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Polymer blends and composites from renewable resources

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Abstract

This article reviews recent advances in polymer blends and composites from renewable resources, and introduces a number of potential applications for this material class. In order to overcome disadvantages such as poor mechanical properties of polymers from renewable resources, or to offset the high price of synthetic biodegradable polymers, various blends and composites have been developed over the last decade. The progress of blends from three kinds of polymers from renewable resources—(1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid; and (3) polymers from microbial fermentation, such as polyhydroxybutyrate—are described with an emphasis on potential applications. The hydrophilic character of natural polymers has contributed to the successful development of environmentally friendly composites, as most natural fibers and nanoclays are also hydrophilic in nature. Compatibilizers and the technology of reactive extrusion are used to improve the interfacial adhesion between natural and synthetic polymers.

Keywords: Polymer; Blend; Composite; Renewable resource; Biodegradable

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Contents

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1. Introduction

Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. Generally, polymers from renewable resources (PFRR) can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Like numerous other petroleum-based polymers, many properties of PFRR can also be improved through blending and composite formation.

The study and utilization of natural polymers is an ancient science. Typical examples, such as paper, silk, skin and bone arts, can be easily found in museums around the world. However, the availability of petroleum at a lower cost and the biochemical inertness of petroleum-based products have proven disastrous for the natural polymers market. It is only after a lapse of almost 50 years that the significance of eco-friendly materials has been realized once again. These ancient materials have rapidly evolved over the last decade, primarily due to the issue of the environment and the shortage of oil. Modern technologies provide powerful tools to elucidate microstructures at different levels, and to understand the relationships between structures and properties. These new levels of understanding bring opportunities to develop materials for new applications. The inherent biodegradability of natural polymers also means that it is important to control the environment in which the polymers are used, to prevent premature degradation. For example, the water solubility of many natural polymers raises their degradability and the speed of degradation, however, this moisture sensitivity limits their application. Another limitation of many natural polymers is their lower softening temperature.

The development of synthetic polymers using monomers from natural resources provides a new direction to develop biodegradable polymers from renewable resources. One of the most promising polymers in this regard is PLA, because it is made from agricultural products and is readily biodegradable. Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which in turn can be obtained by the fermentation of corn, sugar cane, sugar beat [1,2]. PLA is not a new polymer, however, better manufacturing practices have improved the economics of producing monomers from agricultural feedstocks, and as such PLA is at the forefront of the emerging biodegradable plastics industries.

In nature, a special group of polyesters is produced by a wide variety of micro-organisms as an internal carbon and energy storage, as part of their survival mechanism. Poly(β-hydroxybutyrate) (PHB) was first mentioned in the scientific literature as early as 1901 and detailed studies begin in 1925 [3,4]. Over the next 30 years, PHB inclusion bodies were studied primarily as an academic curiosity. The energy crisis of the 1970s was an incentive to seek naturally occurring substitutes for synthetic plastics, which sped up the research and commercialization of PHB. The brittleness of PHB was improved through copolymerization of β-hydroxybutyrate with β-hydroxyvalerate [5,6]. This family of materials, known as poly(3-hydroxybutyric acid-*co*-3-hydroxyvaleric acid) (PHBV), was first commercialized in 1990 by ICI. However, the high price of PHBV is still the major barrier to its wide spread usage.

Like most polymers from petroleum, polymers from renewable resources are rarely used by themselves. In fact, the history of composites from renewable resources is far longer than conventional polymers. In the biblical Book of Exodus, Moses's mother built the ark from rushes, pitch and slime—a kind of fiber-reinforced composite, according to the modern classification of material. During the opium war more than 1000 years ago, the Chinese built their castles to defend against invaders using a kind of mineral particle-reinforced composite made from gluten rice, sugar, calcium carbonate and sand.

Fibers are widely used in polymeric materials to improve mechanical properties. Vegetable fibers (e.g. cotton, flax, hemp, jute) can generally be classified as bast, leaf or seed-hair fibers. Cellulose is the major substance obtained from vegetable fibers, and applications for cellulose fiber-reinforced polymers have again come to the forefront with the focus on renewable raw materials [7–9]. Hydrophilic cellulose fibers are very compatible with most natural polymers. The reinforcement of starch with cellulose fibers is a perfect example of PFRR composites.

The reinforcement of polymers using fillers is common in the production and processing of polymeric materials. The interest in new nanoscale fillers has rapidly grown in the last two decades, since it was discovered that a nanostructure could be built from a polymer and a layered nanoclay. This new nanocomposite showed dramatic improvement in mechanical properties with low filler content. The reinforcement with filler is particularly important for polymers from renewable resources, since most of them have the disadvantages of lower softening temperatures and lower modulus. Furthermore, the hydrophilic behavior of most natural polymers offers a significant advantage, since it provides a compatible interface with the nanoclay.

Many natural polymers are hydrophilic and some of them are water soluble. Water solubility raises degradability and increases the speed of degradation, however, this moisture sensitivity limits their application. Blends and multilayers of natural polymers with other kinds of PFRR can be used to improve their properties. Blends can also aid in the development of new low-cost products with better performance.

These new blends and composites are extending the utilization of polymers from renewable resource into new value-added products.

2. Natural polymer blends

Wide ranges of naturally occurring polymers derived from renewable resources are available for various materials applications [10,11]. Some of them, such as starch, cellulose and rubber, are actively used in products today, while many others remain underutilized. Natural polymers can sometimes be classified according to their physical character. For example, starch and cellulose are classified into different groups, but they are both polysaccharides according to chemical classification. Table 1 lists some natural polymers surveyed by Kaplan [10].

These natural polymers perform a diverse set of functions in their native setting. For example, polysaccharides function in membranes and intracellular communication; proteins function as structural materials and catalysts; and lipids function as energy stores [10]. Nature can provide an impressive array of polymers that have the potential to be used in fibers, adhesives, coatings, gels, foams, films, thermoplastics and thermoset resins.

One of the main disadvantages of biodegradable polymers obtained from renewable sources is their dominant hydrophilic character, fast degradation

Table 1
List of natural polymers

Polysaccharides
- Plant/algal: starch, cellulose, pectin, konjac, alginate, caragreenan, gums
- Animal: hyluronic acid
- Fungal: pulluan, elsinan, scleroglucan
- Bacterial: chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran

Proteins
Soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatine, silks, resilin, polylysine, polyamino acids, poly(γ-glutamic acid), elastin, polyarginyl–polyaspartic acid

Lipids/surfactants
Acetoglycerides, waxes, surfactants, emulsan

Speciality polymers
Lignin, shellac, natural rubber

rate and, in some cases, unsatisfactory mechanical properties, particularly under wet environments. In principle, the properties of natural polymers can be significantly improved by blending with synthetic polymers. Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend. In the 1970s and 1980s, numerous blends of starch with various polyolefins were developed. However, these blends were not biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost. In this section, polymer blends only from natural raw materials are discussed.

Since the majority of natural polymers are water soluble, water has been used as a solvent, dispersion medium and plasticizer in the processing of many natural polymer blends [12]. Since proteins and polysaccharides are the main constituents of natural polymers, their interaction with water and with each other in a water medium give the structure–property relationships in these materials. An analysis of the glass transition temperature and thermal profile gives one of the best illustrations of the role of water in natural polymers.

Natural fiber-reinforced composites are one of the successful examples and will be discussed in detail in a later section.

2.1. Melt processed blends

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and its annual renewal [13]. However, by itself, pure starch is not a good choice to replace petrochemical-based plastics. It is mostly water soluble, difficult to process and brittle when used without the addition of a plasticizer. In addition, its mechanical properties are very sensitive to moisture content. Blending two or more chemically and physically dissimilar natural polymers has shown potential to overcome these difficulties.

Natural rubber has been blended with starch for a number of different applications. Arvanitoyannis et al. [14] reported on biodegradable blends based on gelatinized starch and 1,4-transpolyisoprene (gutta percha) for food packaging or biomedical applications. Components are mixed to an adequate degree of dispersion by thermal pressing. A series of blends of gutta percha with gelatinized starch, with and without plasticizers or compatibilizers, was prepared in an attempt to preserve the excellent biocompatibility of gutta percha. A low amount of plasticizer was incorporated into the blends to improve mechanical properties. The gas and water permeability values of the blends were found to be intermediate values between the two components. Carvalho et al. [15] studied the blending of starch with natural rubber. Thermoplastic starch/natural rubber polymer blends were prepared using natural latex and cornstarch. The blends were prepared in an intensive batch mixer at 150 °C, with the natural rubber content varying from 2.5% to 20%. The dispersion of rubber in the thermoplastic starch matrix was homogeneous because of the presence of the aqueous medium, with rubber particles ranging in size from 2 to 8 μm. The results revealed a reduction in modulus and tensile strength, making the blends less brittle than thermoplastic starch alone. Phase separation was observed in some compositions, which was dependent on rubber and plasticizer content (glycerol). Increasing the plasticizer content made the addition of higher amounts of rubber possible. The addition of rubber was, however, limited by phase separation, the appearance of which depended on the glycerol content. Scanning electron microscopy (SEM) showed good dispersion of the natural rubber in the continuous phase of the thermoplastic starch matrix. The process employed in this investigation called upon the use of both starch and latex in their natural form, without any kind of purification. Moreover, the presence of the non-rubber constituents of the latex was not only responsible for insuring the latex stability, but also for improving the compatibility between the thermoplastic starch and the natural rubber phases. Finally, glycerol seemed to contribute to both the plasticization of the starch and to the improvement of the starch/rubber interface.

Cellulose and starch are some of the most abundant biopolymers on earth. Since the origin of civilization, the excellent chemical and physical properties of these materials have made them a useful component in many applications. However, blends of starch and protein have not shown significant promise in biodegradable materials applications to date. The system of starch/protein, however, has been studied in food field [12,16]. Kokini et al. [16] studied starch conversion and protein/starch interaction during processing, and established a kinetic model for starch gelatinization and the effect of starch/protein interactions. Matveev et al. [12] studied the effect of water on the glass transition of protein, polysaccharides and blends, considering inter-macromolecular hydrogen and dipole–dipole interactions.

Warth et al. [17] used the technology of reactive extrusion to develop starch/cellulose acetate blends. Thermoplastic polysaccharides such as cellulose-2,5-actetate were produced by means of reactive processing technology that grafted cyclic lactones simultaneously onto polysaccharides, hydroxy-functionalized plasticizer, and optionally also onto hydroxy-functional fillers. Organosolv lignin, cellulose, starch and chitin were added for reinforcement of the polymer blends. Compatibility between oligolactone-modified cellulose acetate and fillers were markedly improved when fillers were added during the reactive extrusion process. As a result of the excellent compatibility of poly(ε-caprolactone) with numerous polymers, it has been possible to prepare a wide range of new polymer blends.

