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Review

Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability

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ABSTRACT

Recent environmental regulations, societal concerns and growing environmental understanding throughout the world have triggered renewed efforts in plastic industry to develop new products and processes compatible with our environment. This review outlines the new developments in thermoplastic starch, polyvinyl alcohol based blends and nanocomposites. These materials show a broad and versatile range of physical properties and other advantageous characteristics at acceptable cost and biodegradation rate and can be employed in a wide range of applications. To further improve their properties (such as mechanical properties, moisture sensitivity), some physical or chemical methods such as cross-linking, incorporation of new nanoparticles can be applied. With these new techniques, materials with a great variety of property profiles could be realized and they were even able to compete, both in price and in performance, with synthetic polymeric materials in different applications.

Contents

1. Introduction

Use of plastics has been under attack for some time because of lack of recycling facilities or infrastructure, non-recyclability, non-renewability, non-biodegradability or incorporation of toxic additives. Current trends indicate steady growth will occur in the use of biodegradable plastics with increasing availability of suitable materials and because of societal and legislative pressure (Rasato, 2009).

Starch is a widely used material for making biodegradable plastics. Starch is cheap, renewable and biodegradable, but pure starch lacks the strength, water resistibility, processability and thermal stability. To improve some of these drawbacks, starch was often blended with some biodegradable synthetic polymers such as poly (ε-caprolactone) (PCL), poly (lactic acid) (PLA), polyvinyl alcohol (PVOH), which have good potentials for plastic and packaging applications. PVOH is a material with a high technological potential as a water-processable or melt-processable polymer. Due to its excellent optical and physical properties, PVOH is successfully used in a

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wide range of industrial fields. However, PVOH is relatively expensive, and has low biodegradation rate and poor moisture barrier properties. To reduce cost and to enhance its eco-friendliness, and performance, PVOH is often modified with other polymers (such as starch) and nanoparticles.

Biodegradable plastics are now available based on thermoplastic starch, PVOH, and their blends. These materials provide environmentally advantageous biodegradable alternatives to conventional non-biodegradable materials such as polyethylene (PE) for many applications. This review will highlight the major developments in starch, PVOH based polymer blends, nanocomposites and their biodegradability. The processing and probable applications will also be discussed.

2. Starch based materials

Among all natural biopolymers, starch has been considered as one of the most promising one because of its easy availability, biodegradability, and lower cost. Starch is the major form of stored carbohydrate in plants such as corn, wheat, rice, and potatoes. Starch is composed of a mixture of two polymers of α-glucose – linear amylose and a highly branched amylopectin. Amylose molecules consist of 200–20,000 glucose units which form a helix as a result of the bond angles between the glucose units. Amylopectin is a highly branched polymer containing short side chains of 30 glucose units attached to every 20–30 glucose units along the chain. Amylopectin molecules may contain up to two million glucose units (Ray & Bousmina, 2005).

Starch can be used to form edible or biodegradable films. Different sources of starch, high amylose starch, modified starch (Mali & Grossmann, 2003; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2006; Roth & Mehltretter, 1967; Wolff, Davis, Cluskey, Gundrum, & Rist, 1951) have been used to form self-supporting films by casting from aqueous solution. These films appear to have moderate oxygen barrier properties but poor moisture barrier and mechanical properties, which limit their wide applications.

Starch can also be used as a filler to produce reinforced plastics (Bagheri, 1999; Evangelista, Nikolov, Sung, Jane, & Gelina, 1991). Usually, a small amount of starch (6–30%) was compounded with synthetic polymer, increasing the products' biodegradability.

The starch is not a real thermoplastic, but, in the presence of a plasticizer (water, glycerol, sorbitol, etc.), high temperature, and shearing, it melts and fluidizes, enabling its use in injection, extrusion and blowing equipment, such as those for synthetic plastics. Thermoplastic starch (TPS) products with different viscosity, mechanical strength, water solubility, and water absorption have been prepared by altering the moisture/plasticizer content, amylose/amylopectin ratio of raw material, and the temperature and pressure in the extruder (Mohanty, Misra, & Hinrichsen, 2000). Large amount of researches have been performed on the plasticization of TPS using glycerol (Forssell, Mikkia, Moates, & Parker, 1997), sorbitol (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999), urea, formamide (Ma, Yu, & Jin, 2004), dimethyl sulfoxide (Nakamura & Tobolsky, 1967), and low molecular weight sugars (Kalichevsky, Jaroszkiewicz, & Blanshard, 1993). Plasticizers can increase the flexibility and processability of TPS. The properties of TPS depend a lot on moisture. As water has a plasticizing power, the materials behavior changes according to the relative humidity of the air through a sorption–desorption mechanism (Vilpoux & Avérous, 2004). At the same time, the properties of the materials evolve as time goes by, even if moisture and temperature are controlled, translating into a lower elongation and higher rigidness.

Thermoplastic starch cannot be used in many applications owing to its sensitivity to humidity and inferior mechanical properties. They find use mainly in soluble compostable foams, expanded trays, shape molded parts, and expanded layers as a replacement of polystyrene. BIOTEC (Emmerich, Germany) has commercialized TPS products as Bioplast TPS® for foamed trays and boxes applications. So as to improve the properties of starch biodegradable products, starch was suggested being blended with other biodegradable, renewable or synthetic polymers, such as PCL, PLA and PVOH.

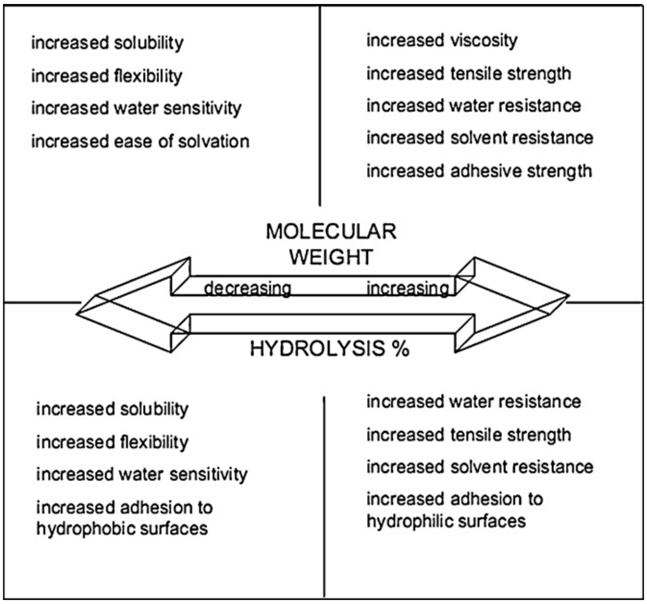

Fig. 1. Effect of molecular weight and hydrolysis level on the physical properties of PVOH (Sekisui Specialty Chemicals America, LLC, 2010).

