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Emerging biodegradable materials: starch- and protein-based bio-nanocomposites

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Abstract This article provides a broad overview on the natural polymer-based bio-nanocomposite properties, processing and application. Bio-nanocomposites prepared with natural biopolymers, such as starch and protein, can be formed using a melt intercalation or a solvent intercalation method. Incorporation of layered silicates into the biopolymer matrices results in improved mechanical properties, water vapor barrier properties, and thermal stability of the resulting bio-nanocomposites without sacrificing biodegradability due to their nanometer size dispersion. Consequently, even though natural polymer-based bio-nanocomposite is in its infancy, it has a huge potential in the future.

Introduction

In recent years the development of biodegradable materials from renewable resources with excellent mechanical and barrier properties has been an important research challenge for the plastics industry. It is estimated that the world's annual consumption of plastic materials has increased from around 5 million tons in the 1950s to nearly 100 million tons today [1]. In the UK, a total of approximately 4.7 million tons of plastic products were used in various economic sectors in 2001. Of the plastics produced, approximately 44% are items that have a relatively short period of use before they are discarded (e.g., disposable cutlery, disposable plates, cups and utensils, diapers, trash bags, beverage containers, agricultural films, fast food containers, medical devices, etc.). The remaining 56% is used in long-term applications (e.g., building and construction, electronics, household items, furniture, transport, toys, etc.) where high stability is required [1].

The main types of plastics that are currently used in all applications are derived from non-renewable petroleum resources, and give non-biodegradable plastic materials. The environmental impact of persistent plastic wastes is of increasing global concern, as in 2005, in the USA, 28.9 million tons of plastics packaging was generated and only approximately 5.7% of plastic is recycled or reused in some way, 94.3% is sent to landfill and discarded or combusted into the environment [2]. While the proportion of plastics recycled or reused is increasing, (for example, in European, polyethylene terephthalate collection recycling rates reached 796,000 tons in 2005, a 15.1% increase over the previous year, according to Petcore, a trade association.) [3, 4], only part of the plastics produced can be practically recovered, and not all plastics are suitable for recycling or re-use (e.g., contamination of plastic by other materials, non-reshaped properties of thermosetting materials, and poor compatibility of co-blend) [5, 6]. Thus, the volume of plastics discarded annually creates a substantial waste disposal issue, and alternative methods to reduce the quantity of persistent plastic wastes are required.

One approach is to make materials from biodegradable materials that can be disposed of through composting or

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feedstock recycling [2, 7]. A number of biodegradable materials have been investigated for use as plastics. Some are naturally occurring polymeric materials (e.g., starches, proteins, cellulose, gums) [8], some are produced by polymerizing organic molecules to form polymers (e.g., polyurethanes by polyols obtained from vegetable oils, polylactic acid by lactide monomer from 100% renewable resources like corn, sugar, and other starch-rich products) [9, 10] and others are manufactured from petrochemicals (e.g., poly(butylene succinate)-PBS, biodegradable aliphatic polyesters-BAPs, poly(ε-caprolactone)-PCL, and poly(vinyl alcohol)-PVA) [11]. The processing properties, properties in finished products and biodegradability of these different materials varies widely [12], however several commonly occurring factors limiting their industrial application have been identified. First, in some instances their mechanical properties are relatively poor compared to many petroleum-based plastics due to the inherent lower stiffness and strength (Table 1). Second, many are relatively sensitive to water, with some materials dissolving rapidly, or a substantial decrease in mechanical when they absorb water, especially in moist environments [13]. Third, the present low level of production and high cost restrict them from wide range of applications [8].

Therefore, there is an urgent need to develop biodegradable plastics made from renewable resources to reduce the quantity of plastic wastes [10], but with properties comparable to petroleum-based plastics. An attractive option is nano-composite materials based on materials of biological origin that are biodegradable materials, which are called bio-nanocomposites.

Polymer-clay nanocomposites have generated enormous interest since Toyota researchers in the late 1980s showed that as little as 5% addition of nano-sized clays to nylons greatly increased their modulus and heat distortion temperature 80 °C [15]. Improvements in a range of properties have followed in epoxy resins [16], PDMS elastomers [17], polyimides, and polycaprolactones [18, 19], polypropylene [20], and many other host polymers. Work in this area has been the subject of several reviews [21–23].

They include bio-nanocomposites based on polysaccharides such as cellulose and starch [24–49], and bio-nanocomposites based on proteins such as dairy protein, soybean protein, and gelatin [50–52]. The use of these materials serve a number of important functions, such as extending the food shelf life, enhancing food quality because they can serve not only as barriers to moisture, water vapor, gases, and solutes, but also serve as carriers of some active substances, such as antioxidants and antimicrobials [53–55].

These bio-nanocomposites are significant due to their nanoscale dispersion with size less than 1,000 nm (a nanometer being billionth of a meter) [56, 57]. Incorporation of nanoparticles into conventional petroleum-based plastics is well known. Addition of relatively low levels of nanoparticles (less than 5%) have been shown to substantially improve the properties of the finished plastic, increasing the deformability and strength, and reducing the electrical conductivity and gas permeability [12].