2.2. Aqueous blends

Many natural polymers cannot be melt processed, either because they degrade on or before melting (softening) or because they are designed to incorporate substances that do not stand high temperature (proteins, drugs, etc.). For these examples, aqueous blending is the preferred technology, particularly in biomedical applications.

Natural polymers are usually biocompatible and non-cytotoxic due to their similarity with living tissues. Biopolymers are an important source of material with a high chemical versatility and with high potential to be used in a range of biomedical applications [18,19]. A great variety of materials derived from natural sources have been studied and proposed for different biomedical uses, namely polysaccharides (starch, alginate, chitin/chitosan) or protein (soy, collagen, fibrin gel) and, as reinforcement, a variety of biofibers such as lignocellulosic natural fibers [20,21]. Starch-based polymers present enormous potential for wide used in the biomedical field, as these natural polymers are totally biodegradable and inexpensive when compared to other biodegradable polymers available [22–25]. Aqueous blends of soluble starch and cellulose acetate have been studied intensively [26–29] because these blends have a range of properties that make them suitable for use in a wide array of biomedical applications, ranging from bone replacement to engineering of tissue scaffolds and drug-delivery systems.

Starch-based thermoplastic hydrogels for use as bone cements or drug-delivery carriers have been developed through blending starch with cellulose acetate [26–28]. Pereira et al. [26] reported on biodegradable hydrogels, based on cornstarch/cellulose acetate blends, produced by free-radical polymerization with methyl methacrylate and/or an acrylic acid monomer. The polymerization was initiated by a redox system consisting of benzoyl peroxide and 4-dimethlyaminobenzyl alcohol at low temperature. Utilizing the biodegradable character of starch-based blends, with the biostability of the acrylic polymers poly(methyl methylacrylate (PMMA) and poly(acrylic acid) [30,31] used as the matrix of these systems, and the incorporation of the well-known ceramic compound hydroxylapatite [32], Espigares et al. [27] developed partially biodegradable acrylic bone cements based on cornstarch/cellulose acetate blends. Varying amounts of a biocompatible, osteoconductive and osteophilic mineral component such as hydroxylapatite were incorporated to confer a bone-bonding character to the bone cements in this type of applications. Arvanitoyannis and Biliaderis [28] reported on aqueous blends of methyl cellulose and soluble starch, plasticized with glycerol or sugars, prepared by casting or by extrusion and hot pressing. The observed T_g depression for these polymer blends was proportional to the plasticizer content (water, glycerol and sugars). Although glycerol had a greater depressing effect on T_g than sorbitol, the latter had a greater impact, as a plasticizer, on the mechanical properties (higher percentage elongation) of the soluble starch/methyl cellulose blends. Generally the tensile strength and flexural moduli of these blends were shown to decrease drastically with an increase in the total plasticizer content.

Lepeniotis et al. [29] prepared dry spin fibers by blending starch acetate (SA) with a degree of substitution (ds) of 2.1–3.0 with cellulose acetate (CA) with a ds of 2.5 to make 25–30 wt% blended solutions in acetone:water. To develop solubility and phase information, a modified central composite face/central composite circumscribe (CCF/CCC) statistical designed experiment at 5–10 wt% solids was completed. This was based on five factors: (1) acetyl value; (2) acetone versus water concentration; (3) ratio of SA to CA; (4) total weight of solids in the solution; and (5) mixing temperature. The resulting solubility information could be used to predict the stability of SA:CA blends at the higher concentration and temperature ranges commonly used for fiber spinning. The most significant factors influencing phase type was found to be SA concentration and the interaction of SA percentage and total solids concentration.

Psomiadou et al. [33] developed edible films made from natural resources—microcrystalline cellulose (MCC), methylcellulose (MC), cornstarch and polyols. Aqueous blends of MCC or MC and cornstarch with or without polyols were prepared by extrusion, hot pressed and studied. After conditioning at different relative humidities, their thermal, mechanical, and water and gas permeability properties were determined. An increase in water or polyol content showed a considerable increase in percentage elongation, but also a decrease in the tensile strength of films. The presence of high cellulose contents increased the tensile strength and decreased the water vapor transmission of the films. The increase in crystallinity with time resulted in decreased gas and water permeability. Peressini et al. [34] studied the rheological properties of starch/methylcellulose-based edible films. The flow curves showed shear-thinning behavior. Mechanical spectra and Cox–Merz superposition of steady-shear viscosity and dynamic viscosity were consistent with polymer solutions containing topological entanglement interactions of chains. Dispersion stability results showed total recovery of the viscoelastic properties of dispersions subject to high strains, as expected for entangled polymers. MC was the main factor influencing the apparent viscosity and viscoelastic properties.

Demirgoz et al. [35] developed a method to control the moisture sensitivity of starch/cellulose acetate blends through chemical modifications. In their work, starch-based blends with CA were chemically modified by chain crosslinking. This modification was based on the reaction between the starch hydroxyl groups and tri-sodium tri-meta phosphate. The resulting compounds were characterized by Fourier transform infrared (FTIR) and the respective properties were assessed and compared to the original materials by means of the hydration degree, the degradation behavior, contact angle measurements and mechanical testing. The results showed that the water uptake of these blends could be reduced by up to 15%, and that simultaneously stiffer materials with a less pronounced degradation rate could be obtained.

Levy et al. [36] reported on the design of a polysaccharide crossbridging protein which was comprised of a cellulose-binding domain from *Clostridium cellulovorans* ($\mathrm{CBD_{clos}}$) and a starch-binding domain from *Aspergillus niger* B1 ($\mathrm{SBD_{Asp}}$). The two genes were fused in-frame via a synthetic elastin gene to construct a cellulose/starch crossbridging protein (CSCP). The CSCP demonstrated a crossbridging ability in different model systems composed of insoluble or soluble starch and cellulose. The fact that different carbohydrate-binding modules maintained their binding capacity over a wide range of conditions, without the need for chemical reactions, makes them attractive domains for designing new classes of polysaccharide-binding domains with potential applications in the biomaterial field.

Other kinds of aqueous blends are made from chitosan. Kweon et al. [37] reported the preparation of aqueous blends of protein with chitosan. *Antheraea pernyi* silk fibroin (SF)/chitosan blend films were prepared by mixing aqueous solution of *A. pernyi* SF and acetic acid solution of chitosan. The conformation of *A. pernyi* SF in blended films was revealed to be a β-sheet structure, mainly due to the effect of using acetic acid as a mixing solvent. Blending with *A. pernyi* SF can enhance the thermal decomposition stability of chitosan. Lazaridou and Biliaderis [38] studied the thermo-mechanical properties of aqueous solution/cast films of chitosan (C), starch/chitosan (SC) and pullulan/chitosan (PC) using dynamic mechanical thermal analysis (DMTA) and large deformation tensile testing. Incorporation of sorbitol (10% and 30% d.b.) and/or adsorption of moisture by the films resulted in substantial depression of the glass transition (T_g) of the polysaccharide matrix due to plasticization. For the composite films there was no clear evidence of separate phase transitions of the individual polymeric constituents or a separate polyol phase; a rather broad but single drop of elastic modulus, E', and a single $\tan\delta$ peak were observed. Tensile testing of films adjusted at various levels of moisture indicated large drops in Young's modulus and tensile strength ($\sigma_{\max}$) with increasing levels of polyol and moisture; the sensitivity of the films to plasticization was in the order of SC > PC > C. Modeling of the modulus data with Fermi's equation allowed comparison among samples for the fall in modulus around the glass transition zone as a function of moisture content under isothermal conditions. Arvanitoyannis et al. [14] developed films of chitosan and gelatin by casting their aqueous solutions (pH ~4.0) at 60 °C and evaporating at 22 or 60 °C (low- and high-temperature methods, respectively). The physical (thermal, mechanical and gas/water permeation) properties of these composite films, plasticized with water or polyols, were studied. An increase in the total plasticizer content resulted in a considerable decrease of elasticity modulus and tensile strength, whereas the percentage elongation increased. The low-temperature preparation method led to the development of a higher percentage of renaturation (crystallinity) of gelatin, which resulted in a decrease, by one or two orders of magnitude, of CO_2 and O_2 permeability in the chitosan/gelatin blends. An increase in the total plasticizer content (water, polyols) of these blends was found to be proportional to an increase in their gas permeability.

Antibacterial starch/chitosan blend film formed under the action of irradiation was reported by Zhai et al. [39]. Starch/chitosan-blended films were prepared by irradiation of compression-molded starch-based mixtures in physical gel state with an electron beam at room temperature. The tensile strength and the flexibility of the starch film were significantly improved after the incorporation of 20% chitosan into the starch film. X-ray diffraction (XRD) and SEM analyses of starch/chitosan blend films indicated that there was an interaction and microphase separation between the starch and chitosan molecules. Furthermore, in order to produce a kind of antibacterial films, the starch/chitosan blend films were irradiated. After irradiation, there was no obvious change in the structure of the starch/chitosan blend films, but antibacterial activity was induced even when the content of chitosan was only 5%, due to the degradation of chitosan in blend films under the action of irradiation.

3. Aliphatic polyester blends

Aliphatic polyesters have been recognized for their biodegradability and susceptibility to hydrolytic degradation. Examples of this group are PLAs, which also have the advantage of controllable crystallinity and hydrophilicity, and therefore overall degradation rate [40–45]. Another family of polyesters being studied widely are poly(hydroxyalkanoate)s (PHAs) that occur in nature. They are produced by a wide variety of micro-organisms as an internal carbon and energy storage, as part of their survival mechanism [46]. Bacterially synthesized PHAs have attracted attention because they can be produced from a variety of renewable resources and are truly biodegradable and highly biocompatible thermoplastic materials. Biosynthesis and characterization of various copolymers, including copolymers of hydroxybutyrate (HB) with 3-hydroxyvalerate (3HV) [47,48], 3-hydroxypropionate (3HP) [49], 3-hydroxyhexanoate (3HH) [50] and 4-hydroxybutyrate (4HB) [51] have been developed. Over 90 different types of PHA consisting of various monomers have been reported and the number is still increasing [52].