3. PVOH based materials

PVOH cannot be made by polymerization of vinyl alcohol, since this species does not exist in the free state. PVOH instead is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups.

Most commercially available PVOH polymer grades are atactic, and the degree of crystallinity and physical properties depends on various factors such as the production processes used to make the precursor polyvinyl acetate and convert it to PVOH, the degree of hydrolysis, the molecular weight, the water content, and the contents and types of plasticizer or other constituents incorporated (Kuraray America, Inc., 2010). Fig. 1 shows how the properties of PVOH-based materials vary depending on the degree of hydrolysis and molecular weight (Sekisui Specialty Chemicals America, LLC, 2010). Partially hydrolyzed grades contain residual acetate groups, which reduce the overall degree of crystallinity. Their formulations generally have lower melting points, easier processability, lower strength and lower water dissolution temperatures than those based on fully hydrolyzed polymers.

PVOH has excellent film forming, emulsifying, and adhesive properties, which has resulted in its broad industrial use, such as water soluble packaging films, paper adhesives, textile sizing agent, and paper coatings (Chang, Jang, Ihn, Lee, & Sur, 2003; Ibrahim, El-Zawawy, & Nassar, 2010). PVOH is a water soluble polymer, so PVOH can be processed by solution casting and orientation to make high performance PVOH films. However, high energy cost of evaporating water limits this application. PVOH is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer, will then reduce its tensile strength, but increase its elongation and tear strength (Kuraray America, Inc., 2010).

PVOH is also not considered as a thermoplastic because the melting temperature exceeds the degradation temperature for fully hydrolyzed grades. Unplasticized PVOH degrades at about 180 °C by eliminating water to form conjugated double bonds (Tsuchiya & Sumi, 1969), while the melting point of PVOH ranges from about 180 to 240 °C depending on its degree of hydrolysis. By using plasticizers, the PVOH's melting temperature can be controlled with an adequate melt flow and improved heat stability, which made it possible for more economical melt extrusion process to be used for PVOH based formulations (Bastioli et al., 1995).

PVOH has been considered to be a truly biodegradable synthetic polymer since the early 1930s. However, the overall number of PVOH-degrading microorganisms is rather limited in comparison to the widespread species able to degrade aliphatic polyesters, such as PHA and PLA (Chiellini, Corti, & Solaro, 1999). The lower rate of biodegradation was also observed for PVOH based materials (Chen et al., 1997; Mao, Imam, Gordon, Cinelli, & Chiellini, 2000). Another factor affecting the wide use of PVOH is its higher cost compared with their daily commodity counterparts like polyethylene, and polypropylene. Blending PVOH with other cheap renewable polymers such as starch could be one of the solutions to improve its biodegradation rate and lower the overall cost.

4. Starch–PVOH polymer blends

4.1. Plasticizers for starch–PVOH blends

Since 1980s, starch–PVOH has been studied primarily for producing films by means of solution casting because PVOH easily degraded during the melt processing. However, from an economic viewpoint, solution processing is likely unacceptable, mainly due to the additional high processing cost and low efficiency in comparison to thermoplastic processing. In order to decrease the melting temperature of PVOH and increase the flexibility and workability of starch and PVOH, a number of plasticizers, e.g. water and polyols have been essayed, which made it possible for conventional thermal processing like extrusion applicable for starch–PVOH compounding.

The conventional plasticizer used for starch and PVOH composites is glycerol and water (Lawton & Fanta, 1994; Liu, Feng, & Yi, 1999), but several other chemicals like sorbitol (Park, Chough, Yun, & Yoon, 2005; Westhoff, Kwolek, & Otey, 1979), urea (Tudorachi, Cascaval, Rusu, & Pruteanu, 2000), citric acid (Park et al., 2005; Zou, Jin, & Xin, 2008), as well as complex plasticizers (Zhou, Cu, Jia, & Xie, 2009) have also been successfully employed.

Liu et al. (1999) compounded starch and PVOH using a single screw extruder. To obtain good processability, they found that glycerol is much more effective than water as a plasticizer for the compounds, but it scarified tensile strength and water barrier properties. To balance these properties, a mixture of glycerol and water (50/50 in weight) was hence suggested as the optimum plasticizer for the compound. With 50/50 ratio of glycerol and water, the melt flow index (MFI) fell on the intermediate point. However, tensile strength reached its maximum value.

Starch–PVOH films containing 51% starch, 17% PVOH, 30% plasticizer, 1% paraformaldehyde and 1% NH_4Cl were investigated by Westhoff et al. (1979). They evaluated various polyols, including glycerol, as plasticizers for starch–PVOH cast film and found that film properties varied with the type of plasticizer used. Glycol glycoside, an experimental polyol made from starch and ethylene glycol, and sorbitol were highly effective plasticizers alone and in combination with small amounts of glycerol. They also noted a loss of methanol-extractable glycerol from aged films, as well as a loss of plasticizer effectiveness in films prepared with high starch loads.

Park et al. (2005) examined glycerol, sorbitol and citric acid as plasticizers for film casting. They reported that in all measurement results, the film adding citric acid was better than glycerol or sorbitol because hydrogen boding at the presence of citric acid with hydroxyl group and carboxyl group increased the inter/intramolecular interactions between starch, PVOH and plasticizers. Similar studies were also performed by Shi et al. (2008). They casted a series of starch–PVOH films with varying concentrations (5–30 wt%) of citric acid. They found that the water absorbance decreased from 33% to 20% as the citric acid percentage increased from 5 to 30 wt%. When 5 wt% citric acid was added, the tensile strength of the sample increased from 39 to 48 MPa, but when more citric acid was added (from 5 to 30 wt%), the tensile strength decreased from 48 to 42 MPa, and the elongation at break increased from 102% to 208%. They contributed this to the plasticizing effect of residual-free citric acid in the blend. As compared to the hydroxyl groups on glycerol, the carboxyl groups on citric were capable of forming stronger hydrogen bonds between citric acid and other components, and these cross-linking and strong hydrogen bonding enhanced the thermal stability of the starch–PVOH films. At the same time, Fourier-transform infrared (FT-IR) spectroscopy showed that an esterification took place between citric acid and starch (or PVOH) during the processing at 140 °C. Such an esterification improved the water resistibility.