Properties of bio-nanocomposites

Bio-nanocomposites are mixture of polymers with nano-sized inorganic or organic fillers with particular size, geometry, and surface chemistry properties. The polymers used are normally hydrocolloids, such as proteins, starches, pectins, and other polysaccharides. Various inorganic nano-particles have been recognized as possible additives to enhance the polymer performance [21, 58, 59]. Nanofillers include solid layered clays, synthetic polymer nanofibers, cellulose nano-whiskers, and carbon nano-tubes. Up to now only the layered inorganic solids like layered silicate have attracted the attention of the packaging industry. This is due to their ready availability and low cost, and also

Table 1 The mechanical properties of polymers used for injection molding: comparison of conventional and thermoplastic starch

Material	Young's modulus (MPa)	Maximum stress/Ultimate tensile strength (MPa)	Strain at break (%)
Conventional polymers[a]			
Low density polyethylene (LDPE)	210	11,000	190
High density polyethylene (HDPE)	911	20.3	380
Polypropylene (PP)	1,900	36.8	120
Poly(ethylene terephthalate) (PET)	2,700	55	130
Thermoplastic starch[b]			
0% Amylose	160	6.5	75
80% Amylose	120	7.5	95
Hydroxypropylated 80% amylose	75	5.5	180

[a] Averaged values supplied by manufacturers' data from http://www.matweb.com

[b] From Chaudhary et al. [14]

their significant enhancement of finished product properties and relative simple processing [12].

When polymers are combined with nanofillers, the resulting in bio-nanocomposites exhibit significant improvements in mechanical properties, dimensional stability, and solvent or gas resistance with respect to the pristine polymer. Bio-nanocomposites also offer extra benefits like low density, transparency, good flow, better surface properties, and recyclability [11, 12, 59].

The enhancement of many properties resides in the fundamental length scales dominating the morphology and properties of these materials. The nanofiller particles have at least one dimension in the nanometer (from 1 to 100 nm) range. It means that a uniform dispersion of these particles can lead to ultra-large interfacial area between the constituents. The very large organic or inorganic interface alters the molecular mobility and the relaxation behavior, improves the mechanical properties of bio-nanocomposites both in solid and melt states, and the thermal stability and melt viscosity of renewable polymers also increase after bio-nanocomposite preparation. The above improved properties are generally attained at low silicate content ($\leq$5 wt%) compared to that of conventional filler field composites [12, 23, 60]. Manias et al. [61] reported that small additions—typically less than 6 wt %—of nanoscale inorganic fillers could promote concurrently several of the polypropylene material properties, including improved tensile characteristics, higher heat deflection temperature, retained optical clarity, high barrier properties, better scratch resistance, and increased flame retardancy [61]. Strawhecker et al. suggested that for a 5% montmorillonite (MMT) exfoliated composite, the softening temperature of nanocomposites increased by 25 °C, the water permeability reduced by 60% and the nanocomposites could retain their optical clarity [62]. For these reasons, these are far lighter in weight than conventional biodegradable composites and make them competitive with other materials for specific applications, especially food packaging [10, 63].

Another advantage of bio-nanocomposite is that it can be biodegraded efficiently. Degradation of a polymer may result from the action of microbes, macroorganisms, photodegradation or chemical degradation [64]. The ‘‘biodegradable’’ materials described in this article are those materials which can be degraded by the action of living organisms, such as bacteria, yeasts, fungi and the ultimate end-products of the degradation process, these being CO_2, H_2O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anerobic conditions [34]. However, these materials vary in their rate of degradation in the environment. They are bio-degradable under controlled conditions after discarding. The most important parameters for controlling degradability are appropriate water activity, pH, nutrients, oxygen, storage time, and temperature [65]. According to some reports, there are different degradation rates at different lifetime. When disposed, they maybe be completely degraded after 3 months, 6 months, or 12 months, causing no harm to the environment [66–68]. For example, at the end of their lifetime, these biodegradable materials introduced in agriculture can be safely buried in the soil for the final complete composting and continues to have the functionality needed for agricultural applications, during the crop cycle [69, 70]. Therefore, bio-nanocomposites appear to have a very bright future for a wide range of applications.

Preparative techniques of bio-nanocomposites

The techniques used to manufacture bio-nanocomposites are based largely on existing techniques for processing plastics or composite materials. There is considerable literature available devoted to developing bio-nanocomposites with different combinations, employing somewhat different technologies appropriate to each. The technologies are broadly classed into three main categories [10, 12, 21, 58, 59].

Solution intercalation

This is based on a solvent system in which the bio-polymer or bio-prepolymer, such as starch and protein, is soluble and the inorganic nanofillers, usually silicate platelets, are swellable. The layered silicate is first swollen in a solvent such as water, chloroform, or toluene. When the bio-polymer and solution of swollen nanoparticles are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in a bio-polymer/layered silicate bio-nanocomposite formation.

In situ intercalative polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step.

Melt intercalation

Recently, the melt intercalation technique has become the standard method for the preparation of polymer/layered silicate bio-nanocomposites. There are many advantages compared with solution intercalation and in situ intercalative polymerization. For example, from a waste perspective, the absence of organic solvents makes direct melt intercalation an environmentally sound. In addition, it is compatible with current industrial processes such as extrusion and injection molding [61, 71–74].

