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The Effects of Novel Additives Used in PVA/Starch Biohybrid Films

*Eyyup Karaogul, Ertugrul Altuntas, Tufan Salan
and Mehmet Hakki Alma*

Abstract

The main aim of this chapter is to indicate the importance of additives and modifications used for PVA/starch biohybrid films. The additives and modifications used to improve the mechanical, thermal, and morphological properties of films are plasticizers, cross-linkers, fillers, physical and chemical treatment, and natural materials as well as thermoplastic starch. Plasticizers are preferred for higher molecular dynamism because of flexibility of functional groups in PVA and starch. Their flexibility is considerably affected by carboxyl and hydroxyl groups of plasticizers. The use of cofunctional groups increases the plasticity, flexibility, and physicochemical and mechanical properties of films. Moreover, cross-linking modifications are also effective to enhance the properties of biofilms. These modifications improve the tensile strength, modulus of elasticity, water resistance, thermal resistance, swelling behavior, and antibacterial activity of films. Fillers are also used to enhance the properties of PVA/starch films. In this way, the properties such as gas barrier, mechanical stiffness, transparency and thermal stability of the filler-added films are improved. The chemical and physical modifications provide stronger hydrogen bonds in films due to increasing carboxyl groups. Thus, the physical, biological, and chemical properties of films are improved because of the changing molecular structure via esterification, etherification, hydrogen bonding, and oxidation.

Keywords: PVA/starch biobased films, modifications, formation methods, physicochemical properties

1. Introduction

Petrochemical-based plastics are being replaced by biobased materials because of being widely eco-friendly. In the last decades, the biobased films have been investigated due to their biodegradability and for being suitable, generally obtainable, and less expensive materials in the industry. The plastics produced from petrochemical sources (e.g., polyesters and polyolefins) have been commonly used in the packaging industry due to their potential features. They are obtainable in large quantities and at low cost, displaying advantageous properties (i.e., good tensile strength, enriched barrier properties, and heat sealing) and applicability in the industry [1, 2]. However, these plastics are totally nonbiodegradable and

expose a serious ecological problem due to hydrophobic properties and very low water vapor transmission rate [2, 3]. The growing public interest on the environment is induced by a growing research on biohybrid films (i.e., biobased films) as alternatives to traditional nondegradable plastics due to the harmful effect of petroleum-based plastic packaging [4]. The eco-friendly polymeric resources can be categorized into three main groups depending on the raw material used: renewable natural, biodegradable synthetic polymers, and microbially produced biopolymers. The renewable natural polymers can be obtained from several sources such as starch, cellulose, chitosan, etc. [5], while biodegradable synthetic polymers such as polyvinyl alcohol, polycaprolactone, polylactic acid, polybutylene succinate, and copolymers are produced by using natural or petroleum-based monomers. On the other hand, microbially produced biobased polymers (e.g., polyhydroxybutyrate and valerate copolymer) are manufactured via various microorganisms.

Starch among all natural biopolymers has been believed to be one of the most suitable biopolymer resources due to its biodegradable, regularly available, and inexpensive features. There are two major polymers of starch: amylose and amylopectin. Amylose is a linear molecule with a spiral structure unlike a branched structure of amylopectin. Moreover, the molecular weight of amylose is commonly a smaller molecule (1–1.5 million), while amylopectin is a large molecule (50–500 million) [6]. Various starches have been used in the biohybrid films because of changing amylose/amylopectin ratio. And these are classified by amylopectin content [7]. In most studies, biobased films have been manufactured from starch of corn, wheat, rice, potato, tapioca, and cassava [8]. Various starch types have been also used to the biobased films because of changing amylose and amylopectin ratio [7–10].

However, the biobased films obtained from starch have demonstrated some disadvantages such as brittleness, low processability, high water sensitivity (i.e., low moisture resistance and hydrophilic character), and poor mechanical properties compared to petroleum-based conventional polymers [37]. Moreover, the starches are not thermoplastic biopolymers due to the intra- and intermolecular hydrogen bonds, because the degradation temperature of starch exceeds the melting temperature [11]. These make them inadequate for some packaging purposes limiting their widespread industrial applications [12–14]. Therefore, physicochemical and biological properties of the starch should be improved. Several modification techniques are needed to improve the mechanical and physical properties to overcome the inadequate features of the starch-based biobased films [15]. Thus, several efforts have been made to improve thermal properties of starch by blending with a plasticizer for its stability, elasticity, and edibility. Despite the above-mentioned modifications and applications, the biodegradable films produced from starch are still limited due to poor mechanical and hydrophilic properties along with susceptibility to the biological attacks. Accordingly, polyvinyl alcohol (PVA) known as synthetic biodegradable polymer and thermoplastic starch was utilized together to obtain excellent compatibility [16]. In several studies, starch was used with polyvinyl alcohol (PVA). As an example, various starches such as corn, potato, rice, and tapioca have been studied in combination with PVA polymers [9, 10].

PVA is an important polymer having superior gas barrier properties along with higher strength, tear, and flexibility than those of natural biobased polymers. Nevertheless, it has weak dimensional stability owing to high water uptake. Furthermore, PVA has relatively high manufacturing cost in comparison with the other commercial polymers in the market. Thus, if PVA is blended with renewable and abundant natural sources like starch, the manufacturing costs can be reduced. This method also resulted in improved moisture resistance and rapid biodegradation [17, 18].

Over the last 10 years, hundreds of studies about PVA/starch biobased films have been carried out on the topic using various production techniques. The researchers

used the PVA and starch together for the purpose of exposing their superior properties and eliminating the poor properties. The main aim of this chapter was to investigate the effects of additives and modifications on the several properties of various novel additives on the PVA/starch-based biodegradable hybrid films. Moreover, the review of the studies was explained in a molecular chemistry point of view in the specific subheadings. So, the results obtained from the literature have been evaluated based on the effect of different novel additives on the several properties of PVA/starch-based biodegradable films.

2. Formation of PVA/starch films

PVA/starch-based biodegradable formulations are produced from polyvinyl alcohol (PVA) and starch known as main compositions with different additives such as plasticizer, cross-linkers, and filling materials. Until now, PVA/starch blend biobased films have been prepared using casting (sol-gel or mixing) and thermal (extruder or extrusion) methods by many researchers in the literature.