In the study of Yoon, Chough, and Park (2006), the effects of different functional groups, that is hydroxyl and carboxyl groups, on the physical properties of starch–PVOH blend films were examined. Glycerol with 3 hydroxyl groups, succinic acid with 2 carboxyl groups, malic acid with 1 hydroxyl and 2 carboxyl groups, and tartaric acid with 2 hydroxyl and 2 carboxyl groups were used as additives. The results of measured tensile strength and elongation verified that hydroxyl and carboxyl groups as functional groups increased the flexibility and strength of the film and they also found that when the additives containing both hydroxyl and carboxyl groups were simultaneously added, the tensile strength and elongation were better than in glycerol added film with hydroxyl groups only.

The mixture of glycerol and urea was used as a complex plasticizer for the thermoplastic starch–PVOH extruded blends (Zhou et al., 2009). Results showed that the complex of glycerol and urea could form more stable and strong hydrogen bonds with water and starch–PVOH molecules than the single plasticizer such as glycerol. The starch–PVOH polymer matrix with complex plasticizer was proved to be a continuous phase and the rheological properties were improved. With successful additives, the ensuing starch–PVOH blends with glycerol/urea (20 wt%/10 wt%) had better mechanical properties, of which the tensile strength, elongation at break could respective reach 7.83 MPa (14% increase) and 203% (77% increased).

4.2. Chemical and physical modification of starch–PVOH blends

In general, blending starch with PVOH improves the mechanical properties of starch-based materials. Mao et al. (2000) extruded corn starch–glycerol–PVOH blends. The results showed that starch–glycerol without PVOH had a tensile strength of 1.8 MPa and elongation at break of 113% at 50% relative humidity (RH), whereas those containing 9.1 wt% of PVOH had a tensile strength and elongation of 4 MPa and 150%, respectively. They mentioned that addition of PVOH to starch–glycerol blends prevented the development of surface cracks, indicating relatively good compatibility of starch and PVOH. Because both starch and PVOH are polar substances having hydroxyl groups (–OH) in their chemical structure, these highly polar hydroxyl groups tend to form inter-

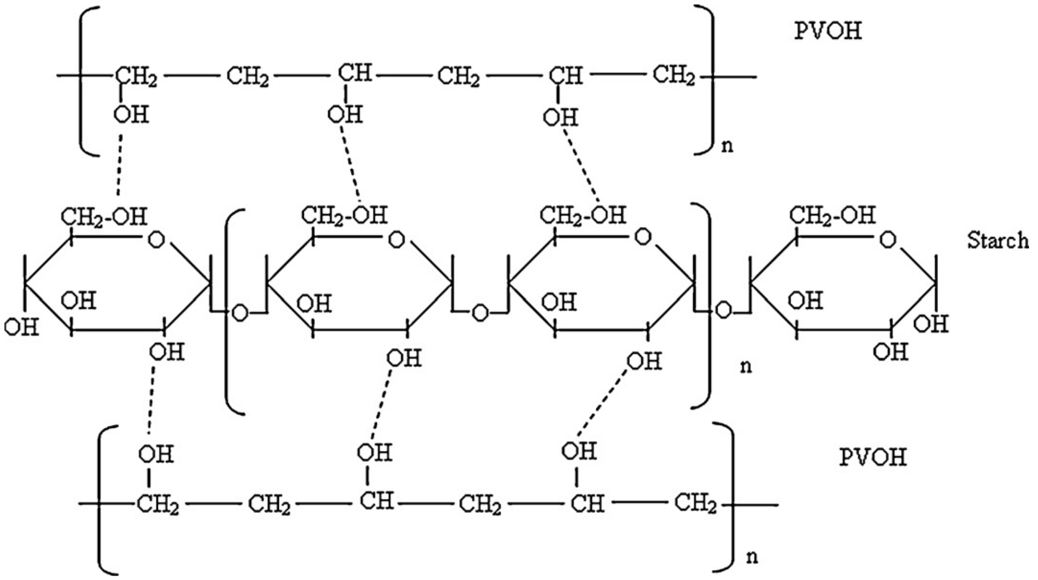

Fig. 2. Possible hydrogen bond formation between starch and PVOH.

molecular and intramolecular hydrogen bonds which improve the integrity of starch–PVOH blends. Fig. 2 shows possible hydrogen bond formation between starch and PVOH. Sin, Rahman, Rahmat, and Samad (2010) investigated the hydrogen bonding interactions in starch–PVOH blends. Semi-empirical AM1 (Austin Model 1) and PM3 (Parameterized Austin Model 3) methods were employed to model the blending. The computed negative binding energies justified the stability of blending. On the other hand, the solubility parameters of starch and PVOH modeling complexes had been found close to each other, which confirmed that starch and PVOH are compatible blends. In addition, vibrational frequency analysis of these molecular complexes has exhibited that hydroxyl group shifted to lower wavenumbers due to formation of hydrogen bonds. The same research group (Sin, Rahman, Rahmat, Sun, & Samad, 2010) also investigated the physical bonding interaction of cassava starch–PVOH blend using differential scanning calorimetry (DSC) method. The results showed that after adding PVOH to cassava starch, the starch–PVOH blend films showed obvious endothermic peaks with onset and end-point temperature higher than neat PVOH film. In addition, the starch–PVOH blends have experimental enthalpy of melting higher than theoretical values. These evidenced that the interactions between starch and PVOH are extensively strong. Siddaramaiah Raj and Somashekar (2004) studied starch reinforced PVOH composites and concluded that increasing the percentage of starch content (up to 10%) in PVOH matrix retains the mechanical properties such as tensile strength (270 kg/cm^2), elongation at break (200%) and burst strength (0.7–0.88). Their results also support the formation of hydrogen bonds between the hydroxyl groups of PVOH and the hydroxyl groups of starch networks.

However, some researchers elucidated their observations in a different way. In the study of Chen, Cao, Chang, and Huneault (2008), the tensile strength, elongation at break, and transparency of starch–PVOH composites decreased rapidly with the increased starch content (up to 40 wt%) (Fig. 3). They attributed this property deterioration to the relatively poor compatibility between starch and PVOH. Liu et al. (1999) also found that incorporation of PVOH into starch could enhance the mechanical properties, but such improvement was very limited, mainly due to the poor interface adhesion between the fibrous PVOH structure and the starch matrix.