This process involves annealing a mixture of the polymer and layered silicate above the softening point of the polymer. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers. A range of bio-nanocomposites with structures from intercalation to exfoliation can be obtained, depending on the degree of penetration of the polymer chains into the silicate galleries [10, 75]. So far, the melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or the solution intercalation method.

Recent advances in melt intercalation have examined effects of chemistry and processing conditions on intercalation and exfoliation [76]. They have seen for twin-screw extrusion that shear rate is important to initially shear apart layers and residence time is important for allowing time for diffusion to fully exfoliate layers. However they note clay chemistry is also very important to be able to initiate the primary breaking up of layers. Optimizing interlayer chemistry, as well as polymer molecular weight and annealing temperatures was also seen as very important in modeling exfoliation and designing optimal nanoclays as demonstrated by Vaia [77, 78]. Through melt intercalation, with lower nanoparticles the mechanical properties and thermal properties of nanocomposites, such as tensile strength, impact strength, and thermal stability properties are improved. At the same time, the storage modulus and glass transition temperature of nanocomposites have also remarkably enhancements [79–81].

Application of bio-nanocomposites

Food packaging

The use of proper packaging materials and methods to minimize food losses and provide safe and wholesome food products have always been the focus of food packaging. In addition, consumer trends for better quality, fresh-like, and convenient food products have intensified during the last decades. Therefore, a variety of active packaging technologies have been developed to provide better quality, wholesome, and safe foods and also to limit package-related environmental pollution and disposal problems [82]. The application of bio-nanocomposites may open a new possibility to solve this problem.

Owing to the nanometer-size particles obtained by dispersion, these bio-nanocomposites can exhibit many advantages [8, 83]. Followings are some examples:

- Biodegradable;
- Enhanced organoleptic characteristics of food, such as appearance, odor, and flavor;
- Reduced packaging volume, weight, and waste;
- Extended shelf life and improved quality of usually non-packaged items;
- Control over intercomponent;
- Individual packaging of small particulate foods, such as nuts and raisins;
- Function as carriers for antimicrobial and antioxidant agents;
- Controlled release of active ingredients;
- Annually renewable resources.

Therefore, bio-nanocomposite packaging materials have great potential for enhanced food quality, safety, and stability as an innovative packaging and processing technology. The unique advantage of the natural biopolymer packaging may lead to new product development in food industry, such as individual packaging of particulate foods, carriers for functionally active substances, and nutritional supplements.

Agricultural applications

The world consumption of plastic materials in agriculture amounts yearly to 6.5 million tons in order to improve crop cultivation and protect agricultural products after harvesting, in the form of greenhouses, tunnels, mulch, silage films, and bale wraps [69, 84]. Therefore, there is a huge amount plastics discarded into the environment, buried in the soil or burnt by farmers releasing of harmful substances with the associated obviously negative consequences to the environment [70]. A solution to this problem can be the introduction in agriculture of biodegradable films, which can be disposed directly into the soil or into a composting system at the end of their lifetime.

When biodegradable raw materials mixed with some nano-grade additives such as TiO_2, layered silicate, and MMT, resulted in bio-nanocomposite or film exhibiting many advantages [69, 70, 85–87].

- Biodegradation in the soil due to the action of microorganisms such as bacteria, fungi, and algae;
- Degradation by the sunlight and water;
- Function as carriers for pesticide resistance;
- Control release of active substance, such as insecticides;
- Controlled degradation, such as biopolymer/TiO_2 nanofilms;

- Enhanced durability and optical properties, such as ultraviolet, visible, infrared;
- Annually renewable resources.

Up to now, degradable or biodegradable materials have been extensively tested in field trials in different countries and for different crops. Successful results have been obtained such as in maize, melon, strawberries, and cotton mulch film applications. The use of biodegradable materials in agriculture can promote sustainable and environmentally friendly cultivation reducing the contamination of the soil, enhancing the protection of the landscape in rural areas against pollution, and increasing the use of renewable non-oil raw materials such as starch. At the end of their lifetime, these biodegradable materials can be safely buried in the soil for the final complete composting and continues to have the functionality needed for agricultural applications, during the crop cycle [69, 70].

Industrial applications

Recently Ruiz-Hickey et al. [88] reviewed a large range of biopolymer nanocomposites utilizing biopolymers such as polysaccharides (cellulose, sucrose, starch, chitosan), many peptides and proteins, nucleic acids (DNA), and mixed and modified biopolymers, with natural and synthetic nanoparticles. The diverse range of possible novel applications included clothes, conductive polymers, bone repair, drug delivery, gene repair, superadsorbent materials, and green packaging applications. They noted that thought must be given to processing soft biomolecules and polymers at relatively moderate temperatures and pressures (such as spin coating and supercritical gas-aided processing) as well as the use of layered-nanomaterials that are capable of intercalation and exfoliation, as well as carrying targeted biomolecules and biochemicals.