In casting method, PVA is dissolved in hot water with the gelatinized starch in order to form intermolecular interaction. The obtained mixture is then stirred in a mechanical high-speed mixer for homogenization [19] over 1000 rpm/min and at 85–95°C temperature, and then some of the additives are added into the mixture under continuous stirring. After removing the bubbles formed during the preparation of biobased films by an aspirator, it is dried at room temperature [20]. The hybrid films are generally heated in an oven at 80–95°C for 1 h to induce the cross-linking reactions [21]. Another approach for the fabrication of PVA/starch blend biobased films is using a single or twin screw extruders. Primarily, the plasticizing starch is mechanically mixed with PVA, and then, PVA/starch blend granules are obtained following the extrusion process under the optimum conditions at various temperature and screw speeds. After that, the biobased films are obtained from the prepared granules by using the blown film extrusion or hot-press molding [4, 22].

In casting method, considerable amounts of water are evaporated from aqueous solutions or suspensions with a high energy-consuming process to obtain PVA/starch hybrid films [23]. The PVA/starch blends are generally produced via solution casting method. Nevertheless, this method has several deficiencies such as low solution density, low manufacturing yield, high energy consumption, etc., which limit its industrial practices [19]. On the other hand, the extrusion films have a great importance due to energy-efficiency process, high productivity, and continuous industrial production possibilities. However, the solution casting method has gained much more attention compared to extrusion process for the production of PVA/starch blend films in scientific publications due to its easy applicability in laboratories [4, 23, 24].

3. Use of additives and modifications in PVA/starch biobased formulations

Various additives such as plasticizers (e.g., glycerol and sorbitol), cross-linkers (e.g., glutaraldehyde and epichlorohydrin), fillers (e.g., silicium dioxide and calcium carbonate), and natural raw materials (e.g., cellulose and chitosan) as well as thermoplastic starch have been used to improve the mechanical, thermal, and morphological properties of PVA/starch-based biodegradable hybrid films. Furthermore, a variety of methods including esterification, oxidation, and etherification were applied in order to modify the starch [25]. These novel additives and the

modifications have been discussed under the following subheadings as plasticizers, cross-linkers, fillers, and chemical and physical modifications.

3.1 Plasticizers

Plasticizers are additives that increase the elasticity. These are the ingredients for nonthermoplastic starch, which are added in order to alter their physical properties. Plasticization takes place in the amorphous zone, which has a higher molecular dynamism. The type and the amount of plasticizer have an important influence on the ability to hinder hydrogen bonding along the polymer chains. The major gain obtained from utilization of plasticizers is that the tensile strength (TS) is decreased, while the elongation at break (E%) increases as well as they become more flexible [26]. One of the most important properties of an efficient plasticizer is to be compatible with the polymer matrix. The plasticizers such as glycerol, polyethylene glycol, urea, ascorbic acid, sorbitol, citric acid, and tartaric acid are usually used [19]. However, the plasticizers in the biobased films cause an increase in permeability to moisture, oxygen, and aromatic compounds [27]. **Table 1** presents the various plasticizers and used methods along with the effects of plasticization on some properties of PVA/starch films.

Water is accepted as a basic plasticizer for PVA/starch biofilms. Physicochemical properties of films could differ based on the changing water content. At the same time, the water is also compatible with other plasticizers. When the plasticizers are added into biofilm formulations, the physical properties are affected due to the increasing relative moisture because of compatibility with water. Possibly, water is absorbed because of polarity compliance to the solubility of other plasticizers added as additives. The plasticizer effect of water could usually be effective when it is used also together or not with an above-mentioned plasticizer. Furthermore, glycerol, sorbitol, and citric acid are generally favored as an efficient plasticizer for PVA/starch films. According to previous studies, the E% increased while TS decreased because of increasing glycerol, sorbitol, and citric acid ratio from 10 to 50% in the biobased films. It was also reported that E% and TS of sorbitol or citric acid-added films were higher than those of the glycerol-added films. However, the water absorption property of the biobased film decreased with the increasing glycerol ratio due to its hydrophobicity [29]. Moreover, the swelling behavior of the film containing glycerol was the lowest compared to the sorbitol- and citric acid-added films due to weaker hydrogen bonding capabilities, unlike the solubility value due to weaker hydrogen bonding capable [8].

Plasticizers added	Characteristics of PVA/starch film and obtained improvement	Processing method	Reference
Water	A large decrease in tensile strength in all the tested films was recorded when the storage relative humidity increased from 15% to 33%.	Casting	[8]
Glycerol	E% increased while TS decreased. TS, E%, swelling behavior, and degree of the compatibility with PVA and starch were lower compared to sorbitol and citric acid. However, solubility was higher.	Casting	[8]
Urea	It had a good interaction, homogeneity, and sensitivity to the water with PVA and starch in comparison with glycerol and sorbitol.	Casting	[28]
Formamide	It was not a good plasticizer and could not improve the compatibility and flexibility of the blend. It exhibited synergistic effects and the compatibility, especially E%, with simultaneously added urea in the blend.	Casting	[19]

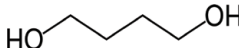
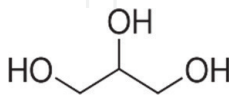
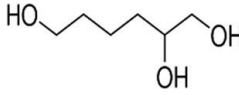
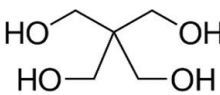
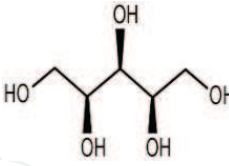
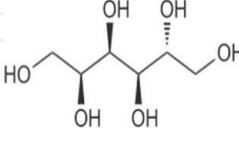
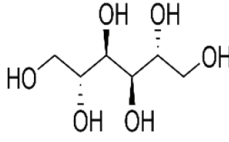

Table 1.
Effect of plasticization on some characteristics of PVA/starch films along with obtained improvements.