3.1. Blends of PLA family

Among the family of biodegradable polyesters, polylactides (i.e. PLA) have been the focus of much attention because they are produced from renewable resources such as starch, they are biodegradable and compostable, and they have very low or no toxicity and high mechanical performance, comparable to those of commercial polymers. However, the thermal stability of PLAs is generally not sufficiently high enough for them to be used as an alternative in many commercial polymers applications [53]. Ikada et al. [54] studied various PLA blends to improve their thermal properties. A stereocomplex is formed from enantiomeric PLAs, poly(L-lactic acid) (PLLA) and poly(D-lactide) (i.e. poly(D-lactic acid) (PDLA)) due to the strong interaction between PLLA and PDLA chains [54]. The stereocomplexed PLLA/PDLA blend has a melting temperature (T_m) (220–230 °C) ca. 50 °C higher than those of pure PLLA and PDLA (170–180 °C), and can retain a non-zero strength in the temperature range up to T_m [55]. Moreover, the PLLA/PDLA blend has a higher hydrolysis resistance compared with that of the pure PLLA and PDLA, even when it is amorphous-made, due again to the strong interaction between PLLA and PDLA chains [56,57]. X-ray diffractometry and differential scanning calorimetry (DSC) elucidated that all the initially amorphous PLA films remained amorphous, even after autocatalytic hydrolysis for 16 (PDLLA film) and 24 (non-blended PLLA and PDLA films, PLLA/PDLA(1/1) blend film) months. Also, the melting peaks observed at around 170 and 220 °C for the PLLA/PDLA(1/1) blend film after the hydrolysis for 24 months were ascribed to those of homo- and stereocomplex crystallites, respectively, formed during heating at around 100 and 200 °C, but not during the autocatalytic hydrolysis.

On the basis of these findings, enantiomeric polymer blending is expected to enhance the thermal stability of the PLLA/PDLA blend in the melt compared with those of the pure PLLA and PDLA. Tsuji and Fukui [53] studied the films of poly(L-lactide) (i.e. PLLA) and poly(D-lactide) (i.e. PDLA), and their equimolar enantiomeric blend (PLLA/PDLA). The films were prepared and the effects of enantiomeric polymer blending on the thermal stability and degradation of the films were investigated isothermally and non-isothermally under nitrogen gas using thermogravimetry. The enantiomeric polymer blending was found to successfully enhance the thermal stability of the PLLA/PDLA films compared with those of the pure PLLA and PDLA films. The ΔE_{td} value of the L/D film was in the range of 205–297 kJ mol^{-1}, which was higher by 82–110 kJ mol^{-1} than the averaged ΔE_{td} value of the L and D films.

Controlling the hydrolytic degradability of PLAs is of great importance, and numerous studies have been undertaken to elucidate the effects of various components in the systems. Shinoda et al. [58] used poly(aspartic acid-*co*-lactide) (PAL) to accelerate the degradation of PLA. PAL, an amphiphilic copolymer obtained from aspartic acid and lactide, was found to be miscible with PLA and produced homogeneous blend films without impairing the inherent mechanical properties of PLA. The blend films maintained sufficient transparency, which is one of the most valuable advantages of pure PLA. The increased hydrophilicity of the surface suggests that PAL and poly(sodium aspartate-*co*-lactide) (PALNa) may be useful as antistatic agents for PLA films. The addition of a small amount of PAL enhanced the degradation rate of PLA in water, soil and compost. The blended PAL resisted hydrolysis unless it contacts water, which ensures that the blend products could have a long shelf life and be useful for a wide variety of applications. PAL was also found to be effective as an additive that increases the non-enzymatic hydrolysis rates of both PBS and polycaprolactone (PCL). PAL also improved the thermal stability of PLA containing an appreciable amount of residual catalyst.

PLLA is usually hard and brittle, which hinders its usage in medical applications, i.e. orthopedic and dental surgery. Poly DL-lactic acid (PDLLA) can degrade quickly due to its amorphous structure, thus the degradation time of PLLA/PDLLA blends can be controlled through various blending ratios. Chen et al. [59] prepared blends of biodegradable PLLA and PDLLA, in addition to a third component, the surfactant—a copolymer of ethylene oxide and propylene oxide—at various ratios using dichloromethane as a solvent. DSC data indicated that PLLA/PDLLA blends without the surfactant had two T_g values. With the addition of the surfactant, there was a linear shift of the single T_g as a function of composition, with lower percentages of PLLA producing lower glass transition temperatures, indicating that better miscibility had been achieved. Dynamical mechanical analysis (DMA) data showed that the 40/60 PLLA/PDLLA blends without the surfactant had high elastic modulus and elongation, and similar results were observed after adding 2% surfactant into the blends. The 50/50 PLLA/PDLLA/2% surfactant blend had the highest elastic modulus, yield strength and break strength compared with other ratios of PLLA/PDLLA/2% surfactant blends. The elongation at break of 50/50 PLLA/PDLLA was similar to that of PLLA. Again, the elongation at break of 50/50 PLLA/PDLLA/2% surfactant was almost 1.2–1.9 times higher than that of 50/50 PLLA/PDLLA and PLLA. Elongation of PLLA increased with the addition of PCL, but the strength decreased at the same time. In conclusion, adding PDLLA and surfactant to PLLA via solution blending may be an effective way to make PLLA tougher and more suitable for use in orthopedic or dental applications.

To achieve a similar outcome, Urayama et al. [60] developed blends of polylactides with high and low L-isomeric ratios of the lactate units (PLA99.0 and 77.0, where the numbers correspond to the L-ratios). The crystallinity of the blends was similar to that of the blends of PLLA and PDLLA. The glass transition behavior was indicative of the compatible nature of both polymers. The tensile modulus of the blends was almost identical irrespective of the blend ratio, while their tensile strength decreased with decreasing composition of PLA99.0. Above the T_g, the storage modulus of the blends dropped from $2–3\times10^9$ to $1–3\times10^6$ Pa and then increased to a different level depending on the crystalline nature of the blends. The biodegradability of the blends increased with decreasing composition of PLA99.0. This difference in degradability can be explained by a random packing model of local helices of the L-sequenced chains for the L-rich PLA samples [60].

3.2. Blends of PHA family

Bacterially synthesized PHAs attract much attention because they can be produced from a variety of renewable resources, and are truly biodegradable and highly biocompatible thermoplastic materials. Therefore, PHAs are expected to contribute to the construction of an environmentally sustainable society. Over 90 different types of PHA consisting of various monomers have been reported and the number is increasing. Some PHAs behave similarly to conventional plastics such as polyethylene and polypropylene, while others are elastomeric [61]. Therefore, blending offers much scope for expanding their range of applications.

The most representative member of this family is poly(3-hydroxybutyrate) (PHB). Due to its biodegradability and biocompatibility, PHA may well serve as a material for tissue engineering [62]. PHA, including fragile PHB, a flexible copolymer consisting of PHBV, and an elastomeric copolymer consisting of 3-hydroxyoctanoate and 3-hydroxyhexanoate (PHOH) may have promising applications as tissue scaffolds and cardiovascular tissue. Chen and colleagues [61,63,64] have systematically studied various PHB blends to suit biomedical applications. The biocompatibility of microbial polyesters PHB and poly(hydroxybutyrate-*co*-hydroxyhexanoate) (PHBHHx) were evaluated in vitro [61]. It was found that the growth of cells L929 was poor on PHB and PLA films, but the growth on the films made by blending PHB and PHBHHx showed a dramatic improvement. Biocompatibility was also strongly improved when these polymers were treated with lipases and NaOH, respectively. However, the effects of treatment were weakened when the PHBHHx content was increased in the blends. It was found that the lipase treatment increased the biocompatibility more than NaOH. After the treatment the biocompatibility of PHB was approximately the same as PLA, while PHBHHx and its dominant blends showed improved biocompatibility compared to PLA. It was also shown that chondrocytes proliferated better on the PHBHHx/PHB scaffolds than on the PHB one [63]. Furthermore, the films made from blending polyesters showed that the elongation to break of the blended PHBHHx/PHB film increased from 15% to 106% when the PHBHHx content in the blend increased from 40% to 60% [63].

Detailed studies have shown that the high degree of crystallization and rapid crystallization rate of PHB generates pores and protrusions on the PHB film surface. This coralloid surface could prohibit the attachment and growth of mammalian cells [65]. The presence of PHBHHx in PHB strongly reduced both the degree of crystallization and the crystallization rate of PHB. The low degree of crystallization of PHBHHx/PHB blends provided films with a fairly regular and smooth surface, which allowed cell attachment and growth, thus strongly improving the biocompatibility of PHB [65]. While these results explained the improvement in biocompatibility brought about by PHBHHx, they also demonstrated the feasibility of using polymer blends of PHBHHx/PHB as scaffold materials for tissue engineering.

Blends of the PHB family are usually compatible and co-crystallization is enhanced. Yoshie et al. [66] studied solid-state structures and crystallization kinetics of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) and PHB/PHB-HV blends. It was found that PHB and HV can co-crystallize, and the content in the co-crystalline phase was determined by high-resolution solid-state ^{13}C NMR spectroscopy. As co-crystallizable blends, both the blends show complete co-crystallization, i.e. the PHB content in the crystalline phase is the same as that of the whole blends, and the blends form a PHB-rich crystalline phase. On the other hand, the PHB/PHB-HV blends forming a PHB-rich crystalline phase had a thicker amorphous layer than that of the PHB-HV copolymers with the same overall HV content. Saad [67] studied the miscibility, melting and crystallization behavior of poly[(*R*)-3-hydroxybutyrate] (PHB) and oligo[(*R*,*S*)-3-hydroxybutyrate]-diol (oligo-HB) blends using a DSC. It was found that the thermograms of blends containing up to 60 wt% oligo-HB showed behavior characteristic of single-phase amorphous glasses with a composition-dependent T_g and a depression in the equilibrium melting temperature of PHB. The negative value of the interaction parameter, determined from the equilibrium melting depression, confirms miscibility between blend components. In parallel studies, glass transition relaxations of different melt-crystallized polymer blends containing 0–20 wt% oligo-HB were dielectrically investigated between –70 and 120 °C in the 100 Hz–50 kHz range. The results revealed the existence of a single α-relaxation process for blends, indicating miscibility between the amorphous fractions of PHB and oligo-HB.