Processing of bio-nanocomposites

Starch-based bio-nanocomposites

In the family of renewable source-based polymeric materials, starch is an inexpensive and abundant natural resource. Currently much research concerns on the materials prepared by starch, because it is biodegradable and renewable [29, 89–91]. Native starch granules exhibit two main types of X-ray diffraction diagrams, the A type for cereal starches and the B type for tuber and amylose-rich starches [92–94]. Another C-type diffraction diagram, which has been shown to be a mixture of A- and B-type diagrams [95], is characteristic of most legume starches [96]. The crystalline V-form characteristic of amylose complexed with fatty acids and monoglycerides, appears upon gelatinization of starch [29]. Native starch is a mixture of amylose and a highly branched amylopectin, and its mechanical and physical properties are poor. The addition of nano-scale particles into thermoplastic starch by chance can change the crystallization kinetics, the crystalline morphology, the crystal forms, and the crystallite size [97]. This difference in crystalline morphology, in turn, can significantly affect the overall mechanical and physical properties of the starch.

Native starch is not a true thermoplastic but it can be converted into a plastic-like material called "thermoplastic starch" [31]. In the presence of plasticizers at high temperature (90–180 °C) and under shear, starch readily melts and flows, allowing for its use as an extrusion, injection molding, or blow molding material, similar to most conventional synthetic thermoplastic polymers. However, pure thermoplastic starch still have the same limitations as native starch, such as high water-sensitivity, poor barrier properties at high moisture contents and poor mechanical properties [32, 33].

Avella et al. [34] showed a good increase in modulus and tensile strength for starch-nanocomposites prepared from cast film dispersions of MMT into plasticized potato starch. The nanocomposite showed good exfoliation, but films however were still quite brittle, without addition of polyester [34].

Wilhelm et al. [35, 36] examined a range of nanoclays (natural kaolonite and hectorite and synthetic layered double hydroxide (LDH) and brucite) in blends of glycerol plasticized starch and oxidized starch and cast as films. Better exfoliation and mechanical property improvement were found in hectorite films where the starch–calcium ion interaction was more favorable. Oxidized starch showed greater intercalation of clay layers [35, 36].

Park et al. [37] and Park et al. [38] reported their efforts to develop environmentally friendly polymer hybrids to improve the properties of thermoplastic starch. Biodegradable thermoplastic starch /layered silicate nanocomposites were prepared by the melt intercalation method. Natural MMT (Cloisite Na^+) and one MMT organically modified with methyl tallow bis-2-hydroxyethyl ammonium cations located in the silicate gallery (Cloisite 30B) were chosen to generate thermoplastic starch/clay bio-nanocomposites. Starch was prepared from natural potato starch by gelatinizing and plasticizing it with water and glycerol. With 5% by weight inclusion of the clays, strong interactions between thermoplastic starch and Cloisite Na^+ led to higher tensile properties and a lower water vapor transmission rate than the pristine thermoplastic starch [37, 38]. Pandey [39] noted in their review that this work by Park et al. [37, 38] was one of the most important advances in developing starch nanocomposites due to the advances in mechanical and barrier properties, and highlights to importance of starch-plasticizer-clay interactions.

Pandey et al. [40] examined the addition sequence of starch, plasticizer (glycerol) and clay (sodium MMT) in heated solutions that were subsequently cast as films. Better mechanical properties were obtained when clay was added to starch and then plasticized, due to more homogeneous dispersion (than compared to addition of clay to plasticized starch), but overall all materials were very brittle compared to conventional plastics [40].

Huang and Yu [41] reported on preparation and properties of starch/MMT nanocomposite prepared with thermoplastic cornstarch and activated MMT by the melt intercalation method using an extruder with various nanofiller concentrations of 0–11% to the starch. Tensile test results indicated that the tensile strength and Young's modulus increased monotonously with increase in nanofiller content up to 8%. Water resistance of the bionanocomposite was also improved [41].

Chiou et al. [42] examined effects of moisture content, screw speed, and temperature on nanoclay dispersion of Na-Cloisite (MMT) and Cloisite 30B (a MMT modified with a quaternary ammonium salt of hydrogenated tallow) in wheat starch using a twin screw extruder. Better dispersion and more water resistance occurred in the Na-Cloisite (more hydrophilic) nanocomposites, where moisture content had the greatest effect on exfoliation. This agreed with earlier work by Chiou et al. [43], where Na-cloisite mixtures had higher shear moduli and better exfoliation than a range of organically treated cloisite clays in wheat, potato, corn and waxy corn starch mixtures [43].

Qiao et al. [44] examined the melt mixing of Na-MMT and an organically modified MMT (OMMT) modified with trimethyl-dodecyl ammonium in acetylated starch, and showed greater dispersibility, tensile strength increase, ultimate elongation decrease and viscosity increase with the organically treated MMT [44].

Chen et al. [45] examined the effects of clay type (MMT, hectorite, organically treated hectorite, kaolinite) in glycerol plasticized potato starch nanocomposites at similar clay volumes, and showed greater exfoliation and modulus increase with the unmodified clays. The effect was greater for the (higher aspect ratio) unmodified MMT [45].

Bagdi et al. [46] examined the effect of organic treatment on MMT nanofiller addition to glycerol plasticized potato starch. Unfortunately limited improvements were seen due to competitive dissolution and absorption of surfactant and plasticizer; however, greatest improvements in strength were seen with amino acid modification over aliphatic amine modification [46].