The homogeneity of PVA/starch biobased films could also be enhanced with the addition of urea, like glycerol. However, urea as a plasticizer showed stronger interactions with starch and PVA in biofilms than those of glycerol and sorbitol [11, 28]. Consequently, urea was considered a better plasticizer to improve the flexibility of PVA/starch films [19]. Furthermore, the crystallinity of biobased films was also decreased by the addition of urea and formamide. These agents could penetrate into the crystallization zone of PVA/starch biobased films during the process forming new hydrogen bonds with starch and PVA molecules, which damage the crystal region of PVA in the biobased films. However, formamide is not a good plasticizer and could not develop the compatibility and flexibility of the biobased films, while the compatibility was improved when it combined with urea. When the additives containing both urea and formamide are simultaneously used, their synergistic effects and the compatibility could occur in the blend. Besides, while TS and young modulus of biobased films were significantly decreased, the E% was substantially improved. With the increasing amount of urea in the biobased films, the sensitivity to water increased, while the melting point of blends decreased. It was likely due to the facilitation of molecular ability of both urea and formamide as a plasticizer [19].

3.2 Effects of functional group type and number of plasticizers on the properties of biobased films

Physicochemical properties of blend films are substantially affected by the functional groups of plasticizers used in PVA/starch biobased films. The total number of both carboxyl and hydroxyl groups in plasticizers were given in **Table 2** along with their behaviors in films. For instance, as regards the hydroxyl and carboxyl groups of glycerol (H.3, C.0) and succinic acid (H.0, C.2), the E% of the glycerol-added film has shown a high enhancement than that of the films containing succinic acid, contrarily to the TS behavior. However, when malic acid (H.1, C.2) in the same carboxyl number with succinic acid (H.0, C.2) was added to the film, the TS and E% were improved compared to glycerol (H.3, C.0) and sorbitol (H.6, C.0) because of the presence of two functional groups. Depending on the increasing functional groups of plasticizer, TS and E% of tartaric acid (H.2, C.2) added biobased films with two same functional groups were greater than those of malic acid, glycerol, and sorbitol [6, 30]. Furthermore, the biobased films containing citric acid (H.1, C.3) were stronger and more flexible than that of containing glycerol [7, 30] and xylitol (H.5, C.0) [31]. On the other hand, when the glycerol and xylitol added films were compared, it was found that xylitol-added biobased films had a higher strength and more elasticity than glycerol-added biobased films due to its 5 hydroxyl groups [31]. Even a few xylitol molecules can play an extra role in plasticizer than others [32]. Similarly, the comparison of glycerol- and sorbitol-added films showed that TS and E% of sorbitol-added film were greater than glycerol [7, 30]. Consequently, E% value increases while TS decreases with an increase in the total functional groups and the amount of these plasticizers in blend films.

The concept of plasticization could be understood with the analysis of different properties such as elongation at break (mentioned above) or glass transition point (T_g). For instance, Aydin et al. reported that the addition of plasticizers reduced the T_g point clearly and the change of plasticizing performances could be observed by increasing T_g point. Apart from the above-mentioned plasticizers, 1,4-Butanediol (H.2, C.0), 1,2,6-Hexanetriol (H.3, C.0), pentaerythritol (H.4, C.0), xylitol (H.5, C.0), and mannitol (H.6, C.0) from 2 to 6 hydroxyl groups have also been investigated based on the changes in T_g point. Among the investigated plasticizers, 1,4-butanediol demonstrated the maximum plasticizing effect for starch and PVA due to small molecular size and geometry [32]. **Table 2** shows the effects of the various plasticizers with different functional groups and number on the properties of PVA/starch films.

Plasticizer added	PVA/starch film characteristics and obtained improvement	Funct. groups		Formula	Reference
		H ¹	C ²		
		Numbers			
1,4-Butanediol	Among the investigated plasticizers with 2 and 6 hydroxyl groups, it showed the highest plasticizing effect for starch and PVA due to small molecular size and geometry.	2	—		[32]
Glycerol	The E% of the glycerol-added film was higher than that of succinic acid on the contrary TS.	3	—		[6]
1,2,6-Hexanetriol	Further penetration into the chain fragment of starch and PVA was prevented because of their larger molecular geometry.	3	—		[32]
Pentaerythritol	Due to molecular size and geometry, its plasticizer efficiency was generally lower than 1,4-butanediol, 1,2,6-Hexanetriol, xylitol, and mannitol.	4	—		
Xylitol	Compared to the glycerol, its TS and E% had more potential ¹ . However, after its continuous addition, penetration capability into molecular chains tended to be lower ² .	5	—		1[31], 2[32]
Sorbitol	Mechanical properties of sorbitol-added films were higher than those of glycerol-added films.	6	—		[30]
Mannitol	It can enhance the thermal stability.	6	—		[32]
Succinic acid	It is too fragile to be used in applications	—	2		[6]

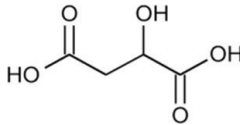
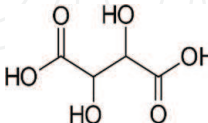
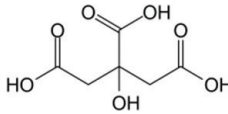
Plasticizer added	PVA/starch film characteristics and obtained improvement	Funct. groups		Formula	Reference
		H ¹	C ²		
		Numbers			
Malic acid	It has a good effect on the TS and E% than those of glycerol, sorbitol, and succinic acid due to both hydroxyl and carboxyl groups.	1	2		[6, 30]
Tartaric acid	Compared to malic acid, glycerol, and sorbitol, it had a higher TS and E%.	2	2		
Citric acid	Due to hydroxyl and carboxyl groups, its TS and E% were stronger than those of glycerol and xylitol.	1	3		[31]

Table 2.
Effect of functional group type and number on the plasticization in PVA/starch films.

