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COMPREHENSIVE REVIEWS IN FOOD SCIENCE AND FOOD SAFETY

Recent advances in starch-based films toward food packaging applications: Physicochemical, mechanical, and functional properties

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Abstract

Interest in starch-based films has increased precipitously in response to a growing demand for more sustainable and environmentally sourced food packaging materials. Starch is an optimal candidate for these applications given its ability to form thermoplastic materials and films with affordable and often sustainably sourced plasticizers like those produced as waste byproducts by biodiesel and agricultural industries. Starch is also globally ubiquitous, affordable, and environmentally benign. Although the process of producing starch films is relatively straightforward, numerous factors, including starch source, extraction method, film formulation, processing methods, and curing procedures, drastically impact the ultimate material properties. The significant strides made from 2015 to early 2020 toward elucidating how these variables can be leveraged to improve mechanical and barrier properties as well as the implementation of various additives or procedural modifications are cataloged in this review. Advances toward the development of functional films containing antioxidant, antibacterial, or spoilage indicating components to prevent or signal the degradation of food products are also discussed.

KEYWORDS
amylopectin, amylose, cellulose, chitosan, sustainable

1 | INTRODUCTION

The widespread use of petrochemical plastics is a growing concern from both economic and ecological points of view. Most modern plastics are sourced from petrochemicals and present significant challenges for primary recycling due to significant loses in mechanical properties upon reprocessing, perpetuating the need for a constant stream of petrochemical resources (Hong & Chen, 2017; Iyer, Zhang, & Torkelson, 2016; Thiounn & Smith, 2020). Continued widespread use of petrochemically sourced plastics has resulted in relentless plastics pollution and pervasive environmental microplastics (Chen, Feng, & Wang, 2020; Rhodes, 2018). In the context of the current review, the widespread use of plastics in food packaging, of which ~40% is made from petrochemical plastics, is a particular concern (Domene-Lopez, Garcia-Quesada, Martin-Gullon, & Montalban, 2019). Of the plastics used in food packaging, polyethylene (PE), a highly biodegradation-resistant and difficult to recycle plastic, is the most commonly used (Brooks Amy, Wang, & Jambeck Jenna, 2018; Gewert, Plassmann, & MacLeod, 2015; Sivan, 2011). Given the geographic disparity in food production and population centers, the need for packaging that protects food from degradation during transport and storage is a long-term concern to support a growing population, necessitating the development of more economically and environmentally friendly surrogates for current plastic food packaging. Compared to traditional petrochemical-based plastics, bioplastics are considerably more biodegradable as well as being inexpensive, ubiquitous worldwide, and providing the potential to help utilize currently produced waste products of forestry, agriculture, and fisheries. There are two primary approaches to bio-based plastics: (1) creating traditional synthetic polymers from biobased feedstocks (such as bio-polyethylene), and (2) the modification of natural polymers to produce so-called "agropolymers" to replace current petroleum-derived polymers (Payne, McKeown, & Jones, 2019; Verbeek & Bier, 2011). The former process typically requires depolymerization of biopolymers into monomeric units or oligomers followed by their successive repolymerization. The energy requirements, multiple processing steps, and poor atom economy are in direct conflict with the principles of green chemistry and currently preclude this approach as a sustainable solution (Anastas & Warner, 1998; Mendieta, Vallejos, Felissia, Chinga-Carrasco, & Area, 2020). The production of agropolymers, on the other hand, has considerably improved atom economy and limits the number of necessary chemical transformations but poses its own set of challenges, such as the reliance on heterogeneous or harsh reaction conditions due to inherently poor solubility and high crystallinity of many biopolymers (Bakshi, Selvakumar, Kadirvelu, & Kumar, 2020; Onwukamike, Grelier, Grau, Cramail, & Meier, 2019; Szabo, Gerber-Lemaire, & Wandrey, 2020; Zhang et al., 2011).

Starch is an enticing biopolymer to supplant conventional plastics in food packaging due to its biodegradability, relative abundance, chemical inertness and resistance to degradation, as well as its excellent film-forming capabilities (Niranjana Prabhu & Prashantha, 2018; Shah, Naqash, Gani, & Masoodi, 2016). The uniqueness of starch compared to other polysaccharides lies in its ability to become a thermoplastic material upon addition of food-safe plasticizers, most commonly polyols (glycerol, sorbitol, xylitol, etc.), sugars (glucose, fructose, etc.), and water (Khan, Bilal Khan Niazi, Samin, & Jahan, 2017). The most common plasticizer used glycerol is a waste byproduct and an economic burden of an ever-growing biodiesel market, while other polyols and sugars can be produced from agricultural waste (Hu, Luo, & Li, 2014; Monteiro, Kugelmeier, Pinheiro, Batalha, & Cesar, 2018; Questell-Santiago, Galkin, Barta, & Luterbacher, 2020). In most preparations of starch-based films, starch is heated in water to its gelatinization temperature to break up the hydrogen bond-supported crystal structure of the granules. Plasticizers are then incorporated so that upon drying, the intermolecular hydrogen bonding between starch chains does not cause the starch to recrystallize, leading to cracks and troughs in the films. Unfortunately, compared to PE, starch films generally have inferior mechanical and barrier properties (Figure 1) (Matweb). A multitude of additives and modification strategies have recently been explored to improve the mechanical and barrier properties of films to make them competitive with current technologies, typically while maintaining the desired high biodegradability (Verbeek & Bier, 2011).