Dean et al. [47, 48] examined a range of premixing procedures on premixed then twin screw extruded high-amylose corn-starch nanocomposites using MMT and synthetic fluoromica nanoclays. Systematic increases in modulus and exfoliation were found and an optimum level of plasticizer and nanoclay were found. Standard premixing showed better results than ultrasonic premixing [47, 48].

McGlashan and Halley [24] examined the melt intercalation of starch-polyester-nanocomposites and its usefulness in the addition of modified MMT in improving mechanical properties, clarity (via disruption of crystallinity) and film blowing processibility of the nanocomposites [24].

Chen et al. [49] examined the melt processing of thermoplastic starch-clay nanocomposite foams and noted the synergistic effects of the urea plasticizer and ammonium treatment of the clay to enhance clay dispersion. Further ammonium treatment was found to enhance regular foaming due to ammonia production [49].

Through these efforts, nanocomposites with superior properties have been successfully made from starch matrix blends in the presence of nanoparticles. WAXD (Wide-angle x-ray diffraction) analyses and TEM (transmission electron microscopy) observations showed that compatible layered nanoparticles could be in a fine-dispersed manner into polymer matrix materials if in good process conditions, and the addition of nanoparticles at lower level (less than 5% wt) could significantly improve the mechanical, physical, and thermal properties of nanaocomposites, such as tensile strength, Young's modulus, elongation, water resistance, and so on [98–103].

As a packaging material, starch-based nanocomposite is a promizing due to its characteristics (shown in Table 2) and its being completely degradable in soil and water, as well as low cost. There are many opportunities for starch-based nanocomposite as film or bag. It could be employed as packaging for fruits and vegetables, snacks or dry products. Therefore, extensive research work, preparation and application regarding starch-based nanocomposite have performed recently.

Protein-based bio-nanocomposites

α-Amino acids are the basic structural units of proteins. Proteins are highly complex polymers, made up of 20 different amino acids. The constituents are linked via substituted amide bonds. In proteins, four levels of protein structure exist: primary, secondary, tertiary, and quaternary. Due to the complexity in their composition and structure, proteins possess multiple function properties, such as solubility, gelation, elasticity, emulsification, and cohesion-adhesion [105, 106]. Proteins are amphoteric molecules, and they can migrate spontaneously to an air–water interface or an oil–water interface. Once at the

Table 2 Characteristics of starch-based nanocomposites

Starch type	Non-starch ingredients	Nanoparticles	Processing conditions	Starch level	Non-starch ingredient level	Nano-particle level	Nanoparticle exfoliation	Tensile strength (MPa)	Young's modulus (MPa)	Strain at break (%)	Effect of water	References
Mixture of: 1. Regular maize 2. Chemically modified high amylsoe maize	Aliphatic polyester Plasticizer	MMT organoclay	Twin screw extrusion to form pellets Single screw extrusion to form blown film	30–70 Starch and plasticizer mixture	30–70 Aliphatic polyester	0–5	Exfoliation only at lowest clay and starch level (1.5% and 30%, respectively) Intercalcation/partial intercalcation at higher clay and starch levels	At all starch levels, increasing level of clay increased tensile strength. At the same clay level, strain at break decreased with increasing level of starch.	Increased markedly from 17 MPa (0% clay) to 65 MPa (5% clay)	At all starch levels, increasing level of clay increased strain at break. At the same clay level, strain at break decreased with increasing level of starch.		McGlashan and Halley [24]
Cara starch	Glycerol	Ca2+ hectorite	Clay hydrated in water Film cast from suspension	70–100	20 Glycerol	0–30	15.0–18.9	–	Increased from 815 MPa (0% clay) to 1,406 MPa (30% clay)	Decreased from 11% (0% clay) to 5% (30% clay).		Wilhelm et al. [35, 36]
Corn starch	Glycerol	Na MMT	Single screw extrusion of starch and glycerol to form pellets Pellets mixed with nanoparticles and re-extruded	75	25 Glycerol	0–30		Maximum stress progressively increased from about 5 MPa (0% MMT) to 15 MPa (25% MMT). There was a large increase to about 27.5 MPa at 30% MMT.		Maximum strain progressively decreased from about 80% (0% MMT) to 17% (25% MMT). Strain decreased slightly to about 17% at 30% MMT.	Irrespective of MMT level, mechanical properties were highly sensitive to moisture content. Maximum stress of all samples was at about a minimum at 20% moisture.	Huang et al. [104]
Potato starch	Glycerol, water, polyester	MMT	Twin screw mixing of starch, then cast films	48–65	35–52	0–4	Yes	6–22	217–1,135	3–60		Avella et al. [34]
Cara starch–native and oxidized	Glycerol	Kaolinite, Hectorite, LDH, Brucite	Suspension mixing then casting	70–100	20	0–30	18–23 A					Wilhelm et al. [35, 36]