3.3. PLA/PHB blends

PLA/PHB blends have been studied with the aim of producing PLA-based materials with a wide range of physical properties and improved processibility [68]. Ohkoshi et al. [68] and Koyama and Doi [69] studied the miscibility of binary blends of bacterial poly[(*R*)-3-hydroxybutyric acid] (P[(*R*)-3HB]) with poly[(*S*)-lactic acid] (P[(*S*)-LA]) of various molecular weights using DSC analysis, which revealed that the structure of P[(*R*)-3HB]/P[(*S*)-LA] blends was strongly dependent on the molecular weight of the P[(*S*)-LA] component. The blends of P[(*R*)-3HB] with P[(*S*)-LA] of M_w values over 20,000 showed two phases in the melt at 200 °C, while the blends of P[(*R*)-3HB] with P[(*S*)-LA] of M_w values below 18,000 were miscible in the melt over the whole composition range. On the basis of the relationship between the miscibility of blends and the molecular weight of the P[(*S*)-LA] component, the difference in the solubility parameters δ_1 and δ_2 of the blend components in the Flory–Huggins equation was estimated to be 0.34 (J cm^{-3}).

Zhang et al. [70] reported that PHB/PLA blends prepared by casting a film from a common solvent at room temperature were immiscible over the range of compositions studied, while the melt-blended sample prepared at high temperature showed some evidence of greater miscibility. The crystallization of PHB in the blends was affected by the level of PLA addition. The thermal history caused a depression of the melting point and a decrease in the crystallinity of PHB in the blends. Compared with plain PHB, the blends exhibited an improvement in mechanical properties. Ohkoshi et al. [68] studied the miscibility and phase structure of binary blends of poly[(*S*)-lactide] (PLA) with atactic poly[(*R*,*S*)-3-hydroxybutyrate] (ataPHB) of different molecular weights using DSC and optical microscopy. DSC thermograms for the blends of PLA and ataPHB with $M_w = 9400$ in the range from 0 to 50 wt% of ataPHB content showed a single glass transition temperature after melting at 200 °C, and the value decreased from 59 to 10 °C with an increase in ataPHB content, indicating that the PLA and low molecular weight ataPHB ($M_w = 9400$) are miscible in the melt at 200 °C within the ataPHB content up to 50 wt%. In contrast, the binary blends of PLA with high molecular weight ataPHB ($M_w = 140{,}000$) showed two glass transition temperatures, indicating that the binary blend was immiscible in the melt. The radial growth rate of PLA spherulites were accelerated by the addition of low molecular weight ataPHB components. X-ray results showed that the level of crystallinity of the PLA components in the melt-crystallized films were increased by the addition of a small amount of ataPHB component, suggesting that the addition of ataPHB-3 component facilitated crystallization of PLA components in the binary blends. The lamellar thickness of PLA crystals decreased slightly with an increase in ataPHB content, suggesting that ataPHB component was incorporated into the interlamellar region of PLA spherulites. The relaxation phenomena were detected at two different temperatures in the dynamic mechanical spectra for PLA/ataPHB blends (containing ataPHB contents over 15 wt%) crystallized at 120 °C, indicating that the partial phase separation of two components occurs in the amorphous phase during the isothermal crystallization process.

3.4. Other polyester blends

Yoo et al. [71] blended poly(*cis*-1,4-isoprene) (PIP) with poly(3-hydroxybutyrate) (PHB) to improve the mechanical properties of the PHB. With the change in the blend composition, there was virtually no shift in the T_g of either PIP or PHB, indicating that PHB and PIP were incompatible. To solve the issue of compatibility, poly(vinyl acetate), which is compatible with PHB, was grafted onto PIP, and the properties of the PHB/PIP-*g*-PVAc blend were characterized. The tensile properties and impact strength of the PHB/PIP-*g*-PVAc blends were found to be superior to the PHB/PIP blends.

He et al. [72] studied the effects of low molecular weight compounds with hydroxyl groups on the properties of PLLA. The spectra of the blends suggested that there were inter-associated hydrogen bonds between the PLLA chains and 4,4′-thiodiphenol (TDP) molecules. The thermal and dynamic mechanical properties of PLLA were greatly modified through blending with TDP, and the PLLA/TDP blends were found to possess a eutectic phase behavior. It was found that the properties of the blends were strongly dependent on the thermal history. In addition to TDP, PLLA blends with other low molecular weight hydroxyl compounds, including aromatic and aliphatic compounds, were also characterized.

Ha and Cho [73] reviewed the recent progress of polymer blends based on microbial polyesters. The blends of poly[(*R*)-3-hydroxybutyrate] (P(3HB)) or poly((*R*)-3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV)) with other synthetic polymers has attracted much interest as one approach to improve the inherent brittleness, as well as to reduce high production costs associated with microbial polyesters. Crystallization behavior, physical properties and biodegradation behaviors of the microbial polyester-containing blends are significantly affected by the nature of the blend partner component, depending on whether it is biodegradable or not and/or whether it is miscible with the microbial polyesters or not.

4. Blends of hydrophobic and hydrophilic polymers

Most natural polymers are hydrophilic materials since they contain either hydroxyl or polar groups. On the other hand, most synthetic biodegradable polymers, especially the aliphatic polyesters, are hydrophobic or sensitive to moisture. Blending these two kinds of polymers together is of significant interest, since it could lead to the development of a new range of biodegradable polymeric materials.

4.1. Starch/PLA blends

Polylactide polymers have gained enormous attention as a replacement for conventional synthetic packaging materials in the last decade. By being truly biodegradable, being derived from renewable resources and by providing consumers with extra end-use benefits such as avoiding paying the ‘green tax’ in Germany or meeting environmental regulations in Japan, PLAs are a growing alternative for packaging material in numerous demanding markets [74].

PLA and starch are both biodegradable polymers derived from renewable sources. Starch, a hydrophilic renewable polymer, has been used as a filler for environmentally friendly plastics for about two decades. PLA is a biodegradable polymer, but its applications are limited by its high cost. Blending starch with PLA is one of the most promising efforts, because starch is an abundant and cheap biopolymer and PLA is biodegradable with good mechanical properties. Starch granules become swollen and gelatinized when water is added or when they are heated, and water is often used as a plasticizer to obtain desirable product properties. Ke and Sun [75] characterized blends of starch and PLA in the presence of various water contents. It was found that the initial moisture content of the starch had no significant effect on its mechanical properties, but had a significant effect on the water absorption of the blends. The thermal and crystallization properties of PLA in the blend were not affected by moisture content. The blends prepared by compression molding had higher crystallinities than those prepared by injection molding. However, the blends prepared by injection molding had higher tensile strengths and elongations and lower water absorption values than those made by compression molding. The crystallinities of the blends increased greatly with annealing treatment at the PLA second crystallization temperature (155 °C). The decomposition of PLA indicated that PLA degraded slightly in the presence of water under the processing temperatures used.

The detailed thermal behaviours of the starch/PLA blends have been studied by DSC [76]. The experimental data was evaluated using the well-known Avrami kinetic model. The Avrami exponent, constant, half-time of crystallization, and degree of crystallinity were obtained. Talc, a nucleating agent, was also blended with PLA at 1% by volume (v/v) as a comparison. Starch effectively increased the crystallization rate of PLA, even at a 1% content, but the effect was less than that of talc. The crystallization rate of PLA increased slightly as the starch content in the blend was increased from 1 to 40%. An additional crystallization of PLA was observed, and it affected the melting point and degree of crystallinity of PLA.

Ke et al. [77] also studied the effect of amylose content in starches on the mechanical properties. Four dry cornstarches with different amylose content were blended at 185 °C with PLA at various starch:PLA ratios using a lab-scale twin-screw extruder. Starch with 30% moisture content was also blended with PLA at a 1:1 ratio. Each extrudate was ground and dried. The powder was mixed with about 7.5% plasticizer, and injection molded (175 °C) into test tensile bars. These were characterized for morphology, mechanical properties and water absorption. Starch performed as a filler in the PLA continuous matrix phase, but the PLA phase became discontinuous as starch content increased beyond 60%. Tensile strength and elongation of the blends decreased as starch content increased, but no significant difference was observed among the four starches at the same ratio of starch:PLA. The rate and extent of water absorption of starch/PLA blends increased with increasing starch. Blends made with high-amylose starches had lower water absorption than the blends with normal and waxy cornstarches.

Park and Im [78] reported blends of PLA with gelatinized starch. Starch was firstly gelatinized with various ratios of water/glycerol using a twin-screw mixer. Gelatinization of starch was found to lead to the destruction or diminution of hydrogen bonding in granules and a decrease in crystallinity of starch. DSC data showed that starch acted as a nucleating agent and glycerol as a plasticizer, contributing to an improvement in the crystallinity in the PLA blends. When the content of starch increased, the size of spherulites in PLA blends was smaller and less regular. In the case of PLA/pure starch blends, voids appeared that were formed by the separation of starch particles from the matrix. These voids were not observed in the PLA/gelatinized starch. Similar blends were also reported by Martin and Averous [79]. The mechanical properties gave a strong indication that a low level of compatibility existed in these blends. The blends showed two distinct T_g values. However, the T_g due to the PLA phase shifted toward the T_g of TPS with the blend composition, indicating some degree of interaction. Microscopic observations revealed non-uniformly dispersed PLA inclusions in the TPS matrix, confirming that phase separation has occurred.

Willett and Shogren [80] studied blends of starch and various thermoplastic resins to produce foams using a twin-screw extruder. Foams of cornstarch with PLA, poly(hydroxyester ether) (PHEE) or PHBV had significantly lower densities and greater radial expansion ratios than the control starch. Blends with other polyesters and CA had densities and expansion ratios between those of the control starch and the other polyesters. Most of the polymer occupied spherical to elongated domains 1–10 μm long, although PLA domains were much smaller. Surface polymer concentrations were larger than the bulk, and correlated with foam expansion and resistance to fragmentation.

Foams were also extruded using blends of PLA or PHEE with high amylose starch (70% amylose), wheat starch and potato starch. The addition of either resin significantly reduced the foam density and increased expansion. At constant relative humidity, compressive strength was a function of foam density only and not the type of resin or starch in the blend. Addition of the resins reduced the water sensitivity of the foams and increased the time needed for complete dissolution. Blends with PLA, PHEE or PHBV produced foams with densities comparable to commercial starch-based loose-fill foams.

Raghavan and Emekalam [81] examined the microstructural aspects of a starch/polyethylene/polylactic acid/vernonia oil composite. Polymer composite films containing different percentages of additives were melt processed and acid hydrolyzed. Scanning electron microscopy of the fracture surfaces of OsO_4 stained composite with vernonia oil showed that the vernonia oil was present at the interface of the starch/polyethylene. Tapping mode atomic force microscopy was used to obtain the pore size of the hydrolyzed polymer composite. The quantity of water passing through the porous acid hydrolyzed composite was found to depend on the thickness of film.