The different plasticizing effect of xylitol and mannitol was attributed to lower penetration capability. Due to larger molecular geometry and size of 1,2,6-Hexanetriol and pentaerythritol, further penetration into the chain fragment of starch and PVA was prevented. Moreover, the plasticizer efficiency of pentaerythritol was generally lower than that of 1,4-butanediol, 1,2,6-Hexanetriol, xylitol, and mannitol. Consequently, the increase in hydroxyl groups and molecular size of the plasticizers such as mannitol caused an improvement in the thermomechanical stability on the contrary of xylitol. For example, the maximum amount of mannitol (due to more hydroxyl number) in the films tends to interact more with the blend, on the contrary, with lower hydroxyl number plasticizers [32]. Based on the literature data obtained, it could be expressed that the molecular structure and geometry of plasticizers could inhibit or support their penetration into the molecular chain segments and reduce or increase inter- and intramolecular interactions, although the number of hydroxyl groups of plasticizers is hydrogen bonding quarters for starch and PVA.

The presence of two type of functional groups could also significantly influence other properties of biobased films. For instance, the citric acid could improve the water stability and inhibit degradation of starch molecules [15]. Due to the very strong interaction of water with glycerol and sorbitol, the solubility values were higher than the plasticizer with carboxyl groups. While the solubility of tartaric and citric acids was easy in water, their solubility value was lower than that of glycerol and sorbitol [7]. Eventually, the degree of swelling and mechanical properties of biofilms could decrease or increase slightly with the increasing content of plasticizer depending on functional groups [30]. However, the degree of swelling of the films without plasticizer was higher than that of films containing additives, while the solubility of films without plasticizer was lower [7].

3.3 Effect of plasticizers added simultaneously into biobased films

When the plasticizers having both hydroxyl and carboxyl groups were simultaneously added into the biobased films, their physicomechanical properties were better than those of plasticizers with only hydroxyl group-containing agents. Yoon et al. reported that as the additives containing both hydroxyl and carboxyl groups were simultaneously added into the formulation, the TS and %E were enhanced compared to the glycerol, having only hydroxyl groups. For instance, %E of the glycerol-succinic acid-added films increased, while only succinic acid-added film showed inadequate potential. The usage of the plasticizer composed of both hydroxyl and carboxyl groups could enhance the flexibility and strength. Moreover, the degree of swelling and solubility values of the comalic acid-/tartaric acid-added films were higher than those of coglycerol-/succinic acid-added films. [6]. This was because the hydroxyl (-OH) group number of malic acid-tartaric acid (7 hydroxyl number) was higher (i.e., having a more hydrophilic character) than glycerol-succinic acid mixture (5 hydroxyl number). %E of the glycerol or sorbitol-succinic acid-added films increased, while %E of succinic acid-added film decreased with increasing amount of additives. Nevertheless, TS of glycerol or sorbitol-succinic acid-added films decreased, while TS of succinic acid-added film diminished with increasing content of additive. The results of TS and %E mentioned above showed that using cohydroxyl/carboxyl group as a functional group increased physico-chemical and mechanical properties of films [30]. Eventually, when the plasticizers having both hydroxyl and carboxyl groups were used simultaneously, TS and %E of the films were found to be better than the films containing plasticizer having only the hydroxyl group [7].

3.4 Cross-linkers

Cross-linking modification method is an effective and frequently applied approach to enhance the physicochemical and mechanical properties of PVA and starch [33]. Cross-linking can be carried out via treatment of granular starch using functional or multifunctional materials, which generated stable ether (R-O-R) or ester (R-CO-OR) linkages with the hydroxyl groups (-OH) in starch [9, 34]. Some of these multifunctional compounds are monosodium phosphate, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin, phosphoryl chloride, a mixture of adipic and acetic anhydrides, and a mixture of succinic anhydride and vinyl acetate. Cross-linker starch showed better compatibility and interaction with PVA than those of unmodified starch; such as, water absorption and TS of starch cross-linked films with sodium trimetaphosphate were higher than those of uncross-linked starch films, unlike E%. Moreover, weight loss in the soil of uncross-linked starch films was higher than that of the cross-linked starch films. Since the weight loss of starch under the soil is related to the amount of moisture, the use of cross-linked starch improves the water resistance of the biobased films [9].

When epichlorohydrin was used for cross-linking, the TS and %E of starch/PVA blend films increased. Thermal degradation of biofilms has been diminished by the cross-linker epichlorohydrin [35]. If sodium carbonate and sodium hexametaphosphate as the other cross-linkers are used, the equilibrium moisture content of the biofilms is significantly reduced by lowering their hydrophilic characteristic. Furthermore, these modifications increase the TS and modulus of elasticity of biofilms, unlike elongation at break [33].

In a study, the usage of sodium trimetaphosphate and sodium tripolyphosphate as the cross-linker enhanced the physicochemical properties such as swelling behavior compared to the uncross-linked starch [8]. Likewise, the swelling of the

biofilms was intensely reduced after utilization of cross-linker epoxidized natural rubber owing to the interaction between the mixtures. Thus, the hydrophilicity of the blend film decreases due to the reduction of the number of free hydroxyl groups in PVA and starch molecule. And, %E of film improves with the addition of cross-linker in blend polymer [36]. Singha and Kapoor have reported that the TS of PVA/starch cross-linked with glutaraldehyde has shown improvement. Moreover, modification with glutaraldehyde also improved the thermal stability of films. Moreover, their antibacterial activities against Gram-positive bacteria compared to Gram-negative bacteria indicated good resistance [15]. Additionally, borax can also be used as a cross-linker for starch and PVA. The enthalpy and crystallinity slightly decreased with increasing concentration of borax due to increasing cross-linking. Also, it improved the TS and %E of biobased films compared to the biobased films without cross-linker. Citric acid as another cross-linker can also be preferred for biobased films. This cross-linker decreases the water absorption of biobased films. So, citric acid also acts not only as a plasticizer but also as a cross-linker [29].

3.5 Fillers used in PVA/starch biobased films

Filled PVA/starch biobased films are the high-potential class of hybrid materials composed of filler incorporated into a biobased matrix [37]. With the aim to attain synergic effects, such a collaboration between environmental biopolymers and fillers is one of the most impressive ways to improve the features of this bioblends [38]. Because of the nature and the geometry of the filler, the properties of biobased films such as gas barrier, mechanical stiffness, transparency, and thermal stability have been enhanced [37, 39].

