric acid was also used to modify the clay and the properties were compared for both the pristine/modified clay-based nanocomposites. The citric acid-modified clay was found to exhibit better mechanical property when compared with clay. The enhancement in properties was attributed to strong interaction among starch and citric acid molecules. Plasticized starch/polypropylene blends' clay nanocomposites were prepared to overcome the disadvantages associated with plasticized starch.[95] In this work, two types of clay, i.e., unmodi-fied/organically modified MMT clays, MMT, and Cloisite 30B were used to reinforce the plasticized starch/polypropylene blends. It was found that the MMT has good dispersion in TPS phase of blends, while the Cloisite 30B can locate within both TPS and polypropylene. With high content of TPS, the clay significantly increased the tensile strength/tensile modulus (by an order of magnitude). This behavior was attributed to the reinforcing effect of clay as well as change in the morphology of the two phases as a result of incorporation of clay. Cassava starch-based biodegradable films and their nanocomposites were also prepared.[96] The effect of incorporation of glycerol (along with the method of incorporation) on tensile/barrier properties of the prepared films (BF) was studied and analyzed in detail. The optimized studies on content of glycerol showed that glycerol and clay content significantly involved in the tensile properties and glass transition temperature. In the case of pristine starch films, the films with lower amount of glycerol exhibited better mechanical and barrier proper-ties. It was concluded from this study that the cassava starch/clay nanoparticles have the potential to be used as novel biodegradable material for packaging applications. Water barrier properties of starch–clay nanocomposite films were studied by incorporating the MMT nanoclay in the polymer matrix using two different morphologies.[97] The effect of clay concentration on the physicochemical properties of the resulting nanocomposite films was studied in detail. It was found that the addition of clay (MMT) content decreased the water permeability due to an increase in the tortuosity and hydrophilicity of the diffusion path caused by clay particles. The opacity was also found to be depen-dent on the used nanoclay dispersion method. The effect of hydrophilicities of different clays on the properties of starch–clay nanocomposites was studied in detail.[98] The nanocomposites in this study were prepared using hydroxypropyl distarch phosphate and five different kinds of clays using the film blowing technique. These nanocomposites were characterized using TEM and XRD. It was confirmed from the study that there was a formation of intercalation nanostructure in the nanocomposites. The prepared nanocomposites demonstrated significant improvement in tensile strength/better barrier properties/water vapor in comparison to the pristine film. The starch–clay films had a lower glass transition temperature ($T_g$) and better heat endurance compared to the contrast film. The microstruc-ture of the films was more homogeneous and smooth with the addition of clays into starch. The clay which had a medium hydrophilic property was more suitable for the preparation of hydroxypropyl distarch phosphate–clay nanocomposite films as an intensifier among all the five clays. Biodegrada-tion of the starch nanocomposites was also studied. The effect of incorporation of amount of glycerol on the tensile and barrier properties of the nanocomposites was studied in detail.[96] The starch used in this work was obtained from cassava starch and the glycerol content was found to significantly affect the barrier and tensile properties.[96] Starch clay nanocomposites were also prepared using acetylation of starch.[99] The nanocomposites were prepared using acetylated corn starch/clay (NaMMT) and with or without addition of PVA (PVOH). In this study also, glycerol was used as a plasticizer. To study the intercalated nanocomposite structure, XRD study was performed in detail in addition to the thermomechanical and mechanical properties. It was found that the addition of clay has a significant reinforcing effect in the starch. Furthermore, the replacement of glycerol with