Table 2 continued

Starch type	Non-starch ingredients	Nanoparticles	Processing conditions	Starch level	Non-starch ingredient level	Nano-particle level	Nanoparticle exfoliation	Tensile strength (MPa)	Young's modulus (MPa)	Strain at break (%)	Effect of water	References
Corn starch	Glycerol, water	MMT	Suspension mixing in excess water then casting	75	20	5	13–26 A		790–825	6–12		Pandey et al. [40]
Mixture of: 1. Regular maize 2. Chemically modified high amylsoe maize	Aliphatic polyester Plasticizer	Organically modified MMT (OMMT)	Twin screw extrusion to form pellets Single screw extrusion to form blown film	30–70	70–30	0–5	15–38 A	4.6–18	14–64	260–>1,500		McGlashan and Halley [24]
Corn starch	Glycerol	Na MMT	Single screw extrusion of starch and glycerol to form pellets Pellets mixed with nanoparticles and re-extruded	75	25 Glycerol	0–30		5–27.5		80–17	Irrespective of MMT level, mechanical properties were highly sensitive to moisture content. Maximum stress of all samples was at about a minimum at 20% moisture.	Huang et al. [104]
Wheat starch	Water	Na Cloisite (MMT) and Cloisite 30B (organically modified-OMMT)	Twin screw extrusion–various processing conditions	95	34–47%	5	18–23 A				Lower water uptake with Na cloisite.	Chiou et al. [42]
Wheat, Potato, Corn and Waxy Corn starch	Water	Na Cloisite (MMT) and Cloisite 10A, 15A and 30B (organically modified-OMMTs)	Twin screw extrusion–various processing conditions	100–90	12%	0–10	11–25 A					Chiou et al. [43]

Table 2 continued

Starch type	Non-starch ingredients	Nanoparticles	Processing conditions	Starch level	Non-starch ingredient level	Nano-particle level	Nanoparticle exfoliation	Tensile strength (MPa)	Young's modulus (MPa)	Strain at break (%)	Effect of water	References
Acetylated tapioca starch	Gycerol	Na Cloisite (MMT) and Cloisite 30B (organically modified-OMMT)	Melt blended in roller mixer after premixing then sheet pressed	66	33	0–5	140–460 A [NB this appears to be too large by factor of 10]	5–10		49–28		Qiao et al. [44]
Potato starch	Glycerol	MMT, Hectorite, Modified Hectorite, Kaolinite	Premixed then twin roll milled	100	30	6–22 wt%	12–18 A					Chen et al. [45]
Wheat starch	Glycerol	Na- MMT and three organic treated MMTs (OMMTs)	Premixed then melt mixed in static mixer	64	36	0–7 vol%	10–18 A	5–7				Bagdi et al. [46]
Potato starch	Urea	Na- MMT and ammonium treated MMTs (NH4MMT)	Twin roll mixed then foamed in mold	100	30	0–10 wt%	exfoliated					Chen et al. [49]
High amylase corn starch	Water	Na- MMT and Synthetic fluoromica	A range of premixing techniques followed by twin screw extrusion	80–85	13–20 wt%	1–3 wt%	10A-exfoliated	12–23	220–550	5–8%		Dean et al. [47]

interface, proteins have an ability to interact with the neighboring molecules and form a strong cohesive, viscoeleastic film that can withstand thermal and mechanical motions [107]. Therefore, traditionally proteins are used in adhesives and as edible films/coatings. Compared with starch, protein films have demonstrated good gas barrier properties and lower water vapor permeability though sometime not entirely hydrophobic or slowly degrading [108]. Proteins show that these properties are advantageous in the preparation of packaging biomaterials. Therefore, the film-forming ability of various proteins has been utilized in industrial applications for a long time [109].

Animal derived sources protein for degradable bio-nanocomposite materials are mainly casein, whey protein, gelatin, collagen, egg white, and fish myofibrillar protein. Due to its water resistance casein has been used in a variety of industrial applications (e.g., glue, plastic, paint, paper coating) for a long time in many countries, such as Ancient Egypt, China, Greece, and Rome. Investigations on the film-forming potential of different plant proteins have mainly focused on soybean protein, corn zein, and wheat gluten [110, 111]. For example, Yu et al. [112] reviewed that through the use of high-powered ultrasonics, soy protein/clay nanocomposites could be produced, which exhibited significant improvement in modulus [112]. Tunc et al. [113] investigated that wheat gluten/MMT nanocomposite films could be prepared by casting. TEM observations showed that MMT nanoparticles were homogeneously distributed within the matrix, but not completely exfoliated. And the results showed that water sensitivity was decreased, the permeability of films toward water vapor and aroma compounds were changed significantly [113].

Milk protein-based bio-nanocomposites

Milk has a protein content of about 33 g/L and casein and whey proteins are the main milk protein [114]. High nutritional quality, water solubility, and emulsification capability of milk proteins make their use in bio-nanocomposite formation very attractive.

Casein is manufactured by adjusting the pH of skim milk to 4.6 and heating to 46 °C to obtain a curd. This disrupts the casein micelle by solubilization of calcium phosphate, releasing individual casein molecules. The curd is then drained, washed (to remove lactose), milled, and dried. Casein has not been as extensively investigated as other protein ingredients, such as soybean protein, gelatin, for their film-forming potential. Whey proteins, accounting for 20% of total milk proteins, are characterized by their solubility at pH 4.6 [87, 115]. Liquid whey, a by-product of cheese manufacture, is produced in large quantities and its annual production is continuously rising. Much of this whey is not utilized, creating serious waste disposal problems. Consequently, significant interest exists in finding new uses for whey proteins, such as bio-nanocomposites.