In a study, the use of silica as a filler has increased the TS of biobased films [40]. With the increase of silica amounts in blend film, the water absorption and water vapor transmission of starch have been decreased. This was due to the complex structure designed by links between silica and hydroxyl groups of starch and PVA. This phenomenon prevented the water molecules from dissolving and developed the water resistance of the biofilm. Furthermore, silica has also improved the compatibility between PVA and starch and formed a rigid structure. Even, according to SEM results, the low amount of silica has provided excellent diffusion and interaction between starch and PVA. On the other hand, filler silica has shown less effect on the biodegradability of the films because of decreasing microorganism penetration rate [9].

Nano-calcitine was preferred as a filler for PVA/starch film because of its positive effects on the physicochemical properties of blend films. As an example, the addition of nano-calcitine into blend film reduced the crystallinity, water solubility, biodegradability, and oxygen permeability. At the same time, it increased TS, limiting oxygen index, decomposition temperature, and water absorption [41]. Simultaneously, addition of nano-SiO₂/TiO₂/CaCO₃ into PVA/starch blends increased the TS of biofilms enhancing the interfacial adhesion through inter- and intramolecular interactions. With nano-TiO₂, an increase in clearness of biofilm was noticeably observed. However, water vapor permeability of biofilms containing nano-SiO₂ was lower than that of biofilms containing nano-TiO₂/CaCO₃ [4, 42]. Therewithal, TS and Young's modulus of biobased films were also increased with filler TiO₂ unlike E% [43].

Zirconium phosphate as another filling material had an attractive effect in the biobased films because of composing new hydrogen links. The addition of zirconium phosphate decreased the moisture uptake, while the degradation temperatures of biobased films increased [44]. The filler clay had an important effect on biobased films due to its hydrophilicity. The use of clay in biofilm increased TS and

heat resistance, enhanced the barrier properties to water vapor, and lowered glass transition temperature [24].

In PVA/starch biohybrid film, natural raw materials were also added as fillers such as cellulose nanofibers, chitosan, and feather keratin. In investigations, cellulose nanofibers blocked the recrystallization of starch by decreasing the mobility of polymer chains. Hence, the physicochemical properties and crystal structure of blend film were significantly enhanced. In relation to this, storage conditions of biobased films improved. Cellulose nanofibers significantly enriched also the stiffness and strength of blend films by the storage conditions [34]. Similarly, the storage conditions of biobased films in natural weathering could be also enhanced by added graphene into PVA and starch [45]. Moreover, when the chitosan known as a natural filler was added to biofilms, their physicochemical properties such as TS, E%, water vapor permeability, and oxygen transmission rate improved. Also, water vapor and oxygen permeability, water uptake, and hydrophobic character of the chitosan-added bioblend film were better than biofilm without chitosan due to its incorporation [46]. As different inorganic salts are used in the biobased films, their crystalline [47], thermal, water vapor barrier, and mechanical properties can be significantly affected via strong hydrogen bonds. For this reason, Jiang et al. have reported that LiCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ salts have provided a good compatibility with PVA and starch [48, 49]. Moreover, the ZnO added biobased films have shown good dispersion, homogeneity, mechanical properties, and water resistance [49]. Another filler salt, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, can show compatibility with PVA and starch. Hence, these salts have presented great destroying effect on the crystalline and good mechanical properties [50].

3.6 Chemical modifications

The chemical modifications applied to the biohybrid films produced from PVA and starch have improved their physical-biological-chemical properties because of the changing molecular structure of blend. For instance, the carboxyl group of PVA and starch has occurred in bioblend films after oxidation of starch with H_2SO_4 and KMnO_4 . After the increase of polar carboxyl groups by oxidation, the hydrogen bonds in blend molecules were stronger than those of nonmodified ones. At the same time, their TS and E% have improved [44]. After modification, hydroxypropyl distarch phosphate converted from starch has shown highest TS and capability of retarding evaporation of water due to being compatible with fillers [4]. In another modification, PVA and starch blend grafted with methylmethacrylate had a higher E% and water desorption. For this reason, polysaccharide chain of starch and OH- groups of PVA are mostly occupied with monomers [51]. However, Yoon et al. depicted that TS increased on the contrary E% after using to blend film modified methylmethacrylate with acrylamide [31].

The plasma and irradiation treatment known as novel modification were also applied to PVA and starch blend films. These treatments can influence physicochemical properties of biohybrid films. Therefore, the treatment can cause a chemical bonding or graft functional groups on the PVA and starch backbone without any additives [52, 53]. Hence, the carbonyl groups of biofilms are improved with plasma treatment by using rotary argon plasma equipment. In addition, while E% of blend films can tolerate, its TS could also be lower. The plasma or irradiating pretreated with PVA and starch exhibited better thermal, processing, and mechanical (tensile) properties and toughness due to the induction of the cross-linking reaction [53]. With irradiated or plasma modifications, biofilms could prolong the storage conditions up to 15 days [54].

3.7 Physical modifications

Physical modification of PVA and starch could be safely used in biohybrid films. In generally, gelatinized, ungelatinized, fast and slow drying, varying amylose contents of raw material starch, changing of PVA and starch ratio, and impregnation of antioxidants were preferred in blend films for this modification. Applying physical modifications to biobased films affects significantly their physicochemical properties. For example, gelatinized starch-polyvinyl alcohol blend films illustrate their uniformity of morphologies than the ungelatinized films, which corresponds well with the intensity of newly formed hydrogen bonds between starch, polyvinyl alcohol, and plasticizer. After the starch was gelatinized, the melting point of blend film decreased because of forming stronger hydrogen bonding interactions at an elevated preparation temperature [11]. At the same time, the gelatinized procedure is believed as a useful way to eliminate the crystalline structure [55]. In the fast (at 50°C) and slow (at 5°C) drying modification of the blend films, solubility, TS, E%, and degree of swelling values of the biobased films are preferable at slow drying than those of fast drying owing to the hydrogen bonding interaction forming at low temperature [56].