Starch is produced by plants as well as certain strains of fungi and algae, which use it for energy storage (Ball, Dirick, Decq, Martiat, & Matagne, 1990; El Halal, Kringel, Zavareze, & Dias, 2019; Mathiot et al., 2019). In general, starch granules are 2 to 100 μm across and can have normal, bimodal, or trimodal size distributions as well as wide-ranging granule morphologies from spherical to polyhedral (El Halal et al., 2019). Starch exists as semicrystalline granules of two polymers, amylose and amylopectin. The two polymers are composed of the same monomers, α-D glucose, connected by glycosidic linkages but differ in how they are connected. Amylose is the more linear form and consists of predominantly (1,4)-α-D linkages as well as a smaller number of (1,6)-α-D branches (Figure 2a) (Bertoft, 2013; Sarka & Dvoracek, 2017; Vamadevan & Bertoft, 2020). The other species, amylopectin, is a highly branched polysaccharide containing numerous 1,4- and 1,6- linkages (Figure 2b). Starch typically contains a higher abundance of amylopectin than amylose, but the ratios can vary drastically depending on the source, thus leading to a range of granule crystallinities (a variety of information on starch from different sources has been summarized in Table 1). Based on the diffraction pattern of the granules, starch can further be divided into its crystal types, primarily so-called "A-type" or "B-type" crystal structures. A-type diffraction patterns show characteristic peaks at 2θ values of ~12, 18, 20, and 23, whereas B-type crystallinity produces peaks at 2θ values of ~5, 11, 20, 22, and 24 (Domene-Lopez et al., 2019; Luchese, Benelli, Spada, & Tessaro, 2018; Maniglia, Tessaro, Ramos, & Tapia-Blacido, 2019). Starch from cereal grains typically produces a more A-type diffraction pattern, whereas starch from root tubers has a more B-type diffraction pattern. The occurrence of peaks for both A- and B-type diffraction patterns is typically referred to as a "C-type" crystal structure (Domene-Lopez et al., 2019; Dries, Gomand, Delcour, & Goderis, 2016; El Halal et al., 2019). A-type crystal structure arises from double helices arranged in a monoclinic unit cell containing four water molecules, whereas B-type diffraction peaks arise from double helices in a hexagonal unit cell containing a central channel with 36 water molecules. Upon plasticization, another crystal type known as "V-type" can arise and is due to amylose interacting with the plasticizer to adopt single helical structures that pack parallel to other single helices of amylose (Dries et al., 2016).

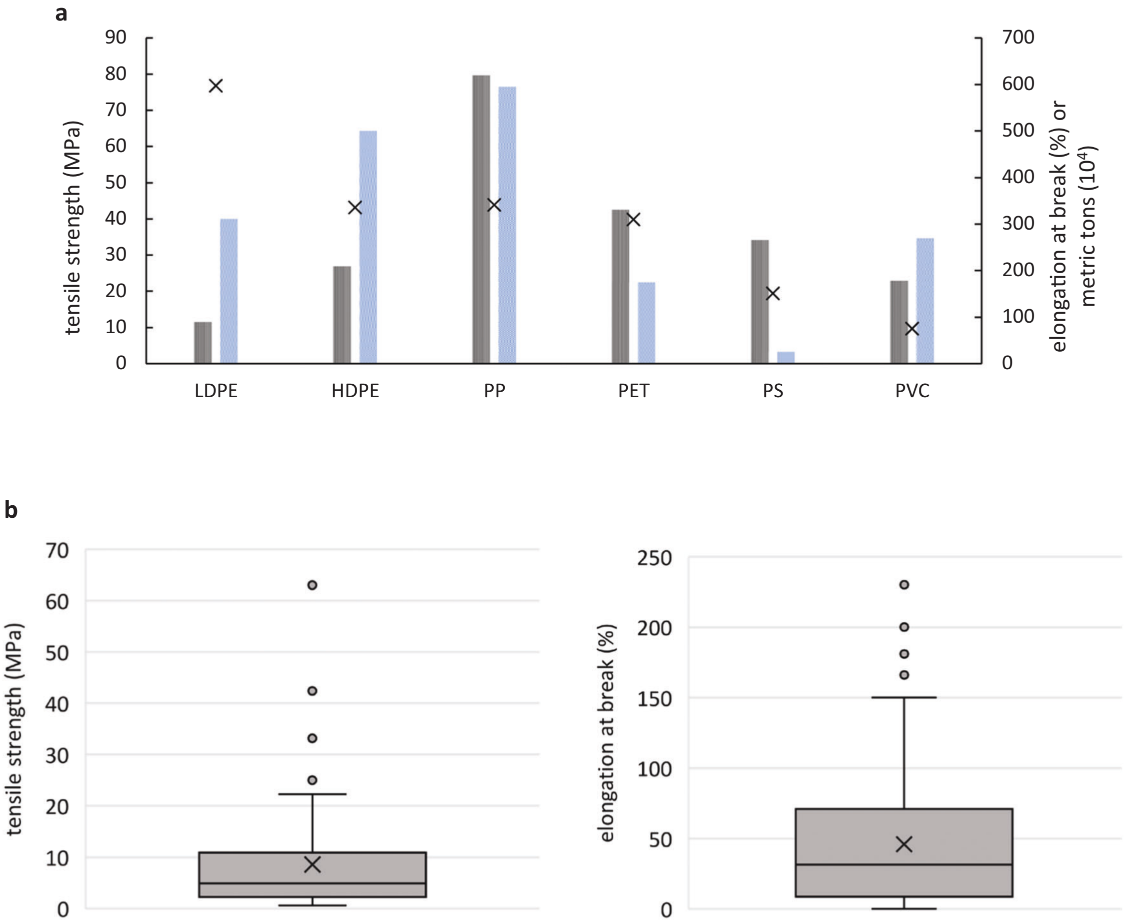

FIGURE 1 Plots showing mechanical properties of (a) various commercial packaging materials organized by their relative market shares reported as average values for extruded material: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC). Gray bars show tensile strength, blue bars show elongation at break, and black X symbols show the metric tons of plastic produced for packaging applications in 2007. Part (b) shows histograms of tensile strength (left) and elongation at break (right) data of plasticized starch films compiled from references in Table 2. While most data are agglomerated in the gray box, outliers are shown as gray circles. The data used to compile the histograms are from starch films compiled containing only plasticizer and water without physical or chemical pretreatment. These histograms display the breadth in reported mechanical properties for simple film formulations. In the presentation of starch film data, 42 references were compiled giving $n = 86$ for both tensile strength and elongation at break statistics (Emblem & Emblem 2012; Matweb)