4.1.1. Compatiblizers used for starch/PLA blends

PLA and starch are two promising candidates for biodegradable polymer blends [82–88]. However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible, leading to poor adhesion between the two components, and hence poor and irreproducible performance. Various compatibilizers and additives have been investigated to improve the interfacial interactions of these blends. Wang et al. [82] used methylenediphenyl diisocyanate (MDI) to improve the interface and studied a blend of 55/45 (w/w) mixture of PLA and dried wheat starch in an intensive mixer with or without a low level of MDI. Blends with MDI had enhanced mechanical properties that could be explained by the in situ formation of a block copolymer acting as a compatibilizer. SEMs showed reduced interfacial tension between the two phases. The presence of MDI also enhanced the mechanical properties of the blend at temperatures above T_g. Water uptake by the PLA/starch blends with and without MDI did not differ.

The blends of PLA with various levels of wheat starch and MDI that were hot mixed at 180 °C then hot-pressure molded at 175 °C to form test specimens, were also studied [83] in terms of their mechanical properties, fracture microstructure and water absorption. Pure PLA had a tensile strength of 62.7 MPa and elongation of 6.5%. The blend with 45% wheat starch and 0.5 wt% MDI gave the highest tensile strength of about 68 MPa with about 5.1% elongation. The blend with 20% starch and 0.5 wt% MDI had the lowest tensile strength of about 58 MPa with about 5.6% elongation. Dynamic mechanical analysis showed that storage modulus increased and $\tan\delta$ decreased as starch level increased, but almost leveled off when the starch level reached 45% or higher. Water absorption of the blends increased significantly with starch content. Yet the blend, if waterproofed on its surface, has potential for short-term disposable applications.

Wang et al. [84] also studied the effect of starch moisture content on the interfacial interaction of an equal-weight blend of wheat starch and PLA containing 0.5% MDI by weight. Starch moisture (10–20%) had a negative effect on the interfacial bonding between starch and PLA. The tensile strength and elongation of the blend both decreased as starch moisture content increased. At 20% moisture level, starch granules embedded in the PLA matrix were observed to be swollen, resulting in poor strength properties and high water absorption by the blend. The effect of physical aging on the properties of the blends with or without MDI was also studied [85]. In this study, blends of PLA (1/1, w/w) and starch with or without MDI were evaluated for thermal and mechanical properties, as well as morphology, during the course of physical aging when stored for up to 12 months at 25 °C and 50% relative humidity. The blends were prepared by thermally blending PLA with wheat starch, cornstarch and/or high amylose cornstarch, with or without MDI. All samples exhibited the phenomena of physical aging. The samples with MDI aged more slowly, showing a slower reduction rate of excess enthalpy relaxation, than those without MDI. The mechanical properties decreased slowly as aging proceeded. The microstructure of these blends showed a reduced interaction between starch and PLA around the interface with aging.

Zhang and Sun [86] used dioctyl maleate (DOM) as a compatibilizer in blends of PLA/starch. Using DOM as a compatibilizer markedly improved the tensile strength of the blend, even at low concentrations (below 5%). When DOM functioned as a plasticizer at concentrations over 5%, significant enhancement in elongation was observed. Compatibilization and plasticization took place simultaneously according to the blends, mechanical properties and thermal behavior. With DOM as a polymeric plasticizer, thermal loss in the blends was not significant. Water absorption of PLA/starch blends increased with DOM concentration. DOM leaching in an aqueous environment was inhibited.

Other compatibilizers were also studied for the starch/PLA blends, such as poly(vinyl alcohol) (PVOH) [87] and PHEE [88]. PVOH containing unhydrolytic residual groups of poly(vinyl acetate) was shown to have a good compatibility with starch. It was added to a starch and PLA blend (50/50, w/w) to enhance compatibility and improve mechanical properties. The increasing molecular weight of PVOH was also shown to affect water absorption. The blend containing gelatinized starch had higher tensile strength. However, gelatinized starch also resulted in increased water absorption. A study of injection molded tensile bars composed of native cornstarch, PLA and PHEE showed that the rates of weight loss increased in the order pure PLA (~0%/year) < starch/PLA (0–15%/year) < starch/PHEE/PLA (4–50%/year), and increased with increasing starch and PHEE contents.

4.1.2. *Reactive blending*

Reactive extrusion is advantageous since it is a solvent-less process that allows the combination of several chemical manipulations in a continuous fashion. Jun [89] reported reactive blends of starch/PLA with a reactive agent during the extrusion process. The affects of the reactive blending were investigated and significant improvements were confirmed by measuring the tensile strength and elongation at break, IR spectra and DSC.

Interfacial compatibilization can be achieved via two different strategies depending on the nature of the polyester chains [90]. In the case of starch/PLA compositions, PLA chains were grafted with maleic anhydride through a free radical reaction conducted by reactive extrusion. The maleic anhydride-grafted PLA chains (MAG-PLA) enhanced the interfacial adhesion with granular starch. As far as starch/PLA blends were concerned, the compatibilization was achieved via the interfacial localization of amphiphilic graft copolymers formed by the grafting of PCL chains onto a polysaccharide backbone such as dextran. The PCL-grafted polysaccharide copolymers were synthesized by controlled ring-opening polymerization of ε-caprolactone, which proceeded via a coordination–insertion mechanism. These compatibilized starch/PLA compositions displayed improved mechanical properties as determined by tensile testing, and more rapid biodegradation as measured by composting testing.

4.2. *Starch/PHB blends*

In recent years there has been considerable interest in the PHA family of biodegradable polyesters. These materials, produced by fermentation, occur as intracellular inclusions within the cytoplasm of many prokaryotic organisms. The most well-known PHA is poly(hydroxybutyrate) (PHB). The principal shortcomings of bacterial PHB that limit its usefulness as a thermoplastic material are its thermal instability and brittleness. For these reasons, there has been much interest recently in the preparation and characterization of blends based on PHB. Willett and Shogren [80] reported on blends of starch and various thermoplastic resins to produce foams. The results showed that foams of cornstarch with PHBV had significantly lower densities and greater radial expansion ratios than the control starch.

Zhang et al. [91] studied blends of poly(3-hydroxybutyrate) (PHB) and starch acetate (SA), and found that the PHB/SA blends were immiscible. Melting temperatures of PHB in the blends showed some shift with an increase of SA content. Melting enthalpy of the PHB phase in the blend was close to the value for pure PHB. The glass transition temperatures of PHB in the blends remained constant at 9 °C. FTIR absorptions of hydroxyl groups of SA and carbonyl groups of PHB in the blends were found to be independant of the second component at 3470 and 1724 cm^{-1}, respectively. Crystallization of PHB was affected by the addition of the SA component, both from the melt on cooling and from the glassy state on heating. Temperature and enthalpy of non-isothermal crystallization of PHB in the blends were much lower than those of pure PHB. Crystalline morphology of PHB crystallized from the melt under isothermal conditions varied with SA content. The cold crystallization peaks of PHB in the blends shifted to higher temperatures compared with that of pure PHB.

Willett et al. [92] utilized grafted copolymers of starch and glycidyl methacrylate (starch-*g*-PGMA) to improve the mechanical properties of composites with PHBV. In general, the tensile and flexural strengths of the composites were greater with starch-*g*-PGMA compared to untreated starch, and increased with increasing graft content. Grafting did not significantly change the modulus and elongation of these blends. All samples gained weight after immersion in water for 28 days. Tensile strength and modulus decreased with water sorption, while the fracture toughness significantly increased with grafted starch. SEMs of cryogenic fracture surfaces showed improved adhesion between the starch-*g*-PGMA and the PHBV matrix.

4.3. *PHB/cellulose derivative blends*

PHB has been blended with other polymers to improve the inherent brittleness as well as to reduce the high production cost of the microbial polyesters. Crystallization behavior, physical properties and biodegradation behaviours of the microbial polyester-containing blends are significantly affected by the nature of the blend partner component, depending on whether it is biodegradable or not and/or whether it is miscible with the microbial polyesters or not. Cellulose derivates have attracted much interest for their compatibility with PHB.

Zhang et al. [93] investigated the miscibility, crystallization and melting behavior, and phase morphology of poly(3-hydroxybutyrate) (PHB) and ethyl cellulose (EC) blends prepared by casting films. The blends showed composition-dependent glass transitions, the temperature position increased with a decrease of PHB content in the blends, and reached the maximum value for the EC component. After melt quenching or cooling via DSC, only a low temperature T_g was found, corresponding to that of the PHB phase in the blends. This T_g remained almost unchanged at about 5 or 9 °C for all the blends. The hydrogen bonding of the hydroxyl groups of EC was found to be stronger than that of the hydroxyl group in EC with carbonyl groups in PHB. Unlike the PHB component, the blends displayed no crystallization when cooled from the melt during the DSC non-isothermal crystallization runs. The growth of PHB spherulites was delayed by EC content. No evidence of phase separation of the blends was observed by SEM studies.

Maekawa et al. [94] studied the phase behavior and crystallization kinetics for the binary blend poly(hydroxybutyrate) (PHB)/cellulose propionate (CP). The results show that the blends are miscible, as evidenced by the observation of a single composition-dependent T_g, a depression of the equilibrium melting temperature of PHB, and a decrease in the spherulitic growth rate of the PHB component. A study of the tensile properties has shown that an improvement in the ductility of PHB is brought about by blending with CP.

El-Shafee et al. [95] studied blends of poly(3-hydroxybutyrate) (PHB) with cellulose acetate butyrate (CAB) by solution casting from chloroform solutions at different compositions. CAB/PHB blends were found to be miscible in the melt state, as evidenced by a single T_g for each composition, a depression in the equilibrium melting point of PHB, and a marked reduction in the spherulites growth rate of PHB in the PHB/CAB blends. The Flory–Huggins interaction parameter (χ_{12}), obtained from melting point depression data, is composition dependent, and its value is always negative. The nucleation factor, K_g, was determined using a Lauritzen–Hoffman model. The K_g values for the PHB in the blends are considerably lower than the K_g value in the pure homopolymer. The phase structure of the blend in the solid state as revealed by single angle X-ray scattering is characterized by the presence of a homogeneous amorphous phase situated mainly in the interlamellar regions of crystalline PHB, and consisting of CAB molecules and uncrystalline PHB chains. Similar results were also reported by Wang et al. [96]. With an increase in CAB content, the degree of crystallinity and the melting temperature of the PHB phase decreased, and this broadened the narrow processability window of PHB. As the elongation at break increased from 2.2% to 7.3%, the toughness and ductility of PHB improved.