With increasing amylopectin contents of starch in blend film, the %E and T_g increased while TS decreased. The linear structure of amylose improved the tensile property of films (especially, the amount of elongation) and the degree of crystallinity. However, because of the amorphous structure of amylopectin, %E of blend film was lower. Increasing amylose ratio in blend film significantly increased %E values as it plays an important role in cross-linking [7]. Moreover, changing rates of PVA and starch illustrated important role in blend films. The TS of the film decreased with increasing starch content in PVA compared to pure PVA film [5]. At the same time, the crystallinity of PVA in blend film decreased importantly compared to pure PVA film. On the other hand, the water absorption of blend film increased with the increasing starch ratio, because the water absorption of PVA is weaker than that of starch [29].

The impregnation of antioxidants into the biofilm is another physical modification technique bringing antioxidative effect in biofilms. For instance, PVA/starch biofilms impregnated with catechin showed antioxidant and antimicrobial properties, while TS and %E of films decreased. Moreover, the biofilm containing catechin hinders lipid oxidation and microbial growth on raw meat during storage condition without substantial change in redness compared with commercial polyethylene pack [57].

4. Conclusion

PVA/starch biohybrid films are widely becoming an eco-friendly alternative to petrochemical-based plastics due to their biodegradability and for being suitable, generally obtainable, and less expensive materials. These biohybrid films have been obtained by using casting (sol-gel or mixing) and thermal processing (extruder or extrusion) methods. A great number of components in PVA/starch biobased films have been added to the matrix in order to improve physicochemical and mechanical properties. Moreover, various additives such as plasticizers, cross-linkers, fillers, and natural raw materials as well as thermoplastic starch have been used to improve the mechanical, thermal, and morphological properties of PVA/starch-based biodegradable hybrid films.

Plasticization in starch and PVA involves place in the amorphous area for higher molecular dynamism as well as their flexibility. Elasticity and other properties of biobased films are significantly affected by the functional groups (carboxyl and hydroxyl groups) of plasticizers. The using of cohydroxyl/carboxyl group as

a functional group increases the flexibility and physicochemical and mechanical properties of films. Cross-linking modifications in biobased films increase amorphous zone in molecular structure. This formation is effective to enhance the physicochemical and mechanical properties. These modifications improve the TS [2], modulus of elasticity [33], water resistance [49], thermal resistance [16], swelling behavior [8], and antibacterial activity of biofilms [15], unlike %E [2]. The filler in PVA/starch biobased films has a high potential class. Nature and the geometry of the filler-added biobased films have enhanced their properties such as gas barrier, mechanical stiffness, transparency, and thermal stability. The chemical modifications occur in the carboxyl group in molecular structure of PVA and starch because of oxidation. With increasing of carboxyl groups, the hydrogen bonds in biobased films were stronger than those of nonmodified ones. This stronger hydrogen bonding has improved physical-biological-chemical properties of biobased films because of the changing molecular structure of blend. Moreover, applied physical modifications to biobased films also significantly affect their physicomachanical properties. Consequently, these modifications applied to starch and PVA cause the esterification, etherification, hydrogen bonding, and oxidation in their molecular structure.

Author details

Eyyup Karaogul^{1*}, Ertugrul Altuntas², Tufan Salan³ and Mehmet Hakki Alma²

¹ Department of Food Engineering, Harran University, Sanliurfa, Turkey

² Department of Forest Industry Engineering, Kahramanmaras Sutcu Imam University, Kahramanmaras, Turkey

³ Department of Materials Science and Engineering, Kahramanmaras Sutcu Imam University, Kahramanmaras, Turkey

*Address all correspondence to: eyyupkaraogul@gmail.com

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References

- [1] Tharanathan RN. Biodegradable films and composite coatings: Past, present and future. *Trends in Food Science and Technology*. 2003;**14**(3):71-78. DOI: 10.1016/S0924-2244(02)00280-7
- [2] Ismail H, Zaaba NF. Effect of additives on properties of polyvinyl alcohol (PVA)/tapioca starch biodegradable films. *Polymer-Plastics Technology and Engineering*. 2011;**50**(12):1214-1219. DOI: 10.1080/03602559.2011.566241
- [3] Klingbeil M. Working Document of Biodegradable Waste Management. Brussels: European Commission; 2000
- [4] Wang W, Zhang H, Dai Y, Hou H, Dong H. Effects of various nanomaterials on the properties of starch/poly(vinyl alcohol) composite films formed by blow extrusion process. *Iranian Polymer Journal*. 2015;**24**(8):687-696. DOI: 10.1007/s13726-015-0359-7
- [5] Azahari NA, Othman N, Ismail H. Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media. *Journal of Physical Science*. 2011;**22**(2):15-31
- [6] Yoon SD, Chough SH, Park HR. Effects of additives with different functional groups on the physical properties of starch/PVA blend film. *Journal of Applied Polymer Science*. 2006;**100**(5):3733-3740. DOI: 10.1002/app.23303
- [7] Yun YH, Yoon SD. Effect of amylose contents of starches on physical properties and biodegradability of starch/PVA-blended films. *Polymer Bulletin*. 2010;**64**(6):553-568. DOI: 10.1007/s00289-009-0158-4
- [8] Lee WJ, Youn YN, Yun YH, Yoon SD. Physical properties of chemically modified starch(RS4)/PVA blend films-Part 1. *Journal of Polymers and the Environment*. 2007;**15**(1):35-42. DOI: 10.1007/s10924-006-0040-5
- [9] Ismail H, Zaaba NF. Effect of unmodified and modified sago starch on properties of (sago starch)/silica/PVA plastic films. *Journal of Vinyl and Additive Technology*. 2014;**20**(3):185-192. DOI: 10.1002/vnl.21344
- [10] Ooi ZX, Ismail H, Abu Bakar A, Aziz NA. Effects of jackfruit waste flour on the properties of poly(vinyl alcohol) film. *Journal of Vinyl and Additive Technology*. 2011;**17**(3):198-208. DOI: 10.1002/vnl.20269
- [11] Luo XG, Li JW, Lin XY. Effect of gelatinization and additives on morphology and thermal behavior of corn starch/PVA blend films. *Carbohydrate Polymers*. 2012;**90**(4):1595-1600. DOI: 10.1016/j.carbpol.2012.07.036
- [12] John MJ, Thomas S. Biofibres and biocomposites. *Carbohydrate Polymers*. 2008;**71**(3):343-364
- [13] Alves V, Costa N, Hilliou L, Larotonda F, Goncalves MP, Sereno A, et al. Design of biodegradable composite films for food packaging. *Desalination*. 2006;**199**(1-3):331-333
- [14] Bastos DC, Santos AEF, da Silva MLJ, Simao RA. Hydrophobic corn starch thermoplastic films produced by plasma treatment. *Ultramicroscopy*. 2009;**109**(8):1089-1093
- [15] Singha AS, Kapoor H. Effects of plasticizer/cross-linker on the mechanical and thermal properties of starch/PVA blends. *Iranian Polymer Journal*. 2014;**23**(8):655-662. DOI: 10.1007/s13726-014-0260-9
- [16] Lum YH, Shaaban A, Mitran NMM, Dimin MF, Mohamad N, Hamid N,