Characteristic peaks for the V-type crystal structure can be observed at 2θ values of 19.6 to 19.8 and 22.1 to 22.7 and are typically quite broad (Domene-Lopez et al., 2019; Dries et al., 2016). Most of the research on starch has been conducted with starch from various cereal grains, potatoes, and cassava because of their ubiquitous production around the world. However, more niche agricultural products like sago, quinoa, mung beans, taro, and even black pepper have also gained attention recently (Abdorreza & Abd Karim, 2013; Arezoo, Mohammadreza, Maryam, & Abdorreza, 2020; Asria, 2016; Chanjarujit, Hongsprabhas, & Chaiseri, 2018; Gutierrez, 2017; Gutierrez & Gonzalez, 2016; Kittipongpatana et al., 2006; Naseri, Shekarchizadeh, & Kadivar, 2019; Zhu, Mojel, & Li, 2017). A recent publication analyzed various pumpkin, lentil, and quinoa starches and found that films prepared from these starches were comparable to potato starch films, emphasizing the potential to utilize a seemingly endless number of agricultural products to produce sustainable, starch-based films (Pajak, Przetaczek-Roznowska, & Juszczak, 2019).

The striking potential of starch-based films has inspired a number of other reviews on the subject.

Some of these reviews have analyzed the impact of blending starch with other synthetic polymers to produce films with good mechanical properties as well as analyzing the impact of the processing and chemical modification of starch to improve film properties (Khan et al., 2017; Niranjana Prabhu & Prashantha, 2018; Shah et al., 2016). By contrast, the current review focuses on delineating the multivariate influences (like those outlined in Section 2.1)

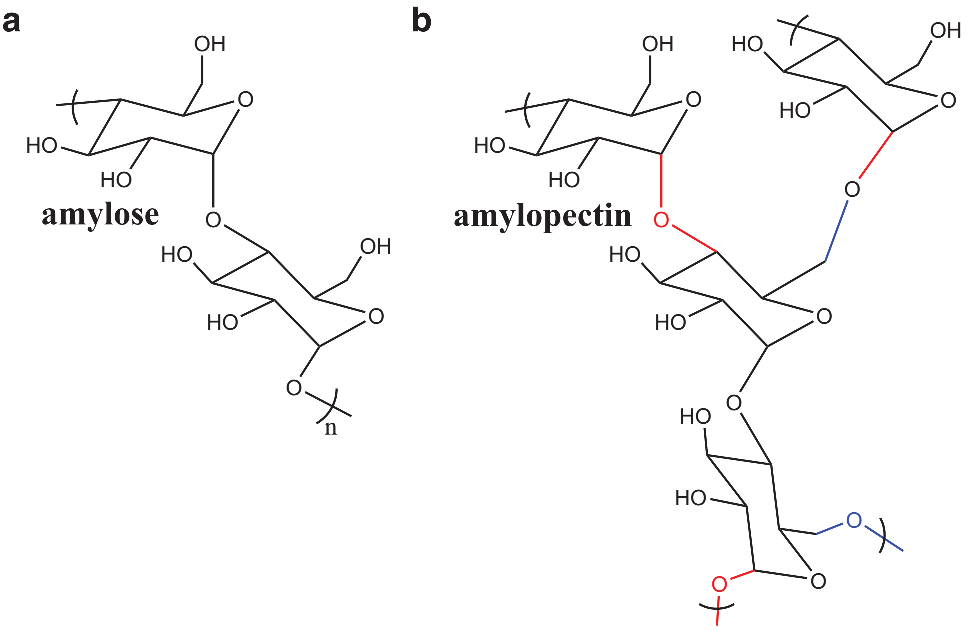

FIGURE 2 The chemical structure of (a) amylose showing only the most common type of linkages, (1,4)-α-D linkages and (b) amylopectin consisting of both (1,4)-α-D linkages (highlighted in red) and (1,6)-α-D linkages (highlighted in blue)

on mechanical and barrier properties between films as well as additives that have been implemented to endow antioxidant or antibacterial properties. This review will also provide a survey of recently developed “smart films” that produce a colorimetric signal in response to food spoilage by-products or pH changes. This review covers advances made between 2015 and 2020 and provides insight into recent accomplishments that have not yet been delineated in other recent reviews. This review intentionally excludes work that has incorporated synthetic polymers or utilizes formulations in which $< 50\%$ of the dry mass is starch in order to more precisely parse out the impact of subtle modifications to formulations.

2 | HURDLES TO DEVELOPING STARCH-BASED FILMS

2.1 | The complexities of starch and starch film processing

Although starch is ubiquitous worldwide, sources of starch can vary drastically by region. The literature on starch films is thus quite diverse, as researchers tend to investigate starches that are sourced in the region where the work is done. Although starches from different sources are chemically similar, there are distinct differences that may dramatically impact film properties (Dai, Zhang, & Cheng, 2019; Luchese, Benelli, et al., 2018). Good films for food packaging should have high tensile strength (TS) and elastic modulus (EM) to provide robustness. A film should also have a reasonable elongation at break (EAB) so that it may be exposed to various stresses during processing and shipping without breaking (Table2, entry 3) (Emblem & Emblem, 2012). Other mechanical properties, such as impact strength and tear strength, are key toward commercialization but are not typically measured in the preliminary steps of film development. Barrier properties are also paramount to prevent spoilage by oxidation and dehydration. In general, a low water vapor permeability (WVP) and oxygen permeability (OP) are typically desired. Films should also be transparent and clear in color to meet the aesthetic demands of consumers. Other considerations include UV transmittance, sensory properties, toxicity, and biodegradability or compostability (Gutierrez, Toro-Marquez, Merino, & Mendieta, 2019; Herniou–Julien, Mendieta, & Gutierrez, 2019; Osorio, Aznar, & Nerin, 2019). Heat sealing is another important property for many packaging applications that hinders the practicality of simple starch film formulations.