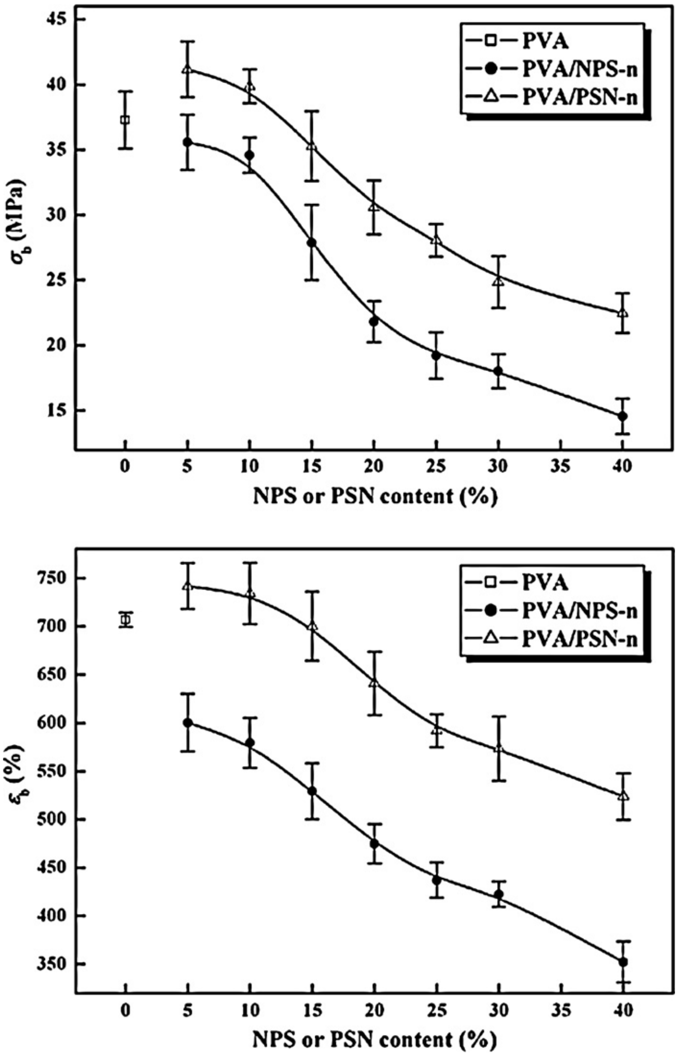

Fig. 3. Tensile strength (σ_b) and elongation at break (ε_b) of PVOH and starch-PVOH composites (NPS is natural pea starch, PSN is pea starch nanocrystals).
Adapted from Chen et al. (2008) with permission from Elsevier.

Another problem with starch–PVOH blends is their poor water barrier properties. Since starch and PVOH molecules have a large number of hydroxyl groups, starch–PVOH composites display a hydrophilic nature. Mao et al. (2000) reported that starch–glycerol–PVOH formulations were very sensitive to relative humidity (RH) and tensile strength decreased significantly with increase of RH.

Based on these observations, attentions had been driven to further improve the properties of starch–PVOH composites (e.g. mechanical and water barrier properties) to meet the demands of extensive applications. Some of the effective means commonly used to modify the starch–PVOH composites for the improvement of properties include: (1) chemically or physically modifying starch or PVOH before the blending processing; (2) using chemical or physical modification to the starch/PVOH composites during or after the blending process, such as acid treatment, cross-linking reactions, surface modification and adding nanoparticles (will be discussed later) to the blends.

Beliakova, Aly, and Abdel-Mohdy (2004) tried grafting of methacrylic acid on starch, PVOH, and a mixture of starch and PVOH, using potassium persulfate/sodium thiosulfate redox initiation system. Applications of these copolymers would help the compatibility of starch–PVOH system. Zhao et al. (2006) prepared methylated cornstarch and blended methylated starch with PVOH. Theoretically, methylation is an effective way to increase the hydrophobicity of starch and to improve the compatibility between starch and PVOH. It was found that methylated starch–PVOH films had higher water resistance than the native starch–PVOH films. Both tensile strength and elongation at break were improved as the degree of substitution of methylated starch increased. In another research by Nabar, Draybuck, and Narayan (2006), different modified starch – hydroxypropylated high amylose cornstarch was used.

Yang, Liu, Wu, Kuo, and Huang (2008) employed two methods, acid modification and plasma treatment to improve the processing ability and mechanical properties of starch–PVOH blends. Maleic anhydride (MA) and citric acid were used as the processing additives and PVOH was treated by argon plasma equipment before the blending process. The results showed that the melt flow index of starch–PVOH blend is increased from 2.3 g/10 min to 32.7 g/10 min by adding MA and to 130 g/min by adding MA and plasma treatment. Glycerol esterified with MA and this esterification reaction enhanced the plasticization of glycerol. Plasma PVOH greatly modified the compatibility of PVOH and starch molecules. The tensile strength of starch–PVOH blend increased from 3.48 to 6.26 MPa by plasma treatment, along with the increase of the yield strength and modulus.

Compared to previous methods, cross-linking is most commonly used to improve the compatibility and properties of starch and PVOH blends. Examples of cross-linking included use of cross-linking reagents such as poly (ethylene-co-acrylic acid) (EAA) (Lawton & Fanta, 1994), glutaraldehyde (Ramaraj, 2007; Yoon, Chough, & Park, 2007), boric acid (Sreedhar, Sairam, Chattopadhyay, Syamala Rathnam, & Mohan Rao, 2005; Yin, Li, Liu, & Li, 2005), epichlorohydrin (Sreedhar, Chattopadhyay, Sri Hari Karunakar, & Sastry, 2006), Hexamethoxymethylmelamine (HMMM) (Chen et al., 1997), and radiation (Follain, Joly, Dole, & Bliard, 2005; Khan, Bhattacharia, Kader, & Bahari, 2006; Zhai, Yoshii, Kume, & Hashim, 2002; Zhai, Yoshii, & Kume, 2003).