- et al. Characterization of urea encapsulated by biodegradable starch-PVA-glycerol. *Journal of Polymers and the Environment*. 2013;**21**(4):1083-1087. DOI: 10.1007/s10924-012-0552-0
- [17] Han XZ, Chen S, Hu XG. Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. *Desalination*. 2009;**240**(1-3):21-26
- [18] Russo MAL, O'Sullivan C, Rounsefell B, Halley PJ, Truss R, Clarke WP. The anaerobic degradability of thermoplastic starch: Polyvinyl alcohol blends: Potential biodegradable food packaging materials. *Bioresource Technology*. 2009;**100**(5):1705-1710
- [19] Yan JA, Tian HF, Zhang YH, Xiang AM. Effect of urea and formamide plasticizers on starch/PVA bioblend sheets. *Journal of Applied Polymer Science*. 2015;**132**(33):1-8. DOI: Artn 4231110.1002/App.42311
- [20] Priya B, Gupta VK, Pathania D, Singha AS. Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre. *Carbohydrate Polymers*. 2014;**109**:171-179
- [21] Yao KH, Cai J, Liu M, Yu Y, Xiong HG, Tang SW, et al. Structure and properties of starch/PVA/nano-SiO₂ hybrid films. *Carbohydrate Polymers*. 2011;**86**(4):1784-1789. DOI: 10.1016/j.carbpol.2011.07.008
- [22] Julinova M, Dvorackova M, Kupec J, Hubackova J, Kopcilova M, Hoffmann J, et al. Influence of technological process on biodegradation of PVA/waxy starch blends in an aerobic and anaerobic environment. *Journal of Polymers and the Environment*. 2008;**16**(4):241-249. DOI: 10.1007/s10924-008-0109-4
- [23] Thunwall M, Kuthanova V, Boldizar A, Rigdahl M. Film blowing of thermoplastic starch. *Carbohydrate Polymers*. 2008;**71**(4):583-590. DOI: 10.1016/j.carbpol.2007.07.001
- [24] Gao W, Dong H, Hou H, Zhang H. Effects of clays with various hydrophilicities on properties of starch-clay nanocomposites by film blowing. *Carbohydrate Polymers*. 2012;**88**(1):321-328. DOI: 10.1016/j.carbpol.2011.12.011
- [25] Yun YH, Wee YJ, Byun HS, Yoon SD. Biodegradability of chemically modified starch (RS4)/PVA blend films: Part 2. *Journal of Polymers and the Environment*. 2008;**16**(1):12-18. DOI: 10.1007/s10924-008-0084-9
- [26] Sothornvit R, Krochta JM. Plasticizer effect on mechanical properties of beta-lactoglobulin films. *Journal of Food Engineering*. 2001;**50**(3):149-155. DOI: Doi 10.1016/S0260-8774(00)00237-5
- [27] Jimenez A, Fabra MJ, Talens P, Chiralt A. Edible and biodegradable starch films: A review. *Food and Bioprocess Technology*. 2012;**5**(6):2058-2076. DOI: 10.1007/s11947-012-0835-4
- [28] Ma XF, Yu JG, He K, Wang N. The effects of different plasticizers on the properties of thermoplastic starch as solid polymer electrolytes. *Macromolecular Materials and Engineering*. 2007;**292**(4):503-510. DOI: 10.1002/mame.200600445
- [29] Zou GX, Ping-Qu J, Liang-Zou X. Extruded starch/PVA composites: Water resistance, thermal properties, and morphology. *Journal of Elastomers and Plastics*. 2008;**40**(4):303-316. DOI: 10.1177/0095244307085787
- [30] Yun YH, Na YH, Yoon SD. Mechanical properties with the functional group of additives for starch/PVA blend film. *Journal of Polymers*

and the Environment. 2006;**14**(1):71-78.
 DOI: 10.1007/s10924-005-8709-8

[31] Yoon SD, Park MH, Byun HS. Mechanical and water barrier properties of starch/PVA composite films by adding nano-sized poly(methyl methacrylate-co-acrylamide) particles. *Carbohydrate Polymers*. 2012;**87**(1):676-686. DOI: 10.1016/j.carbpol.2011.08.046

[32] Aydin AA, Ilberg V. Effect of different polyol-based plasticizers on thermal properties of polyvinyl alcohol: Starch blends. *Carbohydrate Polymers*. 2016;**136**:441-448. DOI: 10.1016/j.carbpol.2015.08.093

[33] Liu Z, Dong Y, Men H, Jiang M, Tong J, Zhou J. Post-crosslinking modification of thermoplastic starch/PVA blend films by using sodium hexametaphosphate. *Carbohydrate Polymers*. 2012;**89**(2):473-477. DOI: 10.1016/j.carbpol.2012.02.076

[34] Panaitescu DM, Frone AN, Ghiurea M, Chiulan I. Influence of storage conditions on starch/PVA films containing cellulose nanofibers. *Industrial Crops and Products*. 2015;**70**:170-177. DOI: 10.1016/j.indcrop.2015.03.028

[35] Kim DH, Na SK, Park JS, Yoon KJ, Ihm DW. Studies on the preparation of hydrolyzed starch-g-PAN (HSPAN)/PVA blend films—Effect of the reaction with epichlorohydrin. *European Polymer Journal*. 2002;**38**(6):1199-1204. DOI: 10.1016/S0014-3057(01)00301-9