The factor that most strongly impacts the physical properties of starch films is the amylose to amylopectin ratio. Most starches are predominantly amylopectin (waxy corn starch can be up to 100% amylopectin) although some sources, such as high amylose corn starch, can have upward of 70% amylose (Lu et al., 2019). In general, it has been observed that higher percentages of amylose lead to more rigid films as denoted by a higher TS and EM and a simultaneous decrease in EAB as a result of an increased crystallinity (Cano, Jimenez, Chafer, Gonzalez,

TABLE 1 List of common starch sources and their physical properties listed in order of global production

Plant	Annual plant production (ref. year)	Starch in plant (%)	Granule size range (μm)	Granule structure	Amylose content (%)	Crystal type (A/B)	Main method of extraction	Refs.
Corn	> 1.13 Gt(2017)	70 to 73	7 to 25	Polyhedral/spherical	0 to 69	A	Steeping with SO_2 followed by wet milling in dilute acid	(FAOSTAT, 2017; Wahl, 1969)
Wheat	> 760 Mt (2019)	65 to 75	10 to 35 / 2 to 10[a]	Lenticular/spherical	0 to 35	A/B	Steeping followed by wet milling	(FAO, 2019; Li et al., 2016)
Rice	480 Mt (2016)	76 to 90	3 to 8	Polyhedral	25	A	Dilute alkaline steeping	(Gani et al., 2017; Van Hung et al., 2016; Ziegler et al., 2017)
Potato	390 Mt (2018)	15 to 20[b]	10 to 100	Polyhedral	20 to 30	B	Wet milling	(Bergthaller, 2004; Bertoft & Blennow, 2016; Nawaz et al., 2020; Singh et al., 2018)
Cassava root	292 Mt (2017)	20 to 30[c]	2 to 30	Oval/spherical	0 to 30	A/B	Wet milling	(FAOSTAT, 2017; Sanchez et al., 2017; Zhu, 2015)
Barley	133 Mt (2016)	62 to 77	1 to 10/ 10 to 40[a]	Lenticular/spherical [a]	25 to 30	A/B	Dry or wet milling, often with additives to soften the grain	(Gous & Fox, 2017; Rittenauer, Kolesnik, Gastl, & Becker, 2016; You & Izydorczyk, 2002; Yu et al., 2017)
Oat	23 Mt (2016)	56 to 65	3 to 10	Polygonal	18 to 29	A	Dilute alkaline extraction, high-shear homogenization in water, protease treatment	(Chu, 2014; Shah, Masoodi, Gani, & Ashwar, 2017; Xu et al., 2017)
Sago	>90 kt (2018)[d]	40[e]	10 to 50	Lenticular/oval	20 to 30	A/B	Milling followed by wet sieving	(Arshad, Zaman, Rawi, & Sarbini, 2018; Ehara, Toyoda, & Johnson, 2018; Karim, Tie, Manan, & Zaidul, 2008; Naseri et al., 2019)

Note: Table adapted from El Halal et al. (2019).

[a] Bimodal distribution represented by A-type/B-type granules.

[b] Starch content of potato is seemingly low due to ~80% water composition of potatoes.

[c] Starch content of cassava is seemingly low due to ~60% water composition of cassava.

[d] Estimated yearly production in Indonesia, the largest producer of sago.

[e] At the optimal stage for harvesting, based on dry mass.

TABLE 2 Mechanical and barrier properties–tensile strength (TS), elongation at break (EAB), elastic modulus (EM), water vapor permeability (WVP), oxygen permeability (OP)–of starch films in which additives or procedural differences influence film properties versus a control film in which no additive or procedural variation was employed