Although the milk protein-based bio-nanocomposites have not been investigated in large-scale in the past, it is hoped that this potential will be explored in the future as protein-nanotechnology advances. For the preparation of milk protein-based bio-nanocomposites, a solvent-casting method or solution intercalation can be used. First, milk proteins and clay solutions are prepared separately. The milk proteins are dissolved in a solvent with high-shear mixing, and a clay solution is prepared by initially swelling and dispersing of layered nanoclay particles in the same solvent as that used for the film-forming solution. To achieve intercalation of the solvent into the stacked layers, the mixture is subjected to high-shear mixing and to ultrasonic treatment [50, 51, 116]. Then the clay solution is added to the milk protein solution in a dropwise fashion. The resulting mixture is subjected to high-shear mixing and ultrasonic treatment again and is cast on to a glass plate. The solution is allowed to dry in ambient or elevated temperature conditions to make a free-standing film. In this process, the intercalation or exfoliation of nanoclay particles in a polymer matrix is a most important step for the preparation of milk protein-based bio-nanocomposite. Hedenqvist et al. [117] reported that the filler content was 0–4.8 vol.% in preparation of whey-protein-isolate/poly(vinylidene pyrrolidone)-coated MMT composite films. TEM showed a partial exfoliation of the nanoparticles. The geometrical impedance factor increased markedly with increasing filler content in accordance with the high aspect ratio of the nanoparticle aggregates. TEM, in combination with model calculations, revealed that the clay sheets were oriented preferentially in the plane of the film which was an important factor underlying the high geometrical impedance factor obtained for the nanocomposites. A small but significant reduction in the fractional free volume of the polymer matrix was observed for the rubbery polymer in the presence of MMT.

Soybean protein-based bio-nanocomposites

The protein content of soybean (38%–44%) is much higher than the protein content of cereal grains (8%–15%) [118]. Most of the protein in soybean can be classified as globulin. The film-forming ability of soybean protein has been noted along with a number of other functional properties, such as cohesiveness, adhesiveness, water and fat absorption, emulsification, dough and fiber formation, texturizing capability, and whippability [30].

Soybean protein extract is precipitated by adjusting the soymilk pH to 4.5, recovered by centrifugation, washed, neutralized with food grade alkali, spray dried [119]. Soybean protein-based film can be formed through the partial denaturation of polypeptide chains by addition of a solvent, alteration of pH, addition of an electrolyte to cause cross-linking, and/or application of heat. Bio-nanocomposites based on soybean protein can be prepared by compositing soybean protein with layered silicate clay materials, resulting in the improvement of mechanical properties of soybean protein-based film, such as water resistance, tensile strength.

Dean and Yu [51] prepared soybean protein-based nanocomposite films and tested their microsturcture and mechanical properties. They prepared the nanocomposite film by blending water with glycerol and adding Cloisite Na^+, then ultrasound treated for an hour. The Cloisite Na^+ suspension was combined with soybean protein isolate (SPI) using a high-speed mixer, then extruded using a twin screw extruder at 140 °C [51]. The results showed that the most significant improvement was elastic modulus. Nanocomposite films both without and with ultrasonic treatment increased in tensile strength, by 23% and 47%, respectively [51].

Rhim et al. [120] also prepared composite films of SPI and various clays (OMMT, bentonite, talc powder, and zeolite). The suspension of clays was prepared by adding the clay mineral sample to a mixture of distilled water and glycerol, vigorously mixed then sonicated. SPI was then dissolved in the clay suspension and heated before casting and drying. The resulting soybean protein/clays bio-nanocomposites had a significantly ($p < 0.05$) increase in tensile strength, while water vapor permeability and water solubility decreased significantly ($p < 0.05$) than the conventional SPI film [120].

Chen et al. [121] successfully prepared SPI/Na^+- MMT plastics. The results revealed that the heterogeneous distribution of the surface positive charges provided the positive-charge-rich domains for the soy globulins bearing net negative charges to anchor into the negatively charged MMT galleries. There were electrostatic attraction and hydrogen bonding interactions on the interfaces of the soy protein and MMT, which led to the good dispersion of the phyllosilicate layers in the protein matrix. The highly exfoliated MMT layers with a dimension of 1–2 nm in thickness were randomly dispersed in the protein matrix containing MMT lower than 12 wt %, whereas the intercalated structure was predominant when the MMT content was higher than 12 wt %. Consequently, the fine dispersion of the MMT layers and the strong interactions between SPI and MMT created the significant improvement of the mechanical strength and thermo-stability of the SPI/MMT plastics [121].

Yu and Cui [122] reported the preparation of rectorite/SPI biodegradable nanocomposite sheets. He suggested that rectorite was highly exfoliated and intercalated in SPI matrix depending on the characteristic structure of rectorite and SPI as well as the motion ability of molecular chain provided by the process of solution mixing and melting compression. At the same time, the exfoliated rectorite lamellae resulted in enhancement of strength and modulus of SPI plastics, which may dissolve the shortcoming of plasticization to some extent. The highest strength happened on 12 wt % rectorite loading, which reached 12.92 MPa by almost twice of pure SPI plastics [122].