Lawton and Fanta (1994) observed that the elongation of starch–PVOH–glycerol films could be improved by adding a small amount of (EAA). A mixture of 55.6% starch, 2.8% EAA, 28.3% PVOH and 13.3% glycerol was believed to be close to the optimum formulation obtain films having at least 100% elongation and tensile strength of 25 MPa, while still maintaining starch concentrations above 50%. The reason for the increase was because EAA could form helical inclusion complexes with both starch and PVOH. Then starch and PVOH could conceivably bound together through simultaneous complex formation with single EAA molecule. Formation of such a starch–EAA–PVOH complex, even in minor amounts, might enhance the compatibility of starch and PVOH significantly and thus improve film properties.

Ramaraj (2007) reported a study that has modified PVOH films by cross-linking with glutaraldehyde and blending with 10–50 wt% starch by a solution casting process. The cross-linked starch–PVOH composite films showed significant improvement in tensile strength, tensile modulus, tear and burst strengths, and solubility resistance over the uncrosslinked films, which was also agreed by Yoon et al. (2007). They found that the starch granules in the PVOH matrix without cross-linking acted as stress concentrators, often inducing cracks which resulted in low strength and elongation. However, strong adhesion existed between PVOH matrix and starch and a covalent bond likely to be formed at the PVOH/starch interface in the presence of glutaraldehyde. Thus, the mechanical and other properties of the blend were improved greatly with the cross-linking agent.

Starch–PVOH blends with different composites were prepared and cross-linked with borax by *in situ* and post-treatment methods (Sreedhar et al., 2005). Various amounts of glycerol and poly(ethylene glycol) were added to the formulations as plasticizers. The results suggested that for starch–PVOH blends treated with borax, glass transition temperature (T_g) was lower than T_g of pure PVOH and thermal stability was higher than that of the pure blends. The mechanical properties of the starch–PVOH blends were also improved after treatment with borax and were higher than those of the pure blends. Yin et al. (2005) casted starch, PVOH films cross-linked by boric acid. They concluded that boric acid was an excellent cross-linking agent for starch and PVOH. The obtained starch–PVOH films had good transmittance, mechanical properties, and water resistance. Increasing the concentration of boric acid (from 0 to 1.5 wt%) improved the extent of cross-linking between starch and PVOH and thus strengthened the bonding of the two kinds of molecules. However, when the concentration of boric acid was too high, cross-linking occurring among the same kinds of molecules was more likely to happen, which led to quick drop of film properties such as transmittance, mechanical strength and elongation, and water resistance.

The cross-linking of starch–PVOH blends by epichlorohydrin was carried out in the presence of plasticizer with different concentration of epichlorohydrin (Sreedhar et al., 2006). The authors found a decrease in intensity of the –OH band upon cross-linking of the blends with epichlorohydrin, which led to a decrease of T_g and loss tangent (δ) values. At the same time, the cross-linking increased the rubbery moduli in the blends from the dynamic mechanical thermal analysis.

In another study by Chen et al. (1997), starch–PVOH films were cast with or without cross-linking agent HMMM in the absence of plasticizer. The results showed that starch–PVOH films cross-linked with 5% HMMM exhibited good water resistance with improved tensile properties. Cross-linked films exposed to aqueous medium for several weeks showed little or no disintegration. Cinelli, Chiellini, Gordon, and Imam (2003) and Imam, Cinelli, Gordon, and Chiellini (2005) did similar research by blending starch, PVOH, and lignocellulosic fibers, cross-linked by HMMM. They had the same observations about the water resistance of the blends. In their findings, natural fibers could also be an important ingredient to improve the properties of starch–PVOH blends. Usually, natural fibers can be added to the composites to impart stiffness, increase degradability, and lower the cost to the final item.

Besides cross-linking agent, photo-curing technique proved to be an important method for cross-linking polymers because their functional groups undergo light induced reactions. Khan et al. (2006) prepared sago starch–PVOH films by casting and cured the

Table 1
Summary of cross-linking method and cross-linking reagents used for improving the compatibility and properties of starch–PVOH composites.

Cross-linking method or cross-linking reagents	Properties of the starch–PVOH composites after cross-linking	References
Poly (ethylene-co-acrylic acid)	Increase of elongation and tensile strength	Lawton and Fanta (1994)
Glutaraldehyde	Improvement in tensile strength, tensile modulus, tear and burst strengths, and solubility resistance	Ramaraj (2007), Yoon et al. (2007)
Borax or boric acid	Higher thermal stability, higher tensile strength, decrease of elongation at break	Sreedhar et al. (2005), Yin et al. (2005)
Epichlorohydrin	Decrease of glass transition temperature and loss tangent value, increase of rubbery moduli	Sreedhar et al. (2006)
Hexamethoxymethylmelamine	Improvement of water resistance and tensile strength	Chen et al. (1997), Cinelli et al. (2003), Imam et al. (2005)
Photo curing (ultra violet)	Higher tensile strength and lower brittleness, decrease of water absorption	Follain et al. (2005), Khan et al. (2006)
Gamma and electron beam irradiation	Increase of gel strength, decrease of melting point and melting enthalpy	Zhai et al. (2002, 2003)

films under ultra violet (UV) radiation. They used two monomers 2-ethyl 2-hydroxymethyl 1,3 methacrylate (EHMPTMA) and 2-ethylhexylacrylate (EHA) and a photoinitiator for the cross-linking reactions. Excitation of photoinitiator produced reactive radicals that initiate subsequent reactions in the polymer blends thus facilitating cross-linking between the two polymer chains. The results showed that UV radiated films had high tensile strength and low brittleness. It was found that the tensile strength of the monomer UV radiated film could be increased up to 46% compared to the non-treated one.

Zhai et al. (2002, 2003) prepared a series of starch–PVOH hydrogels by changing the composition and the dose under gamma and electron beam irradiation. The results showed that there was a grafting reaction between starch and PVOH molecules besides the cross-linking of PVOH molecules under irradiation, and the amylose of starch was a key reactive component. After starch–PVOH blend system was irradiated, PVOH radicals reacted easily with other PVOH molecules to form cross-linked PVOH networks and starch radicals reacted with PVOH molecules to initiate graft reaction. With the increasing of the dose of irradiation, the gel strength increased quickly, but decreased slightly at high dose due to the degradation of the hydrogels.

Table 1 summarized the cross-linking method and cross-linking reagent used for improving the compatibility and properties of starch–PVOH composites. Cross-linking reactions enhanced not only the mechanical properties but also the thermal properties of starch–PVOH blends by reinforcing the intermolecular binding with the introduction of covalent bonds to supplement natural intermolecular hydrogen bonds.