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
Corn Starch								
1	Corn (30%)/glycerol	N/A[a]	ND[b]	ND[b]	ND[b]	+45%[c]	ND[b]	(Sifuentes-Nieves et al., 2019)
		HMDSO plasma treatment	ND[b]	ND[b]	ND[b]	REF[d]	ND[b]	
	Corn (50%)/glycerol	N/A[a]	ND[b]	ND[b]	ND[b]	+125%[c]	ND[b]	
		HMDSO plasma treatment	ND[b]	ND[b]	ND[b]	REF[d]	ND[b]	
	Corn (70%)/glycerol	N/A[a]	ND[b]	ND[b]	ND[b]	+70%[c]	ND[b]	
		HMDSO plasma treatment	ND[b]	ND[b]	ND[b]	REF[d]	ND[b]	
2	Corn[e]/N/A[f]	Film-forming solution pH = 3	−25%[c]	−5%[c]	−35%[c]	ND[b]	ND[b]	(Sakkara et al., 2020)
		Film-forming solution pH = 5	REF[d]	−10%[c]	REF[d]	ND[b]	ND[b]	
		Film-forming solution pH = 7	−25%[c]	−30%[c]	−20%[c]	ND[b]	ND[b]	
		Film-forming solution pH = 9	−40%[c]	−10%[c]	−30%[c]	ND[b]	ND[b]	
		Film-forming solution pH = 11	−35%[c]	REF[d]	−35%[c]	ND[b]	ND[b]	
3	Corn (28.5)/glycerol	2 wt% film-forming solution	−15%3][c]	−65%[c]	0%[g]	ND[b]	ND[b]	(Luchese, Benelli, et al., 2018)
		3 wt% film-forming solution	0%[g]	−45%[c]	−35%[c]	REF[d]	ND[b]	
		4 wt% film-forming solution	REF[d]	REF[d]	REF[d]	0%[g]	ND[b]	
		5 wt% film-forming solution	−20%[c]	0%[g]	0%[g]	+50%[c]	ND[b]	
4	Corn[e]/glycerol	N/A[a]	REFERENCE MATERIAL[j]					(Hu et al., 2019)
	Debranched corn[e]/glycerol	N/A[a]	+225%[h]	−75%[h]	ND[b]	−15%[h]	−20%[h]	
	Hydroxypropylated corn[e]/glycerol	N/A[a]	−40%[h]	+245%[h]	ND[b]	+10%[h]	+5%[h]	
	Dual-modified corn[e]/glycerol	N/A[a]	+50%[h]	+45%[h]	ND[b]	−10%[h]	−10%[h]	
5	Corn (26.5%)/glycerol	Debranched and borax crosslinked waxy corn starch nanoparticles (5 wt%)	+35%	+20%	+65%	−45%	ND[b]	(Lu et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Debranched and borax crosslinked waxy corn starch nanoparticles (10 wt%)	+45%	+10%	+70%	−55%	ND[b]	
6	Corn (28%)/glycerol and xylitol	CNF (5 wt%)	+5%	+10%	+40%	−10%	ND[b]	(Li et al., 2018)
		CNF (10 wt%)	+25%	+20%	+70%	−20%	ND[b]	
		CNF (15 wt%)	+30%	+40%	+140%	−35%	ND[b]	
		CNF (20 wt%)	+10%	+10%	+115%	−30%	ND[b]	
7	Corn (32.5%)/glycerol	CNC from bamboo (2 wt%)	+250%[h]	−40%[h]	ND[b]	ND[b]	ND[b]	(Chen et al., 2019)
		CNC from bamboo (4 wt%)	+315%[h]	−50%[h]	ND[b]	−25%[h]	−35%[h]	
		CNC from bamboo (6 wt%)	+265%[h]	−60%[h]	ND[b]	ND[b]	ND[b]	
		CNC from bamboo (8 wt%)	+205%[h]	−60%[h]	ND[b]	ND[b]	ND[b]	
		CNC from bamboo (10 wt%)	+235%[h]	−50%[h]	ND[b]	ND[b]	ND[b]	
		CNC from cotton linter (2 wt%)	+215%[h]	−35%[h]	ND[b]	ND[b]	ND[b]	
		CNC from cotton linter (4 wt%)	+130%[h]	−35%[h]	ND[b]	−20%[h]	−25%[h]	
		CNC from cotton linter (6 wt%)	+255%[h]	−25%[h]	ND[b]	ND[b]	ND[b]	
		CNC from cotton linter (8 wt%)	+200%[h]	−35%[h]	ND[b]	ND[b]	ND[b]	
		CNC from cotton linter (10 wt%)	+245%[h]	−60%[h]	ND[b]	ND[b]	ND[b]	
		CNC from sisal (2 wt%)	+35%[h]	+15%[h]	ND[b]	ND[b]	ND[b]	
		CNC from sisal (4 wt%)	+155%[h]	−25%[h]	ND[b]	−20%[h]	−15%[h]	
		CNC from sisal (6 wt%)	+150%[h]	−55%[h]	ND[b]	ND[b]	ND[b]	
		CNC from sisal (8 wt%)	+155%[h]	−35%[h]	ND[b]	ND[b]	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		CNC from sisal (10 wt%)	+145%[h]	−35%[h]	ND[b]	ND[b]	ND[b]	
8	Corn (27%)/glycerol	Oxidized sucrose (1 wt%)	+25%[h]	−25%[h]	ND[b]	−25%[h,i]	−10%[h,i]	(Balakrishnan et al., 2019)
		Oxidized sucrose (1 wt%) + CNF (5 wt%)	+255%[h]	+15%[h]	ND[b]	−20%[h,i]	−20%[h,i]	
		Oxidized sucrose (2 wt%)	+210%[h]	−5%[h]	ND[b]	ND[b]	ND[b]	
		Oxidized sucrose (2 wt%) + CNF (5 wt%)	+475%[h]	+40%[h]	ND[b]	ND[b]	ND[b]	
		Oxidized sucrose (3 wt%)	+215%[h]	−5%[h]	ND[b]	−30%[h,i]	−40%[h,i]	
		Oxidized sucrose (3 wt%) + CNF (5 wt%)	+445%[h]	−70%[h]	ND[b]	−15%[h,i]	−50%[h,i]	
9	Corn (25%)/N/A[f]	CNF (3 wt%)	+15%[h]	+95%[7]	+5%[7]	ND[b]	ND[b]	(Li et al., 2019)