Gelatin-based bio-nanocomposites

Gelatin is prepared by the thermal denaturation of collagen, isolated from animal skin and bones, with very dilute acid. It can also be extracted from fish skins. There are two types of gelatin (type A and B), depending on whether or not the preparation involved an acid or alkaline pretreatment that converts asparagines and glutamine residues to their respective acids and results in higher viscosity. Acid pretreatment (type A gelatin) utilizes pigskin, while alkaline treatment (type B gelatin) makes use of cattle hides and bones [30]. The breakdown of collagen to gelatin proceeds in two steps: (1) thermal denaturation, occurring at approximately 40 °C, which cleaves hydrogen and electrostatic bonds, and (2) hydrolytic breakdown of covalent bonds [123].

Gelatin has been known to form clear, flexible, strong, and oxygen-impermeable films when cast from aqueous solutions containing a plasticizer, such as glycerin or sorbitol. Film-forming applications of gelatin in the pharmaceutical and food industry include microencapsulation and manufacture of tablet and capsule coatings. Gelatin is also tested for the preparation of a bio-nanaocomposite with layered silicate such as MMT in order to improve the mechanical and water resistance properties of the polymer [52].

Zheng [52] prepared gelatin/MMT bio-nanocomposite using a solution intercalation method. Gelatin (type B, extracted from bovine skin) solution was prepared separately by dissolving gelatin deionized water, heated to 70 °C, and a suspension of ultrasound pre-treated MMT was added. Then the mixture was cast, giving an intercalated or partially exfoliated bio-nanocomposite. The tensile strength and Young's modulus were improved notably (up to 60% and 80%, respectively), which varied with the MMT content as well as the pH of the gelatin matrix. The wet mechanical strength was also significantly improved in the bio-nanocomposite, which was mainly attributed to nanodispersion of MMT in the gelatin matrix and the barrier effect of MMT sheets to solvent molecules [52].

Kim et al. [124] examined the preparation of hydroxyapatite (HA) precipitate/gelatin matrix nanocomposites as promizing bone regenerative materials, by employing an electrospinning method. The HA precipitate/gelatin matrix nanocomposites were lyophilized and dissolved in an organic solvent, and then electrospun under controlled conditions. With this process, a continuous fiber with a diameter of the order of hundreds of nanometers was successfully generated. The internal structure of the nanofiber featured a typical nanocomposite, i.e., HA nanocrystals well distributed within a gelatin matrix. These nanocomposite fibers improved the bone-derived cellular activity significantly when compared to the pure gelatin equivalent [124].

Li et al. [125] examined nano-hydroxyapatite/gelatin composites in order to provide good biocompatibility and integration with bone tissue. In this work, nano-hydroxyapatite was formed in situ on the surface of chitosan–gelatin (CG) network films in tris-buffer solution containing $Ca(NO_3)_2$-Na_3PO_4). Results suggested that carboxyl groups and amino groups played crucial roles for HA formatting on the surface of CG network films and the average size of nano-hydroxyapatite crystalline decreasing with enhancing Gel content and increase with the increasing calcium and phosphate concentration. These nano-hydroxyapatite/ polymer composites showed good biocompatible and had biodegradable characteristics that might render them useful as components in tissue replacement material [125].

Conclusions

Nanocomposites are a new generation of polymers emerging into every aspect of our lives. They show great promise for potential applications as high-performance biodegradable materials, which are entirely new types of materials based on plant, animal, and other natural materials. When disposed of in compost, these are safely decomposed into CO_2, water, and humus through the activity of microorganisms. The CO_2 and water could become corn or sugar cane again through plant photosynthesis. Many consumer plastic products may be replaced by the natural bio-polymer-based plastics, which may be used for disposal plastic bag, cup, plates, contains and utensils, and others plastic products. These biodegradable plastics can be treated like food waste, which also gets in the plastics stream, so whatever is used to handle or separate food waste will be effective for biodegradable plastics. Also most biodegradable plastics will dissolve in warm water. Therefore, biodegradable materials offer a possible alternative to the traditional non-biodegradable polymers, especially in short life-time application and when their recycling is difficult and/or not economical. Thus, there is a considerable interest in replacing some or all of the synthetic plastics by biodegradable materials in many applications.

Although these materials have strong future prospects, their present low level of production and high costs restrict them from a wide range of applications. The most important factors to the formation of renewable plastics-based industries include cost reduction of biodegradable polymers, the improvement of mechanical strength and water resistance, as well as public and political acceptance.

In order for renewable polymer-based bio-nanocomposites to meet a wide range of applications, bio-nanocomposite formulation must be further researched and modified so that mechanical and other properties can be easily manipulated, depending on the end-users' requirements. We believe that the next generation of packaging materials will be to fit the requirements of preserving fruit, vegetable, beverage, wine, chocolate, and other foods. By adding appropriate nano-particles, it will be possible to produce packages with stronger mechanical, barrier and thermal performance. To food safety, nano-structured materials will prevent the invasion of bacteria and micro-organisms. Embedded nano-sensors in the packaging will alert the consumer if a food has gone bad. To the agriculture, the use of biodegradable materials can promote sustainable and environmentally friendly cultivation and reduce the contamination of the soil and pollution of landscape in rural areas. In all, natural polymer-based film materials originating in controlled bio-nanocomposites pave the way to a much broader range of applications, and open a new dimension for plastics and composites in the future.

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