5. Starch–PVOH based nanocomposites

To further improve the moisture barrier and mechanical properties of starch–PVOH blends, polymer nanocomposite concept could be an option to be applied to the blended system.

5.1. *Starch based nanocomposites*

A number of researchers have investigated ways to improve the properties of thermoplastic starch using nanocomposites and details have been reviewed by Raquez, Nabar, Narayan, and Dubois (2007) and Chivrac, Pollet, and Avérous (2009). De Carvalho, Curvelo, and Agnelli (2001) provided a first insight in the preparation and characterization of thermoplasticized starch–kaolin composites by melt intercalation techniques. Park et al. (2002) and Park, Lee, Park, Cho, and Ha (2003) reported an increase in elongation at break and tensile strength by more than 20% and 25%, respectively, and a decrease in water vapor transmission rate by 35% for potato starch/montmorillonite (MMT) nanocomposites on addition of 5% clay. In addition, the decomposition temperature was increased indicating a better thermal stability for starch/MMT nanocomposites. Wilhelm, Sierakowski, Souza, and Wypych (2003) observed a 70% increase in tensile strength of Cará root starch/hectorite nanocomposite films at 30% clay level. However, the percentage of elongation decreased by 50%. Avella et al. (2005) reported the preparation of starch/MMT-nanocomposite films for food packaging applications. Mechanical characterization results showed an increase of modulus and tensile strength. Tang, Alavi, and Herald (2008a,b) studied starch based nanocomposites using melt extrusion method. The results showed that nanocomposites with lower amount of glycerol (<10%) led to the lower water vapor permeability and higher tensile strength, indicating the hydrogen bonds established between glycerol and clay platelets could disturb the clay exfoliation process. Chivrac, Pollet, Schmutz, and Averous (2008) used cationic starch as clay organo-modifier to promote the clay exfoliation process. After organo-modification, this nanofiller was incorporated into glycerol plasticized wheat starch by mechanical kneading to produce nano-biocomposite materials. According to Chivrac et al. (2008), no diffraction peak was observed by X-ray diffraction, suggesting an exfoliated morphology (Fig. 4). They assumed that this dispersion state was achieved due to the preferential interactions established between the hydroxyl groups of the different starch-based biomacromolecules. Besides inorganic silicate clay nanofillers, nanowhiskers and nanotubes has also been used for reinforcement of starch based materials. Neus Angles and Dufresne (2000), Neus Angles and Dufresne (2001) have prepared nanocomposite materials using glycerol–plasticized starch and a colloidal suspension of tunicin whisker as the reinforcing phase. They reported a lower water uptake and improved thermal and mechan-

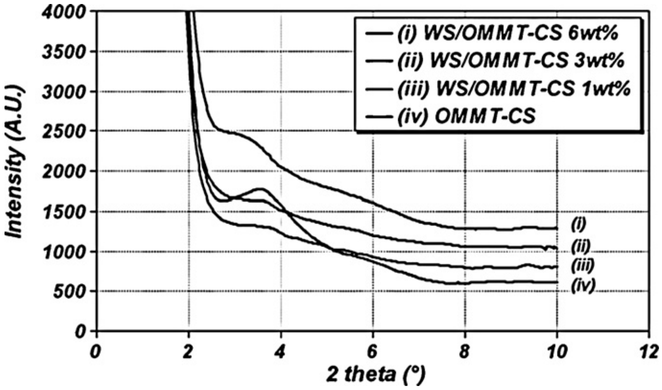

Fig. 4. XRD patterns for OMMT–CS and wheat starch/OMMT–CS nanocomposites with 1, 3, and 6 wt% of clay inorganic fraction (OMMT is organo modified MMT, CS is cationic starch).
Adapted from Chivrac et al. (2008) with permission from Elsevier.

ical properties. Cao, Chen, Chang, and Huneault (2007) studied the utilization of multiwalled carbon nanotubes (MWCNTs) as filler-reinforcement to improve the performance of plasticized starch by solution casting methods. The results indicated that the MWCNTs dispersed homogeneously in the starch matrix and formed strong hydrogen bonding with starch molecules. Compared with the pure starch, the tensile strength and Young's modulus were increased 66% and 89% with an increase of MWCNTs content from 0 to 3.0 wt%, respectively, without sacrificing the elongation of break.

5.2. PVOH based nanocomposites

A large variety of nanocomposites have been prepared using PVOH as a matrix and nanoreinforcement like layered silicate (Grunlan, Grigorian, Hamilton, & Mehrabi, 2004; Strawhecker & Manias, 2000), nanocrystals or whiskers (Chen et al., 2008; Kvien & Oksman, 2007; Sriupayo, Supaphol, Blackwell, & Rujiravanit, 2005), and carbon nanotubes (Probst, Moore, Resasco, & Grady, 2004; Ryan et al., 2007; Shaffer & Windle, 1999). The preparation methods are usually solution casting or *in situ* polymerization. Strawhecker and Manias (2000) first explored the PVOH/MMT nanocomposite materials spanning the complete range of MMT loadings. They reported that the inorganic layers promoted a new crystalline phase different than neat PVOH, characterized by higher melting temperature and different crystal structure. The new crystal phase improved mechanical, thermal, and water transmission properties. For a 5 wt% MMT exfoliated composites, the softening temperature increased by 25 °C and the Young's modulus tripled with a decrease of only 20% in toughness, whereas there was also a 60% reduction in the water permeability. Grunlan et al. (2004) reported that at a concentration of 10 wt% MMT, the oxygen permeability of PVOH decreased below 0.001 $\text{cm}^3\ \text{mil/m}^2\text{/day}$ at 55% RH and haze and clarity changed from 0.4 and 100% to 80 and 23%. Sriupayo et al. (2005) prepared and characterized α-chitin whisker reinforced PVOH nanocomposite films with or without heat treatment. Improved thermal stability, tensile strength and water resistance were observed. The presence of α-chitin whiskers was found to decrease the elongation at break and they did not have any effect on the crystallinity of PVOH matrix. Chen et al. (2008) reported the preparation and characterization of pea starch nanocrystals reinforced PVOH nanocomposites. Kvien and Oksman (2007) prepared unidirectional reinforced nanocomposite by orientation of cellulose whiskers in PVOH. Ibrahim et al. (2010) synthesized cellulose nanospheres from cotton linter and linen and casted a series of PVOH-nanocellulose films. From their studies, improved physical properties were observed. Shaffer and Windle (1999) investigated PVOH–MWNT composites using dynamic mechanical and thermal analysis (DMTA) while Probst et al. (2004) studied the crystallization dynamic of PVOH/single walled carbon nanotube (SWNT) composites. The mechanical measurements found that the polymer modulus doubled at a nanotube concentration of approximately 60 wt% (Shaffer & Windle, 1999) while the crystallization temperature of PVOH was found to rise with the addition of SWNT nanotubes (Probst et al., 2004). The results indicated that carbon nanotubes acted as crystal nucleation sites with the PVOH matrix. Ryan et al. (2007) reported a 4.5 fold increase in the Young's modulus of PVOH with the addition of carbon nanotubes. Their study suggested that in semi-crystalline polymer like PVOH and nanotube systems, the formation of nanotube induced crystalline polymer domains was the dominant reinforcement mechanism and no stress transfer to the nanotubes.