		Montmorillonite (3 wt%)	+5%[h]	+20%[7]	+10%[7]	ND[b]	ND[b]	
		Montmorillonite (3 wt%) + CNF (1 wt%)	+25%[h]	+30%[h]	+25%[h]	ND[b]	ND[b]	
		Montmorillonite (3 wt%) + CNF (3 wt%)	+30%[h]	+50%[h]	+30%[h]	ND[b]	ND[b]	
		Montmorillonite (3 wt%) + CNF (5 wt%)	+45%[h]	+50%[h]	+35%[h]	ND[b]	ND[b]	
		Montmorillonite (3 wt%) + CNF (7 wt%)	+40%[h]	+15%[h]	+35%[h]	ND[b]	ND[b]	
		Montmorillonite (5 wt%)	+15%[h]	+5%[h]	+20%[h]	ND[b]	ND[b]	
		Montmorillonite (5 wt%) + CNF (1 wt%)	+20%[h]	+15%[h]	+20%[h]	ND[b]	ND[b]	
		Montmorillonite (5 wt%) + CNF (3 wt%)	+30%[h]	+40%[h]	+25%[h]	ND[b]	ND[b]	
		Montmorillonite (5 wt%) + CNF (5 wt%)	+40%[h]	+50%[h]	+35%[h]	ND[b]	ND[b]	
		Montmorillonite (5 wt%) + CNF (7 wt%)	+45%[h]	+60%[h]	+35%[h]	ND[b]	ND[b]	
10	CHPTAC esterified corn, DS = 0.04 (67%)/glycerol	Montmorillonite	+10%	−50%	ND[b]	−10%	ND[b]	(Wang et al., 2018)
		Organic montmorillonite	0%[g]	−40%	ND[b]	+10%	ND[b]	
	CHPTAC esterified corn, DS = 0.11 (67%)/glycerol	Montmorillonite	+30%	−40%	ND[b]	−10%	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Organic montmorillonite	0%^{g}	0%^{g}	ND^{b}	+10%	ND^{b}	
	CHPTAC esterified corn, DS = 0.16 (67%)/glycerol	Montmorillonite	−20%	−40%	ND^{b}	+20%	ND^{b}	
		Organic montmorillonite	−30%	−30%	ND^{b}	0%^{g}	ND^{b}	
	CHPTAC esterified corn, DS = 0.20 (67%)/glycerol	Montmorillonite	+100%	−30%	ND^{b}	+10%	ND^{b}	
		Organic montmorillonite	0%^{g}	0%^{g}	ND^{b}	0%^{g}	ND^{b}	
	Corn (28%)/glycerol	Microalgae-*Nanochloropsis gaditana*	0%^{g}	0%^{g}	−20%	−50%	−70%	(Fabra et al., 2018)
11		Microalgae- *Spirulina*	0%^{g}	−40%	0%^{g}	−50%	+80	
		Microalgae- *Scendescmus*	0%^{g}	−60%	0%^{g}	−50%	+60	
12	Corn^{e}/glycerol	Orange peel oil/zein microcapsules (11 wt%)	+10%	0%^{g}	ND^{b}	−35%	−15%	(Wang, Zhang, Ahmed, Qin, & Liu, 2019)
		Orange peel oil/zein microcapsules (43 wt%)	+30%	+15%	ND^{b}	−45%	−30%	
		Orange peel oil/zein microcapsules (100 wt%)	+30%	+20%	ND^{b}	−55%	−35%	
13	Corn (25%)/glycerol	1 wt% starch in film-forming solution	−70%^{c}	−80%^{c}	−90%^{c}	0%^{g}	ND^{b}	(Ortega et al., 2019)
		1 wt% starch in film-forming solution + 143 ppm AgNP	−70%^{c}	−75%^{c}	−85%^{c}	REF^{d}	ND^{b}	
		3 wt% starch in film-forming solution	−50%^{c}	−50%^{c}	−75%^{c}	+40%^{c}	ND^{b}	
		3 wt% starch in film-forming solution + 143 ppm AgNP	REF^{d}	−50%^{c}	REF^{d}	+190%^{c}	ND^{b}	
		5 wt% starch in film-forming solution	−55%^{c}	REF^{d}	−75%^{c}	+155%^{c}	ND^{b}	
		5 wt% starch in film-forming solution + 143 ppm AgNP	−55%^{c}	−5%^{c}	−65%^{c}	+200%^{c}	ND^{b}	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
14	Corn (25%)/glycerol	Chitosan, low M_n	+95%	0%^{g}	−90%	0%^{g}	ND^{b}	(Bof et al., 2015)
		Chitosan, mid M_n	−55%	+230%	0%^{g}	0%^{g}	ND^{b}	
		Chitosan, high M_n	+105%	−125%	−90%	−70%	ND^{b}	
15	Corn (28%)/glycerol	N/A^{1}	−30%^{3}	−35%^{3}	0%^{g}	+80%^{c,h}	ND^{b}	(Tavares et al., 2019)
	Cassava (18%)/glycerol	N/A^{1}	REF^{d}	REF^{d}	0%^{g}	REF^{d,h}	ND^{b}	
	Corn (28%)/glycerol	Carboxymethyl cellulose	+90%	+850%^{2}	0%^{g}	−50%^{h}	ND^{b}	
	Cassava (18%)/glycerol		0%^{g}	0%^{g}	0%^{g}	−40%^{h}	ND^{b}	
Cassava Starch								
16	Cassava^{e}/glycerol and gallic acid^{11}	CNF from canola straw (2.5 wt%)	+710%^{h}	−15%^{h}	ND^{b}	−15%	ND^{b}	(Zhao et al., 2019)
		CNF from canola straw (5.0 wt%)	+870%^{h}	−30%^{h}	ND^{b}	−30%	ND^{b}	
		CNF from canola straw (7.5 wt%)	+1095%^{h}	−45%^{h}	ND^{b}	−45%	ND^{b}	
		CNF from canola straw (10 wt%)	+1165%^{h}	−50%^{h}	ND^{b}	−35%	ND^{b}	
17	Cassava^{e}/glycerol	Chitosan (0.37 wt%)	0%^{g}	0%^{g}	+40%	ND^{b}	ND^{b}	(Dang & Yoksan, 2015)