4.4. *Chitosan/PLA blends*

Chitosan is a natural polymer, non-toxic, edible, biodegradable, derived by deacetylation of chitin and is the second most abundant biopolymer in nature after cellulose. Chitosan has been used in edible coatings or films to extend the shelf life of foodstuffs, e.g. fruit, meat, and fish and seafood. However, its high sensitivity to moisture limits its applications for packaging. One strategy to overcome this drawback is the blending of chitosan with moisture-resistant polymers, while maintaining the overall biodegradability of the products. Suyatma et al. [97] reported on biodegradable film blends of chitosan with PLA by solution mixing and film casting. The main goal of these blends was to improve the water vapor barrier of chitosan by blending it with a hydrophobic biodegradable polymer from renewable resources. The incorporation of PLA with chitosan improved the water barrier properties and decreased the water sensitivity of chitosan film. However, the tensile strength and elastic modulus of chitosan decreased with the addition of PLA. Mechanical and thermal properties revealed that chitosan and PLA blends are incompatible, consistent with the results of FTIR analysis that showed the absence of specific interaction between chitosan and PLA.

4.5. *PHB/chitosan and PHB/chitin blends*

Ikejima et al. [98] developed films of blended microbial poly(3-hydroxybutyric acid) (PHB) with α-chitin and chitosan as completely biodegradable polyester/polysaccharide composites. DSC revealed that the crystallization of PHB in these blends is suppressed when the proportion of polysaccharide is increased. The same tendency was evident from the FTIR band intensity of the carbonyl stretching absorption from PHB. Chitosan was found to have a stronger ability to suppress the crystallization of PHB than α-chitin. PHB in the blends was found by ^{13}C NMR spectroscopy to be trapped in the 'glassy' environment of the polysaccharide. Upon blending with PHB, the chitosan resonances are significantly broadened as compared to the chitin resonances. It is suggested that hydrogen bonds may be formed between the carbonyl groups of PHB and the amide NH groups of chitin and chitosan.

The crystallization behavior and environmental biodegradability were also investigated for the films of bacterial poly(3-hydroxybutyric acid) (PHB) blends with chitin and chitosan [99]. The blend films showed XRD peaks that arose from the PHB crystalline component. It was suggested that the lamellar thickness of the PHB crystalline component in the blends was large enough to show detectable XRD peaks, but was too small to show an observable melting endotherm in the DSC thermogram and the crystalline band absorption in the FTIR spectrum. In the PHB/chitin and PHB/chitosan blends, thermal transition temperatures of PHB amorphous regions observed by dynamic mechanical thermal analysis were almost the same as that of neat PHB. Both the PHB/chitin and the PHB/chitosan blend films biodegraded in an environmental medium. Several blend films showed faster biodegradation than the pure-state component polymers.

Cheung et al. [100] studied the phase structure of poly (*R*)-(3-hydroxybutyrate) (PHB)/chitosan and poly (*R*)-(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(HB-*co*-HV))/chitosan blends using ^{1}H CRAMPS (combined rotation and multiple pulse spectroscopy). ^{1}H T_1 was measured with a modified BR24 sequence that yielded an intensity decay to zero mode rather than the traditional inversion-recovery mode. Single exponential T_1 decay is observed for the β-hydrogen of PHB or P(HB-*co*-HV) at 5.4 ppm and for the chitosan at 3.7 ppm. T_1 values of the blends are either faster than or intermediate to those of the plain polymers. The $T_{1\rho}$ decay of β-hydrogen is bi-exponential. The slow $T_{1\rho}$ decay component is interpreted as the crystalline phase of PHB or P(HB-*co*-HV). The degree of crystallinity decreases with increasing wt% of chitosan in the blend. The fast $T_{1\rho}$ of β-hydrogen and the $T_{1\rho}$ of chitosan in the blends either follow the same trend as or are faster than the weight-averaged values based on the $T_{1\rho}$ of the plain polymers. Together with the observation by DSC of a melting point depression and one effective T_g in the blends, the experimental evidence strongly suggests that chitosan is miscible with either PHB or P(HB-*co*-HV) at all compositions.

Acrylic acid was grafted to ozone-treated poly(3-hydroxybutyric acid) (PHB) and PHBV membranes. The resulting membranes were further grafted with chitosan or chitooligosaccharide (COS) via esterification [101]. Acrylic acid grafting can increase biodegradability, whereas chitosan and COS grafting can reduce the biodegradability.

5. Multilayer composites

Natural polymers such as starch and protein are potential alternatives to petroleum-based polymers for a number of applications. An inherent problem with the use of natural polymers (e.g. thermoplastic starch) as biodegradable materials is their sensitivity to moisture. One approach toward solving this problem is to laminate thermoplastic starches with water-resistant, biodegradable polymers. Of the different techniques for lamination, co-extrusion or multilayer extrusion has many advantages, such as the entire process is completed in a solvent-free single step.

5.1. Multilayer extrusion

Multilayer co-extrusion has been widely used in the past decades to combine the properties of two or more polymers into one single multilayered structure [102–105]. Much progress in multilayer extrusion has been made and new technology can provided capabilities to co-extrude materials with viscosity ratios up to 40:1. It is also possible to co-extrude materials with melt temperature differences as high as 80 °C without causing damage or thermal degradation to heat-sensitive materials. The layer thickness can also be adjusted to produce minimal skin layers of 2% [106].

A numerical simulation of multilayer co-extrusion flows has been undertaken for polymer melts used in producing multilayered plastic sheets [106]. Viscosity data and other material properties are used for typical melts and adhesives applied in co-extrusion. Industrial designs have been employed for the feed-block geometry and multi-manifold vane flat dies. The analysis is based on the lubrication approximation theory, which treats the flow locally as fully developed. A Newton–Raphson iterative scheme is employed to solve the equations for a pressure-drive flow of a number of layers ($N \leqslant 11$). For a given total flow rate ratios (or correspondingly total sheet thickness and individual layer thickness), the solution provides the interface locations and individual pressure drops that each extruder has to supply. The shear stresses at the channel walls are checked as a criterion for proper design. The die design or melt combinations are altered to produce smooth shear stresses with no humps or discontinuities at the points of confluence. Adiabatic temperature rises are also computed based on the pressure drops in the system. Such an analysis provides a quick qualitative insight into the proper design and melt combinations for multilayer sheet co-extrusion.

Co-extrusion produces multilayer materials comprised of two or more separate polymers. In one case, the middle layer was comprised of low-cost thermoplastic starch and the two external layers were made of another biodegradable polymers. These kinds of multilayer products decrease the moisture sensitivity and improve the mechanical properties of starch-based materials. Wang et al. [104] studied the effects of extrusion and formulation variables on the structure and properties of starch/polyester laminates. Three-layer polyester/starch/polyester sheets were prepared using a twin-screw extruder for the starch/water center layer, a single-screw extruder for the outer polyester layers, and a feed-block and coat-hanger-type sheet dye. Overall sheet and coating thicknesses were more uniform as coating polymer viscosity decreased, the starch melt viscosity increased and feed-block/die temperature increased. Peel strengths were 1–2 orders of magnitude larger for high molecular weight compared to low molecular weight PCL. High peel strengths were associated with rough, wavy interfaces (interfacial instability). The addition of a plasticizer such as glycerol and sorbitol to the starch decreased peel strengths. Peel strengths varied little with type of polyester coating, except perhaps for polylactic acid and polyesteramide, which were more difficult to peel. Some possible applications of laminated starch include food packaging and the controlled release of drugs and pesticides.

5.2. *Interfaces between multi-layers*

One of the key issues to develop a multi-layers composite is the interfaces between materials. Multilayer films based on plasticized wheat starch (PWS) and various biodegradable aliphatic polyesters have been prepared through flat film co-extrusion and compression molding [107]. PLA and PHBV were chosen as the outer layers of the stratified polyester/PWS/polyester film structure. The main goal of the polyester layers was to significantly improve the properties of PWS in terms of its mechanical performance and moisture resistance. Since no specific compatibilizer or tie layer was added, the properties of subsequent films relied on the compatibility between the respective materials only. The effects of glycerol content in PWS, polyester type and film composition on the mechanical properties and adhesion strength of multilayers were investigated, and the conditions for optimal product performance were examined. These multilayer films may be suitable for applications in food packaging or disposable articles.

A co-extruded starch/PLA polymeric film was developed [108]. The main mechanical properties of this film were Young's modulus at 2340 MPa, elongation at break at 50%, and contact angle at 118°. Mineralization of the material's carbon content was carried out using the appropriate experimental methods of the International Standard Organisation. Independent of the biodegradation medium used, the percentage of mineralization was better than the required 60% value for the definition of a biodegradable material. Moreover, repartitioning of the material's carbon between the various degradation products produced was quantified throughout the duration of experimental runs. The presence of starch was found to facilitate biodegradation of the polylactic component, especially in liquid media.

6. Fiber-reinforced composites

Fiber-reinforced plastics have successfully proven their value in various applications because of their excellent specific properties, e.g. high strength and stiffness, and low weight. Fiber-reinforced composites have been discussed and reviewed by many authors previously, and many books are available. In that respect, natural fibers are of basic interest since they not only have the functional capability to substitute the widely used glass fibers, but they also have advantages from the point of view of weight and fiber–matrix adhesion, specifically with polar matrix materials. They have good potential for use in waste management due to their biodegradability and their much lower production of ash during incineration.

Wollerdorfer and Bader [8] investigated the influence of plant fibers such as flax, jute, ramie, oil palm fibers and fibers made from regenerated cellulose on the mechanical properties of biodegradable polymers. The so-called biocomposites were produced by embedding natural fibers (e.g. flax, hemp, ramie) into a biopolymeric matrix made of derivatives from cellulose, starch, lactic acid, etc. [9,109]. Bledzki and Gassan [7] reviewed a number of composites reinforced by cellulose-based fibers. The article gave a survey of physical and chemical treatment methods that improved the adhesion between the cellulose fiber and conventional polymers. The different treatments changed a number of properties of the natural fibers, such as the degree of hydrophilicity, so that moisture effects in the composite could be reduced. To produce hydrophobic properties in natural fibers, a special treatment, termed acetylation, was introduced. This section will focus on fiber-reinforced composites from renewable resources: natural fibers and natural matrix. One of the most important advantages of using natural fibers to reinforce natural polymers is their compatibility.