5.3. Starch–PVOH based nanocomposites

Compared to starch nanocomposites and PVOH nanocomposites, nano-reinforced starch–PVOH blends are not widely studied.

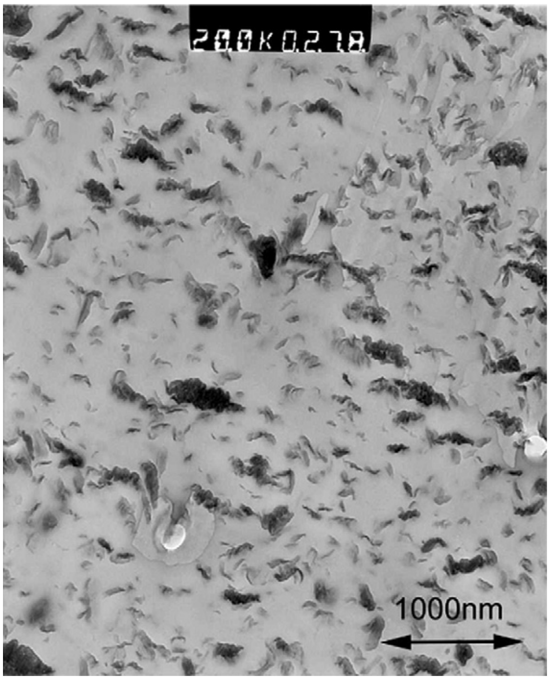

Fig. 5. TEM micrographs of amylocorn starch-PVOH nanocomposite with 5 wt% of PVOH and 2.5 wt% of MMT content.
Adapted from Dean et al. (2008) with permission from Elsevier.

Dean, Do, Petinakis, and Yu (2008) produced a series of thermoplastic starch/PVOH/montmorillonite micro- and nanocomposites which exhibit intercalated and exfoliated structures through extrusion processing (Fig. 5). A small amount of PVOH (up to 7 wt%) and montmorillonite (up to 5 wt%) were used and the improvement of tensile strength (up to 67% increase) and tensile modulus (up to 85% increase) were reported. They attributed the improvements in properties to both interfacial interactions of filler and matrix and the disruption of the recrystallization process. Vasile et al. (2008) prepared starch/PVOH/montmorillonite composites by the melt mixing method. They revealed the morphology and thermal behavior changes for the nanocomposites. In their study, the suppression of T_g and T_m was observed for the nanocomposites, which led to a morphology with a low or very low content of the crystalline phase and a compatibility of the components, based on chain entanglements. At low loadings (<5 wt%), the inorganic fillers were well dispersed through the starch–PVOH matrix, meaning the nanocomposites formed were mostly exfoliated hybrids. Pascu, Popescu, and Vasile (2008) prepared starch/PVOH/MMT nanocomposites and subjected them to surface modification by physical treatments such as dielectric barrier discharge (DBD) exposure and coating with proteins (albumin) or polysaccharide (chitosan), for improving their biocompatibility. By controlling the number and type of nanoparticles introduced in the starch–PVOH blends, and by applying adequate treatment methods, the enhancement of the surface characteristic could be obtained. Majdzadeh Ardakani and Nazari (2010) extruded starch–PVOH–clay nanocomposites and examined three types of cation or modifier (Na^+, alkyl ammonium, and citric acid) for montmorillonite. The prepared nanocomposites with modified MMT indicated a mechanical improvement in the properties in comparison with pristine MMT. The clay modified with citric acid, represented better mechanical properties in comparison with pristine MMT, which could be attributed to the interactions between citric acid and starch–PVOH chains. Tang, Zou, Xiong, and Tang (2008) prepared starch/PVOH/nano-silicon dioxide (nano-SiO_2) films by solution casting. The results indicated that an intermolecular hydrogen bond and a chemical bond C–O–Si were formed between the nano-SiO_2 and starch–PVOH polymer matrix, which increased the miscibility and compatibility of starch and PVOH. Both tensile strength and water resistance were improved. Yang et al. (2010) fabricated oxidized starch/PVOH/exfoliated α-zirconium phosphate (α-ZrP) composites using a solution casting method. α-ZrP exhibits great advantages over MMT clay, including a much higher purity and surface energy, ease of intercalation, and ease of exfoliation. Tensile strength and elongation at break of the nanocomposite films increased from 6.6 to 15.1 MPa and from 35% to 53% as the α-ZrP content increased from 0 to 1.5 wt%. Higher loading levels of a-ZrP resulted in aggregations of α-ZrP and deterioration of stress and elongation. The presence of a-ZrP also decreased the moisture uptake and increased the degradation temperatures of the nanocomposites. The improvement in the properties may have resulted from the formation of synergistic interactions and hydrogen bonding between a-ZrP and polymers.

6. Biodegradability of starch–PVOH blends and nanocomposites

Starch can be readily metabolized by a range of microorganisms to fermentation products such as ethanol (Bai, Anderson, & Moo-Young, 2008; Jamai, Ettayebi, El Yamani, & Ettayebi, 2007), hydrogen (Tadasa & Takeda, 1986; Yang & Shen, 2006) and methane (Amon et al., 2007). PVOH is also susceptible to biological degradation, however, the process was slow (Gartiser, Wallrabenstein, & Stiene, 1998). Furthermore, the overall number of PVOH-degrading microorganisms was rather limited in comparison to the widespread species able to degrade aliphatic polyesters, such as PHA and PLA (Chiellini et al., 1999).