		Chitosan (0.73 wt%)	+30%	−40%	+80%	ND^{b}	ND^{b}	
		Chitosan (1.09 wt%)	+60%	−60%	+150%	ND^{b}	ND^{b}	
		Chitosan (1.45 wt%)	+100%	−70%	+150%	ND^{b}	ND^{b}	
18	Hydroxypropyl cassava (20%)/glycerol	Waxy corn starch and κ-carrageenan nanoparticles (1 wt%)	+110%	−25%	ND^{b}	−10%	ND^{b}	(Fang et al., 2020)
		Waxy corn starch and κ-carrageenan nanoparticles (3 wt%)	+130%	−45%	ND^{b}	−30%	ND^{b}	
		Waxy corn starch and κ-carrageenan nanoparticles (5 wt%)	+150%	−50%	ND^{b}	−20%	ND^{b}	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Waxy corn starch and κ-carrageenan nanoparticles (7 wt%)	+175%	−60%	ND[b]	−20%	ND[b]	
		Waxy corn starch and κ-carrageenan nanoparticles (9 wt%)	+210%	−70%	ND[b]	−15%	ND[b]	
19	Crosslinked cassava[e] /glycerol	Starch nanocrystals (2 wt%)	+30%	−25%	+10%	0%[g]	ND[b]	(Dai et al., 2020)
		Starch nanocrystals (4 wt%)	+65%	−45%	+15%	−25%	ND[b]	
		Starch nanocrystals (6 wt%)	+70%	−60%	+30%	−40%	ND[b]	
		Starch nanocrystals (8 wt%)	+60%	−70%	+25%	−35%	ND[b]	
20	Cassava (26.7%)/glycerol	2 wt% film-forming solution	−70%[c]	−55%[c]	−85%[c]	0%[g]	ND[b]	(Luchese, Benelli, et al., 2018)
		3 wt% film-forming solution	−70%[c]	−10%[c]	0%[g]	0%[g]	ND[b]	
		4 wt% film-forming solution	−70%[c]	REF[d]	−95%[c]	REF[d]	ND[b]	
		5 wt% film-forming solution	REF[d]	−70%[c]	REF[d]	0%[g]	ND[b]	
		6 wt% film-forming solution	−60%[c]	−65%[c]	−75%[c]	+155%[c]	ND[b]	
21	Cassava[e] /glycerol	Oxidized cassava starch (20 wt%)	+55%	0%[g]	+40%	ND[b]	ND[b]	(Oluwasina, Olaleye, Olusegun, Oluwasina, & Mohallem, 2019)
		Oxidized cassava starch (40 wt%)	+65%	+95%	+55%	ND[b]	ND[b]	
		Oxidized cassava starch (60 wt%)	+65%	+105%	+60%	ND[b]	ND[b]	
22	Cassava (15.6%)/glycerol	N/A[a]	REF[d]	REF[d]	REF[d]	REF[d]	ND[b]	(Dai et al., 2019)
	Esterified cassava[e] /glycerol	N/A[a]	+75%[c]	+185%[c]	−30%[c]	−15%[c]	ND[b]	
	Crosslinked cassava[e] /glycerol	N/A[a]	+490%[c]	+240%[c]	+30%[c]	−20%[c]	ND[b]	
	Oxidized cassava[e] /glycerol	N/A[a]	+260%[c]	+60%[c]	+225%[c]	0%[g]	ND[b]	
23	Cassava (10%)/glycerol	Conditioned at 53% humidity	REFERENCE MATERIAL[j]					(Sapper et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Xanthan gum (9 wt%), conditioned at 53% humidity	+50%[c,h]	0%[g]	+40%[c,h]	0%[g]	−30%[c]	
		Xanthan gum (25 wt%), conditioned at 53% humidity	+140%[c,h]	−65%[c,h]	+465%[c,h]	−15%[c]	−25%[c]	
		Acyl gellan gum (9 wt%), conditioned at 53% humidity	+175%[c,h]	−35%[c,h]	+265%[c,h]	−15%[c]	−25%[c]	
		Acyl gellan gum (25 wt%), conditioned at 53% humidity	+275%[c,h]	−40%[c,h]	+395%[c,h]	−5%[c]	−35%[c]	
		Pullulan (9 wt%), conditioned at 53% humidity	0%[g]	−60%[c,h]	+280%[c,h]	+45%[c]	+15%[c]	
		Pullulan (25 wt%), conditioned at 53% humidity	0%[g]	−75%[c,h]	+300%[c,h]	+50%[c]	+35%[c]	
	Cassava (10%)/glycerol	Conditioned at 75% humidity	REFERENCE MATERIAL[j]				ND[b]	(Sapper et al., 2019)
		Xanthan gum (9 wt%), conditioned at 75% humidity	+240%[c,h]	−40%[c,h]	+650%[c,h]	0%[g]	ND[b]	
		Xanthan gum (25 wt%), conditioned at 75% humidity	+225%[c,h]	−60%[c,h]	+495%[c,h]	−5%[3]	ND[b]	
		Acyl gellan gum (9 wt%), conditioned at 75% humidity	+215%[c,h]	−70%[c,h]	+40%[c,h]	0%[g]	ND[b]	
		Acyl gellan gum (25 wt%), conditioned at 75% humidity	+220%[c,h]	−60%[c,h]	0%[g]	0%[g]	ND[b]	
		Pullulan (9 wt%), conditioned at 75% humidity	+215%[c,h]	−60%[c,h]	+315%[c,h]	−20%[c]	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Pullulan (25 wt%), conditioned at 75% humidity	+300%[c,h]	−55%[c,h]	+385%[c,h]	−25%[c]	ND[b]	
	Cassava (10%)/glycerol	Conditioned at 53% humidity for 1 week	REFERENCE MATERIAL[j]			ND[b]	ND[b]	(Sapper et al., 2019)