6.1. Starch reinforced with cellulose fibers

Starch reinforced by cellulose is a typical example of natural polymer composites. These materials have the advantages of being renewable, biodegradable, abundantly available and inexpensive, and as such they have attracted great attention in the last two decades. Like many other fiber-reinforced composites, improving mechanical properties is one of the major driving forces to reinforce starch-based materials using cellulose fibers. Wollerdorfer and Bader [8] reported that reinforced thermoplastic wheat starch was four times better (37 N/mm^2) than without fibers. The reinforcement of cellulose diacetate and starch blends caused a stress increase of 52% (55 N/mm^2) and 64% (25 N/mm^2), respectively. Enhanced properties were obtained by using various natural cellulosic fibers, such as sisal, cotton, bamboo, jute, straw, kenaf and wood. Compared to inorganic fillers, composites based on nature fibers offer a number of benefits. These include a renewable nature, a wide variety of fillers available throughout the world, low energy consumption, low cost, low density, high specific strength and modulus (desirable fiber aspect ratio), high sound attenuation, comparatively easy processability (due to their flexibility and non-abrasive nature, which allow high filling levels, resulting in significant cost savings), and a relatively reactive surface (which can be used for grafting specific groups) [110]. The products according to their processing methods are reviewed as follows.

6.1.1. Hot press molding and foaming

Romhány et al. [111] reported on thermoplastic starch-based composites containing flax fibers in unidirectional and crossed-ply arrangements, produced by hot pressing using the film stacking method. The mechanical response and failure mode of the composites strongly depended on the flax content and the flax fiber lay-up. It was established that the tensile strength increased with increasing flax fiber content (up to 40 wt%), but stayed almost constant above that value. In the case of 40 wt% unidirectional fiber reinforcement, the tensile strength of the composite was three times greater than that of the pure starch matrix. The flax fiber reinforcement increased the tensile modulus of the pure starch by several orders of amplitude.

Matsui et al. [112] used a mixture of 90% cassava bagasse (non-extracted starch) and 10% Kraft paper for producing composites. Kraft paper was added as a source of long fibers, in order to improve the mechanical properties of the material. The material prepared had similar characteristics to the molded fiber packaging made using recycled paper, as used in egg boxes. However, cassava bagasse had advantages over recycled paper, in view of the fact that it is obtained from known and renewable sources.

Alvarez et al. [113] reported on biodegradable polymers based on starch reinforced by short sisal fibers with a range of fiber content of 5–15 wt%. Equations obtained from microscopic mass balances for diffusion in solids were used to predict the absorbed humidity in both components (the sisal fibers and biodegradable polymer) and in the composites as a function of time. Different model predictions of the composite diffusion coefficients as a function of filler concentration were also examined, and they were found to be in agreement with the experimental results.

Curvelo et al. [114] used cellulosic fibers from *Eucalyptus urograndis* pulp as reinforcement for thermoplastic starch in order to improve its mechanical properties. The composites were prepared with regular cornstarch plasticized with glycerin and reinforced with short cellulosic fibers (16% w/w) from bleached pulp. The fibers were added to the thermoplasticized starch directly in an intensive batch mixer at 170 °C. The mixture was hot pressed to 2–3 mm thick plates and then cut to prepare the specimens for mechanical tests. The composite showed an increase of 100% in tensile strength and more than 50% in modulus with respect to the non-reinforced thermoplastic starch. SEMs of fractured surfaces revealed very good adhesion between the fibers and the matrix. The results obtained clearly showed the advantages in the use of thermoplastic starch reinforced with cellulosic fibers, a natural, cheap and abundant material. Carvalho et al. [115] characterized compounds of conventional cornstarch and glycerol reinforced with cellulose fibers by high performance size exclusion chromatography. The compounds and composites were prepared in an intensive batch mixer at 150–160 °C, with glycerol and fiber contents in the range of 30–50 wt% and 1–15 wt%, respectively. The results showed that an increase in glycerol content reduced starch degradation, whereas an increase in fiber content led to increased degradation. The changes in the chromatographic profiles were more pronounced in the high molecular weight fraction, corresponding to amylopectin. The polydispersity index of the matrix was lower than that of native starch, due to selective breakage of large amylopectin molecules as a result of shear-induced fragmentation.

Starch-based foams have been developed to replace the expanded polystyrene foam packaging currently in use. Starch-based foams are water sensitive, and thus their mechanical properties are susceptible to changes in relative humidity. Lawton et al. [116] added fiber to baked cornstarch foams to improve their mechanical properties. Foam trays were made with the fiber content of the batter ranging from 2.5 to 45 wt%. The starch/fiber composite foam trays were formed by heating a starch-based batter inside a closed mold. The trays were stored at different relative humidities (5%, 20%, 50%, 81% and 93%) for 1 week prior to mechanical testing. The strength of the foam trays increased as the fiber content of the trays was increased (up to a maximum fiber content of about 15 wt%). Trays containing between 15 and 30 wt% fibers had no significant difference in tray strength. Trays containing more than 30 wt% fiber had lower tray strength. The lower tray strength was thought to be due to the lack of uniform fiber distribution at high fiber content. Displacement of the trays at break was also affected by fiber content.

6.1.2. *Extrusion*

Ganjyal et al. [117] reported on the formation of starch acetate/corn fiber foams prepared by extrusion. Cornstarch was acetylated to introduce thermoplastic properties. Cornstalks were treated with sodium hydroxide to remove the lignin and to obtain purified cellulose fibers. Starch acetate was blended with treated fiber at concentrations of 0%, 2%, 6%, 10% and 14% (w/w) and extruded at 150 °C in a co-rotating twin-screw extruder with 12–18% w/w ethanol content and 5 wt% talc as a nucleating agent. Fiber incorporation at the lower concentrations enhanced the physical properties of the foams. Fiber contents greater than 10% decreased expansion, and increased density and shear strength. Good compatibility between starch and corn fiber was observed.

6.1.3. *Injection molding*

Funke et al. [118] reported that different types of starch were processed in blend systems with natural plasticizers and commercial fibers by conventional extrusion and injection molding techniques. Blend systems with 2–7% fibers resulted in an increase in tensile strength and water resistance of these products. Averous et al. [119] studied the interactions between leafwood cellulose fibers and a plasticized wheat starch matrix. After extrusion and injection molding, the properties of the different plasticized starch (TPS)-based composites were analyzed. DMTA analysis showed a strong evolution of the main relaxation temperature, which could be linked to the existence of cellulose/starch interactions resulting in a decrease of starch chain mobility. This phenomenon was consistent with the evolution of mechanical behavior. SEM observations also correlated that hypothesis. Similar results were also found for starch-based materials reinforced by lignocellulose fibers [120] using extrusion and injection processing. The results were consistent with static mechanical behavior, which varies according to the filler content (up to 30 wt%), natural fiber (cellulose versus lignocellulose) and fiber length (from 60 μm to 1 mm). It was also shown that the addition of cellulose fillers improved the thermal resistance of these biocomposites.

6.2. *Other starch/cellulose composites*

Cellulose microfibrils were used as a cheap and environmentally friendly filler to provide thermal stabilization and decrease the water uptake of starch-based materials, preserving the aptitude of processing of plasticized materials and biodegradability [121]. It was found that a strong increase in thermomechanical stability could be obtained with only a few percent of filler, whereas the water sensitivity linearly decreased with cellulose microfibril content. Another problem that limits the use of starch is its brittleness due to the anarchical growth of amylose crystals with time. It was shown that crystallization of amylose could be oriented by the presence of cellulose.

Starch-based composites reinforced with cellulose acetate have also been considered as biomaterials. Marques et al. [122] evaluated their cytotoxicity and cell adhesion. The results showed that starch-based polymers exhibited a cytocompatibility that might allow for their use as biomaterials. Alvarez and Valquez [123] studied the thermal behavior of cellulose derivatives/starch blends with different short sisal fiber content, using TGA/DTGA under dynamic conditions. Two peaks were found: the first close to 334 °C and the second at 369 °C. The apparent activation energy value of the first peak slightly increased as well as the maximum temperature value. The apparent activation energy values for the second peak decreased as well as the maximum temperature value. The addition of the sisal fibers did not produce a high effect on the thermal degradation of the composite materials in comparison with the matrix alone. Lundquist et al. [124] developed three preforming techniques to prepare pulp fiber-reinforced cellulose diacetate preforms: namely filtration forming, solvent impregnation, and co-mingling with polymer fibers. These techniques eliminate all thermomechanical steps inducing premature degradation of the fibers, prior to final processing.

6.3. Aliphatic polyester reinforced with natural fibers

Shanks et al. [125] studied natural fiber/biopolymer composites using flax and poly(3-hydroxylbutyrate) bipolyesters (PHB). The biopolyesters consisted of the homopolyester PHB and its copolymers with 5% and 12% 3-hydroxyvalerate (PHV). The adhesion between the fibers and the polyesters was found to be better than for analogous polypropylene composites. Wetting of the fibers by the polyesters was observed using SEM. Nucleation was increased by the fibers and a silane-coupling agent used as an adhesion promoter. The melting temperature was influenced by the promoted adhesion and copolymerization. The bending modulus was increased in the composites and dynamic mechanical analysis provided storage modulus of as much as 4 GPa at 25 °C, with a smaller component as the loss modulus. The maximum in the loss modulus curve was taken as T_g, and this increased in the composites. The influence of the silane-coupling agent was found to be beneficial for the material properties of the biopolyester/flax composites. An earlier study showed that flax and PHB had good interfacial adhesion, which was decreased when plasticizers were present [126]. Some plasticizer migrated from the flax to the PHB and caused complex changes in the glass transition, crystallization and crystallinity of the PHB.

Avella et al. [127] reported on the thermal and mechanical behavior of a biotechnological polyester PHBV reinforced with wheat straw fibers. In order to improve the chemico-physical interactions between the components, the reinforcing agent has previously been submitted to treatment with high-temperature steam, leading to fibers richer in cellulose and more reactive. The addition of straw fibers has been found to increase the rate of PHBV crystallization, while it does not affect the crystallinity content. Furthermore, comparison of the mechanical properties has shown that the composites exhibit higher Young's moduli and lower values of both stress and strain to break than the neat matrix of PHBV. It was observed that the presence of straw did not affect the biodegradation rate evaluated in liquid environments and in long-term soil burial tests. In the composting simulation test, the rate of biodegradation is reduced for composites with more than 10% straw content. The morphology of the composites has also been investigated and correlated to the biodegradation process. Le Digabel et al. [128] used lignocellulosic fractions from wheat straw as natural fillers in composites of a biodegradable polyester (poly(butylene adipate-*co*-terephthalate)). A reinforcing effect of wheat straw residues was found for the composites.