[36] Riyajan SA, Sukhlaaied W. Surface modification and swelling behavior of biodegradable polymer blends from PVA, starch and epoxidized natural rubber. *KGK, Kautschuk Gummi Kunststoffe*. 2012;**65**(9):30-34

[37] Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: A

review from preparation to processing. *Progress in Polymer Science*. 2003;**28**(11):1539-1641. DOI: 10.1016/j.progpolymsci.2003.08.002

[38] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Materials Science and Engineering R*. 2000;**28**(1-2):1-63. DOI: 10.1016/S0927-796x(00)00012-7

[39] Gain O, Espuche E, Pollet E, Alexandre M, Dubois P. Gas barrier properties of poly(epsilon-caprolactone)/clay nanocomposites: Influence of the morphology and polymer/clay interactions. *Journal of Polymer Science: Polymer Physics*. 2005;**43**(2):205-214. DOI: 10.1002/polb.20316

[40] Ismail H, Zaaba NF. The mechanical properties, water resistance and degradation behaviour of silica-filled sago starch/PVA plastic films. *Journal of Elastomers and Plastics*. 2014;**46**(1):96-U19. DOI: 10.1177/0095244312462163

[41] Kisku SK, Sarkar N, Dash S, Swain SK. Preparation of starch/PVA/CaCO₃ nanobiocomposite films: Study of fire retardant, thermal resistant, gas barrier and biodegradable properties. *Polymer-Plastics Technology and Engineering*. 2014;**53**(16):1664-1670. DOI: 10.1080/03602559.2014.919650

[42] Tang S, Zou P, Xiong H, Tang H. Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films. *Carbohydrate Polymers*. 2008;**72**(3):521-526. DOI: 10.1016/j.carbpol.2007.09.019

[43] Sreekumar P, Al-Harthi MA, De S. Reinforcement of starch/polyvinyl alcohol blend using nano-titanium dioxide. *Journal of Composite Materials*. 2012;**46**(25):3181-3187. DOI: 10.1177/0021998312436998

- [44] Yang YJ, Liu CH, Chang PR, Chen Y, Anderson DP, Stumborg M. Properties and structural characterization of oxidized starch/PVA/alpha-zirconium phosphate composites. *Journal of Applied Polymer Science*. 2010;**115**(2):1089-1097. DOI: 10.1002/app.31099
- [45] Bin-Dahman OA, Jose J, Al-Harathi MA. Effect of natural weather aging on the properties of poly(vinyl alcohol)/starch/graphene nanocomposite. *Starch-Starke*. 2017;**69**(7-8):1600005
- [46] Akter N, Khan RA, Tuhin MO, Haque ME, Nurnabi M, Parvin F, et al. Thermomechanical, barrier, and morphological properties of chitosan-reinforced starch-based biodegradable composite films. *Journal of Thermoplastic Composite Materials*. 2012;**27**(7):933-948. DOI: 10.1177/0892705712461512
- [47] Jiang X, Luo Y, Hou L, Zhao Y. The effect of glycerol on the crystalline, thermal, and tensile properties of CaCl₂-doped starch/PVA films. *Polymer Composites*. 2016;**37**(11):3191-3199. DOI: 10.1002/pc.23517
- [48] Jiang X, Li H, Luo Y, Zhao Y, Hou L. Studies of the plasticizing effect of different hydrophilic inorganic salts on starch/poly (vinyl alcohol) films. *International Journal of Biological Macromolecules*. 2016;**82**:223-230. DOI: 10.1016/j.ijbiomac.2015.11.046
- [49] Akhavan A, Khoylou F, Ataeivarjovi E. Preparation and characterization of gamma irradiated starch/PVA/ZnO nanocomposite films. *Radiation Physics and Chemistry*. 2017;**138**(Supplement C):49-53. DOI: 10.1016/j.radphyschem.2017.02.057
- [50] Jiang X, Zhao Y, Hou L. The effect of glycerol on properties of chitosan/poly(vinyl alcohol) films with AlCl₃·6H₂O aqueous solution as the solvent for chitosan. *Carbohydrate Polymers*. 2016;**135**(Supplement C):191-198. DOI: 10.1016/j.carbpol.2015.08.094
- [51] Parvin F, Rahman MA, Islam JMM, Khan MA, Saadat AHM. Preparation and characterization of starch/PVA blend for biodegradable packaging material. *Multi-Functional Materials and Structures III*. 2010;**123**:125:351-354. DOI: 10.4028/www.scientific.net/AMR.123-125.351
- [52] Zhai ML, Yoshii F, Kume T, Hashim K. Syntheses of PVA/starch grafted hydrogels by irradiation. *Carbohydrate Polymers*. 2002;**50**(3):295-303. DOI: 10.1016/S0144-8617(02)00031-0
- [53] Yang SY, Huang CY. Plasma treatment for enhancing mechanical and thermal properties of biodegradable PVA/starch blends. *Journal of Applied Polymer Science*. 2008;**109**(4):2452-2459. DOI: 10.1002/app.28338
- [54] Senna MM, El-Shahat HA, El-Naggar AWM. Characterization of gamma irradiated plasticized starch/poly(vinyl alcohol) (PLST/PVA) blends and their application as protected edible materials. *Journal of Polymer Research*. 2011;**18**(4):763-771. DOI: 10.1007/s10965-010-9473-6
- [55] Chen P, Yu L, Simon GP, Liu X, Dean K, Chen L. Internal structures and phase-transitions of starch granules during gelatinization. *Carbohydrate Polymers*. 2011;**83**(4):1975-1983. DOI: 10.1016/j.carbpol.2010.11.001
- [56] Park HR, Chough SH, Yun YH, Yoon SD. Properties of starch/PVA blend films containing citric acid as additive. *Journal of Polymers and the Environment*. 2005;**13**(4):375-382. DOI: 10.1007/s10924-005-5532-1
- [57] Wu JG, Wang PJ, Chen SC. Antioxidant and antimicrobial effectiveness of catechin-impregnated PVA-starch film on red meat. *Journal of Food Quality*. 2010;**33**(6):780-801. DOI: 10.1111/j.1745-4557.2010.00350.x