polyvinyl alcohol resulted in enhanced mechanical strength as a result of the strong hydrogen bonding between polyvinyl alcohol and starch. Starch–MMT clay nanocomposite were also prepared using screw extruder technique for packaging applications.[100] Citric acid was used to modify the surface characteristics of MMT to have a better compatibility among the silicate layers and starch modification. The extent of modification was confirmed using XRD analysis through the expanded microstructure of citric acid-modified MMT (CMMT). In this work, the effect of different reaction parameters including amount of PVA/CMMT, screw speed along with the temperature profile in the extruder on the tensile strength was studied using Taguchi experimental design. It was concluded from the study that PVA/CMMT content and screw speed has the significant effect on the overall properties, especially on the tensile strength property. Antimicrobial nanostructured starch-based nanocomposite films were also prepared for packaging applications by directly synthesizing silver nanoparticles in starch and in clay/starch solutions using chemical reduction method.[101] In this study, the effect of incorporation of clay and silver nanoparticles was investigated in detail. Different kinds of nanocomposite films such as silver nanoparticles/starch nanocomposite (Ag-NPs/ST-NC), MMT modified with a quaternary ammonium salt C30B/starch nanocomposite (C30B/ST-NC), and both silver nanoparticles/C30B/starch nanocomposites (Ag-NPs/C30B/ST-NC) were produced.
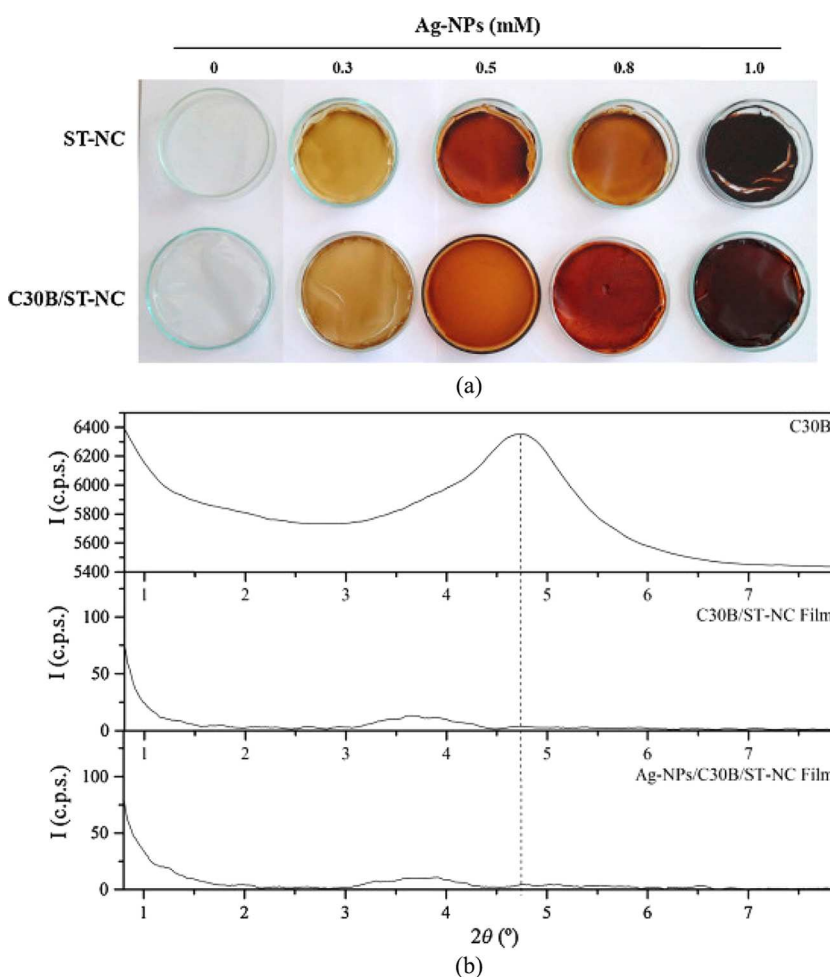


Figure 5.    (a). Nanostructured starch films. (b) X-ray diffraction patterns of organo-modified clay C30B, C30B/ST-NC and Ag-NPs/ C30B/ST-NC films. Reprinted with permission from Abreu et al.[101] Copy right 2015 Elsevier.

Figure 5(a) shows the nanostructured starch films. The effect of amount of different concentrations of silver nanoparticles (Ag-NPs) (0.3, 0.5, 0.8 and 1.0 mM) was also studied. Different characterization techniques such as XRD and SEM were used to confirm the presence of Ag-NP-enhanced clay dispersion [Figure 5(b)]. In addition, other properties such as barrier properties (water vapor/oxygen permeability's), color and opacity measurements, contact angle, and dynamic mechanical analysis were also evaluated. All these measurements were correlated with the incorporation of C30B and Ag-NPs. Subsequently, the antimicrobial activity of the starch films was studied against *Staphylococcus aureus, Escherichia coli*, and *Candida albicans* without significant differences between Ag-NPs' concentrations and it was observed that all the films exhibit promising antimicrobial properties.

## Conclusion

In this article, a review of most important and recent research on development of biodegradable nanocomposites based on polymer/clay, starch/polymer, and starch/clay nanocomposites were exposed. Particularly, the investigation was focused on influences of starch and clay with different biodegradable polymer and starch/clay nanocomposites from renewable source. Some of the different methods of preparation of clay–polymer and starch-based nanocomposites and starch/clay nanocomposites paid significant attention for the further studies. Many physicochemical properties such as structure, mechanical property, biodegradation, gas barrier, and water permeability have been presented. From the literature about the improvement of nanocomposites, the biodegradable nanocomposites from renewable sources have more importance than synthetic polymer-based nanocomposites. More interestingly, starch–clay nanocomposites have achieved better mechanical property and tensile strength for packaging materials. From the result of literature works cited in this work, it can be concluded that to improve the barrier, mechanical and thermal properties of starch/clay matrix, the next consideration need to be taken into account includes morphological and chemical properties of plasticizers and nanofillers. Furthermore, increasing application of synthetic polymer-based nanocomposites affects the human population and standard of living. Therefore, use of starch/clay nanocomposites may alter all the limitations of synthetic polymers. As a result of the current progress in sustainable nanocomposites, starch/clay nanocomposites have more importance and that may lead to more research work in the particular field of developing nanocomposites.

## Acknowledgment

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