7. Novel nanocomposites

Since the pioneering work by the Toyota group [129–131], polymer nanocomposites have attracted an increasing amount of attention. Polymer nanocomposites, in particular polymer/silicate nanocomposites, have been shown to exhibit significant improvements in properties compared with pure polymers or conventional composites [132]. The inclusion of well-dispersed nanosilicates in polymers has led to a vast array of changes in properties, including increased storage modulus, increased tensile and flexural properties, and decreased permeability and flammability [132,133]. In general, polymer/layered silicate nanocomposites are of three different types, namely: (1) intercalated nanocomposites, for which insertion of polymer chains into a layered silicate structure occurs in a crystallographically regular fashion, with a repeat distance of a few nanometers, regardless of the polymer-to-clay ratio; (2) intercalated nanocomposites, for which intercalated and stacked silicate layers flocculated to some extent due to the hydroxylated edge–edge interactions of the silicate layers; and (3) exfoliated nanocomposites, for which the individual silicate layers are separated in the polymer matrix by average distances that depend only on the clay loading [133].

7.1. *Starch/nanoclay composites*

A number of researchers have presented work in the field of starch nanocomposites. Park et al. [134,135] reported on the preparation and properties of gelatinized starch/montmorillonite (MMT) clay nanocomposites using both naturally occurring sodium MMT and a number of alkyl ammonium-modified clays. XRD and transmission electron microscopy (TEM) showed an intercalated structure for the starch/sodium MMT, however the modified clays appeared either unchanged or agglomerated in structure [134,135]. Park et al. [134] also found that the unmodified sodium MMT/starch nanocomposite also exhibited the greatest increase in modulus of all the clays used. Park et al. [135] also investigated the effect of clay content on the barrier properties of the nanocomposites, and found that increasing clay content led to an improvement in barrier properties.

Huang et al. [136] also investigated the formation of MMT-reinforced glycerol/plasticized thermoplastic starch using melt extrusion. SEM showed well-dispersed MMT platelets. FTIR indicated cooperation existed between MMT and starch molecules and hydrogen bonds that formed between the reactive hydroxyl groups of MMT and the hydroxyl groups of starch molecules. The mechanical and thermal properties of the starch nanocomposites formed showed significant improvements.

Wilhelm et al. [137] have also investigated the formation of starch/clay nanocomposites, using a Ca^{2+} hectorite. Solution cast starch/clay nanocomposites showed no XRD due to the first basal spacing, indicating almost total exfoliation in the starch matrix. Although this was a good result, starch does require some kind of plasticizer to reduce the brittleness of the starches. When glycerol was added by itself to the clay, the interplanar distance increased to 18.5 Å, however a peak at 9.3 Å also appeared corresponding to the d-001 spacing for the dehydrated clay.

Fischer and Fischer [138,139] also investigated starch/clay nanocomposites. In this work, a number of experimental pathways were investigated, including the dispersion of Na^+MMT clay in water, followed by blending in an extruder at a temperature of 85–105 °C with a premixed powder of potato starch, glycerol and water. The resulting material appeared to be fully exfoliated and exhibited a reduction in hydrophilicity, and improved stiffness, strength and toughness.

Another group of starch-based nanocomposites is those that are blended with biodegradable polyesters. McGlashan and Halley [140] studied the dispersion of nanoclays in a number of different biodegradable starch/polyester blend formulations. The crystallization temperature of the nanocomposite blends was found to be significantly lower than the base blend, probably due to the clay platelets inhibiting order, and hence crystallization, of the starch and polyester. The best dispersions were found in the 30 wt% starch blends, and the level of delamination depended on the ratio of starch to polyester and the amount of organoclay added.

Kalambar and Rizvi [141] also investigated starch nanocomposites blends and successfully made starch/PCL blends in the presence of MMT nanoclay. Reactive extrusion results showed that the addition of a modified nanoclay at the 3 wt% level increased elongation almost fourfold over that of pristine starch/PCL blends. The nanocomposites have better solvent-resistant properties because of the resistance to diffusion offered by the clay platelets in the polymer matrix [141].

7.2. *Protein/nanoclay composites*

Dean et al. [142–144] studied a number of plasticized soy protein/clay nanocomposites and, through the use of high-powered ultrasonics, produced an exfoliated-type nanocomposite, which exhibited significant improvement in modulus. Water is commonly used in the processing of many natural polymers, and it also interacts strongly with the ions generally found in the intergallery spacing of layered nanoclays. Ultrasonics can produce tiny bubbles, which can collapse violently, releasing significant energy that can be used to exfoliate clay. A unique technology to exfoliate nanoclay using a clean additive (water) and clean energy (ultrasonics) has been developed.

7.3. *PLA nanocomposites*

A number of researchers have developed polylactide-based nanocomposite materials. Ray et al. [145] prepared PLA/organically modified layered silicate nanocomposites by melt extrusion. Using oligo-(-caprolactone) (o-PCL) as a compatibilizer, the effect of compatibilizer in nanocomposites was investigated by focusing on two major aspects: morphological analysis and mechanical property measurements. An intercalated nanocomposite was produced that exhibited improvements in material properties in both solid and melt states [145].

Pluta et al. [146] investigated PLA/MMT nanocomposites by studying dispersions of modified and unmodified MMT prepared by melt blending. XRD showed that the good affinity between the organomodified clay and the PLA was sufficient to form an intercalated structure in the nanocomposite. TGA showed that the PLA-based nanocomposites exhibited improvement in their thermal stability in air.

Ray et al. [147] also investigated PLA/MMT nanocomposites. MMT modified with trimethyl octadecylammonium cation was used as an organically modified layered silicate for the nanocomposite preparation. All the nanocomposites exhibited superior improvement in practical materials properties such as storage modulus, flexural modulus, flexural strength, heat distortion temperature and gas barrier property, compared to that of neat PLA. The biodegradability of neat PLA and a representative nanocomposite was also studied under compost, and the rate of biodegradation of neat PLA significantly increased after nanocomposite preparation [147].

Chang et al. [148] studied the dispersion of two organoclays (a MMT modified with hexadecylamine (C16-MMT) and a fluorinated-mica modified with hexadecylamine (C16-Mica)) in PLA. Solution intercalation was used to produce nano-dispersions of organoclays in the PLA. Increased tensile strength and modulus were observed up to a maximum clay content of 4 wt% of the C16-MMT. In contrast, the initial modulus and tensile strength of PLA nanocomposites containing the C16-Mica increased continually with increasing clay content up to 8 wt%.

Chang et al. [149] also compared the C16-MMT to dodecyltrimethyl ammonium bromide-montmorillonite (DTA-MMT) and the commercially available Cloisite 25A in the preparation of PLA nanocomposites. From morphological studies using TEM, most clay layers were found to be dispersed homogeneously in the matrix polymer, although some clusters or agglomerated particles were also detected. The authors also found the degradation temperature (at a 2% weight loss) of the PLA nanocomposite films with C16-MMT and Cloisite 25A decreased linearly with an increasing amount of organoclay. The O_2 permeability values for all the nanocomposites for clay loadings up to 10 wt% were less than half the corresponding values for pure PLA, regardless of the organoclay employed.

A number of authors have also studied the dispersion of both unmodified and organically modified MMT in poly(ethylene glycol) (PEG) plasticized PLA [150,151]. Paul et al. [150] found from all the clays studied that at constant filler level, the MMT organo-modified by bis-(2-hydroxyethyl)-methyl (hydrogenated tallowalkyl) ammonium cations produced the greatest increase in thermal stability. Increasing the amount of clay was shown to delay the onset of thermal degradation of the plasticized polymer matrix. It was also shown via wide-angle X-ray scattering and DSC analysis, that competition exists between the PEG and PLA for intercalation into the interlayer spacing of the clay.

8. Concluding remarks

The study and utilization of natural polymers is an ancient science. The use of these materials have rapidly evolved over the last decade primarily due to the issue of the environment and the shortage of oil. Modern technologies provide powerful tools to elucidate microstructures at different levels, and to understand the relationships between the structure and properties. However, there is still a long way to go in research to obtain ideal polymeric blends and composites from renewable resources.

This review outlines the significance of the research and development that has been undertaken in the field of polymer blends from renewable resources. The three general classifications of this materials group include: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid; and (3) polymers from microbial fermentation, such as polyhydroxybutyrate. A wide range of naturally occurring polymers that are derived from renewable resources are available for various materials applications. One of the main disadvantages of biodegradable polymers obtained from renewable sources is their dominant hydrophilic character, fast degradation rate and, in some cases, unsatisfactory mechanical properties particularly under wet environments. Since most natural polymers are water soluble, the methods of both melting and aqueous blending have been used in many natural polymer blends.

Aliphatic polyesters have been recognized for their biodegradability and their susceptibility to hydrolytic degradation. Among the family of biodegradable polyesters, polylactides (i.e. polylactic acids) have been the focus of much attention because they are produced from renewable resources such as starch, they are biodegradable and compostable, and have very low or no toxicity and high mechanical performance comparable to those of commercial polymers. The higher price of aliphatic polyesters limits their general application. Blending hydrophilic natural polymers and aliphatic polyesters is of significant interest, since it could lead to the development of a new range of biodegradable polymeric materials. However, aliphatic polyesters and hydrophilic natural polymers are thermodynamically immiscible, leading to poor adhesion between the two components. Various compatibilizers and additives have been developed to improve their interface. One alternative way is the technology of multilayer extrusion.

Natural fibers are of basic interest since they have the ability to be functionalized and also have advantages from the point of view of weight and fiber-matrix adhesion, specifically with polar matrix materials. They have good potential for use in waste management due to their biodegradability and their much lower production of ash during incineration. Starch reinforced by cellulose is a typical example of natural polymer composites. Nanocomposites consisting of nanoclays and biodegradable polymers have also been investigated more recently and have shown to exhibit superior mechanical and thermal properties. The dispersions of nanoclays in polymers from renewable resources have been enhanced via chemical surface modification and the use of novel ultrasonic methods.

The future growth and sustainability of polymers and composites from renewable resources is reliant on continued research, in particular in the fields of compatibilizing mechanisms, surface modification and advanced processing techniques, and it is through an understanding of these that they are expected to replace more and more petroleum-based plastics.

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