Several researches have been conducted on the biodegradation of starch–PVOH blends or their nanocomposites. Chen et al. (1997) observed that the rate of biodegradation in starch–PVOH cast films was negatively correlated with the PVOH content in compost, however, films containing both starch and PVOH degraded much faster than pure PVOH. Mao et al. (2000) reported starch glycerol samples incubated in compost lost up to 70% of their dry weight within 22 days. However, the weight loss was only 59% in starch–glycerol formulations with added PVOH, suggesting that the addition of PVOH slowed the degradation process in the samples. Russo et al. (2009) investigated the degradability of thermoplastic starch and PVOH blends under anaerobic conditions to simulate the most common disposal environment for household wastes. They concluded that predominantly PVOH remained at the end of the digestion and that starch was almost entirely degraded. However, the PVOH content significantly impacted the rate of starch solubilisation. Chai, Chow, Chen, Chuang, and Lu (2009) evaluated biodegradability of modified starch–PVOH blends and followed with bio-reactivity kinetic models. The results showed that the degradability of PVOH was enhanced with addition of the starch. Based on the kinetic models, the growth rate of the microorganism was found to be increasing with the increase of the content of starch in the PVOH–starch blends in the first order reaction fashion. Cinelli et al. (2003) characterized the biodegradability of PVOH, starch, and lignocellulosic films with or without cross-linking agent. Results showed that films generally biodegraded within 30 days in compost, achieving 50–80% mineralization. Both neat PVOH and blends that had been cross-linked exhibited comparatively slow degradation and stimulating effect of lignocellulosic fillers on the biodegradation of PVOH in blends.

Tang, Zou, et al. (2008) studied the biodegradability of nano-SiO_2 reinforced starch/PVOH nanocomposite films. With 5% nano-SiO_2 (SPS5), the weight loss could be up to 60%, which was very close to the weight loss of starch–PVOH without nano-SiO_2 (Fig. 6). This might indicated that nanoparticles had no significant influence on biodegradability of films. However, Spiridon, Popescu, Bodarlau, and Vasile (2008) studied degradation of clay–starch–PVOH nanocomposite films and concluded that the biodegradation of films depended on both type and content of nanoparticles and the nanoparticles hindered the rate of biodegradation.

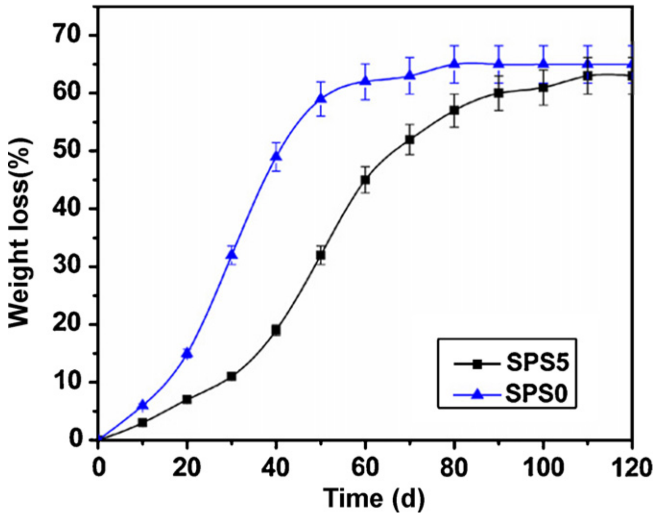

Fig. 6. The weight loss of starch-PVOH films with 0% of SiO_2 (SPS0) and 5% SiO_2 (SPS5) in 120 days.
Adapted from Tang, Zou et al. (2008) with permission from Elsevier.

7. Applications and future prospects

In general, starch–PVOH blends are biodegradable materials and have many advantages. They can be used in multiple applications. Starch–PVOH blends are being explored for replacement of LDPE films in applications where mechanical properties are critical for intended use and good moisture barrier properties are not necessary. This type of product has already been commercialized by Novamont SA (Novara, Italy) and marketed as water-soluble laundry bags. Starch–PVOH films can also be used in biomedical and clinical field (such as drug control release carrier and biomembrane) (Shi et al., 2008), while chemically bounded composites can be used as recyclable sizing agents (Hashem, Kesting, Hebeish, Abou-Zeid, & Schollmeyer, 1996). Starch–PVOH has been considered for expanded foams as loose-fill packaging materials for replacement of polystyrene foams. According to Vilpoux and Avérous (2004), a blend with 95% of hydroxypropylated high amylose corn starch and 5% of PVOH is used as a commercial alternative to the PS. Although starch–PVOH blends are sensitive to moisture, they are superior materials providing barriers to oxygen and carbon dioxide. They also can act as flavor and aroma barriers, which is important for supermarkets and convenience stores to prevent food picking up flavor and odors from other products. The resistance of PVOH-based materials to most organic compounds and solvents also protects packaged products from secondary contamination by printing inks etc. They can be co-extruded with other biodegradable plastics such as PLA, PHA to make completely biodegradable multi-layer barrier structures.

Starch–PVOH nanocomposites could be a solution to further improve physical properties of starch–PVOH blends, especially moisture barrier properties and thermal stability, which will advance the use of starch–PVOH composites in much more diverse applications. Some promising data have been already presented from our research group by using some modified nanoparticles such as synthetic hectorite, surface coated MMT (Tang & Alavi, 2010). Research continues into different types of nanofillers (i.e.

carbon nanotubes), allowing new nanocomposite structure with different improved properties. Polymer nanocomposites represent a stimulating route for creating new and innovative materials, also in the area of biopolymer and biopolymer based blends. Once production and material costs are reduced, companies will be using this technology to increase their product's stability and shelf life so that higher quality products can be delivered to their customers while saving money.

8. Conclusions

Technology is now available for the production, processing, converting and forming of a variety of biodegradable thermoplastic formulations based on thermoplastic starch and PVOH blends. These materials show a broad and versatile range of physical properties and other advantageous characteristics at acceptable cost and biodegradation rate and can be employed in a wide range of applications. To further improve their properties, some physical or chemical methods such as cross-linking, incorporation of nanoparticles can be applied. With these new techniques, materials with a great variety of property profiles can be realized and can compete, both in price and in performance, with synthetic polymeric materials in different applications.

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