		Conditioned at 75% humidity for 1 week	−60%[3,7]	+185%[3,7]	−80%[3,7]	ND[b]	ND[b]	
		Conditioned at 53% humidity for 5 weeks	−40%[3,7]	−50%[3,7]	−115%[3,7]	ND[b]	ND[b]	
		Conditioned at 73% humidity for 5 weeks	−60%[3,7]	+25%[3,7]	−65%[3,7]	ND[b]	ND[b]	
24	Cassava[e] /glycerol	*Lycium ruthenicum* anthocyanins (1 wt%)	+15%	ND[b]	ND[b]	−25%	ND[b]	(Qin et al., 2019)
		Lycium ruthenicum anthocyanins (2 wt%)	+5%	−10%	ND[b]	−30%	ND[b]	
		Lycium ruthenicum anthocyanins (4 wt%)	+5%	−15%	ND[b]	−35%	ND[b]	
25	Cassava[e] /glycerol	Chinese bayberry extract (1 wt%)	+40%	−10%	ND[b]	−10%	ND[b]	(Yun et al., 2019)
		Chinese bayberry extract (2 wt%)	+35%	0%[g]	ND[b]	0%[g]	ND[b]	
		Chinese bayberry extract (3 wt%)	+25%	+5%	ND[b]	−5%	ND[b]	
		Chinese bayberry extract (4 wt%)	+10%	+15%	ND[b]	−15%	ND[b]	
Potato Starch								
26	Potato starch (20.1 wt%)/glycerol	Lauric acid (2 wt%)	REFERENCE MATERIAL[j]				ND[b]	(Wang et al., 2019)
	Potato starch-lauric acid complex prepared by ultrasonic radiation (22.2 wt%)/glycerol	N/A[1]	+10%[c]	−35%[c]	ND[b]	0%[g]	ND[b]	
	Potato starch-lauric acid complex prepared in DMSO (27.5 wt%)/glycerol	N/A[1]	+20%[c]	−45%[c]	ND[b]	−10%[c]	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
	Potato starch-lauric acid complex prepared by debranching with pullulanase (35.4 wt%)/glycerol	N/A[1]	+60%[c]	−30%[c]	ND[b]	−30%[c]	ND[b]	
27	Potato[e]/glycerol	Citric acid (5 wt%)	0%[g]	+10%	ND[b]	−10%	ND[b]	(Wu et al., 2019)
		Citric acid (10 wt%)	+30%	+25%	ND[b]	−25%	ND[b]	
		Citric acid (15 wt%)	+30%	+30%	ND[b]	−30%	ND[b]	
		Citric acid (20 wt%)	+10%	+55%	ND[b]	−25%	ND[b]	
28	Potato[e]/glycerol	Butylated hydroxy toluene (5 wt%)	+290%	−85%	+1585%	−35%[i]	ND[b]	(Nisa et al., 2015)
		Green tea extract (5 wt%)	+20%	−30%	+25%	−25%[i]	ND[b]	
29	Potato (27%)/glycerol	Rice straw extracts (5 wt% substituted for an equal amount of plasticizer)	+155%	−85%	+815%	−15%	−70%	(Menzel, Gonzalez-Martinez, Vilaplana, Diretto, & Chiralt, 2019)
		Rice straw extracts (7.5 wt% substituted for an equal amount of plasticizer)	+210%	−90%	+1120%	−20%	−80%	
		Rice straw extracts (10 wt% substituted for an equal amount of plasticizer)	ND[b]	ND[b]	ND[b]	−5%	−95%	
Sweet Potato/Yam Starch								
30	Potato, sweet (25%)/glycerol and pectin	Nano-TiO_2 (0.5 wt%)	+10%	−15%	+15%	−10%	ND[b]	(Dash et al., 2019)
		Nano-TiO_2 (1 wt%)	+15%	−30%	+40%	−20%	ND[b]	
		Nano-TiO_2 (2 wt%)	+15%	−35%	+60%	−20%	ND[b]	
		Nano-TiO_2 (3 wt%)	+25%	−40%	+85%	−25%	ND[b]	
		Nano-TiO_2 (4 wt%)	+30%	−55%	+100%	−30%	ND[b]	
31	Chinese yam (25%)/D-sorbitol	0.8 wt% plasticizer	−45%[c,h]	−75%[c,h]	−15%[c,h]	+160%[c,h]	+220%[c,h]	(Cheng et al., 2019)
		1.6 wt% plasticizer	−40%[c,h]	−45%[c,h]	−5%[c,h]	+125%[c,h]	+150%[c,h]	
		2.4 wt% plasticizer	REF[d]	−30%[c,h]	REF[d]	+85%[c,h]	+95%[c,h]	
		3.2 wt% plasticizer	−10%[c,h]	−15%[c,h]	−5%[c,h]	+45%[c,h]	+35%[c,h]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		4.0 wt% plasticizer	−20%[c,h]	REF[d]	−15%[c,h]	REF[d]	REF[d]	
32	Chinese yam (25%)/glycerol	0.8 wt% plasticizer	−45%[c,h]	−75%[c,h]	−75%[c,h]	+85%[c,h]	+165%[c,h]	(Cheng et al., 2019)
		1.6 wt% plasticizer	−30%[c,h]	−45%[c,h]	−40%[c,h]	+60%[c,h]	+130%[c,h]	
		2.4 wt% plasticizer	REF[d]	−30%[c,h]	REF[d]	+40%[c,h]	+70%[c,h]	
		3.2 wt% plasticizer	−5%[c,h]	−15%[c,h]	−25%[c,h]	+25%[c,h]	+20%[c,h]	
		4.0 wt% plasticizer	−20%[c,h]	REF[d]	−35%[c,h]	REF[d]	REF[d]	
	Chinese yam (25%)/D-sorbitol	4.0 wt% plasticizer	REF[d]	−4%[c,h]	REF[d]	REF[d]	REF[d]	(Cheng et al., 2019)
	Chinese yam (25%)/glycerol	4.0 wt% plasticizer	−70%[c,h]	REF[d]	−55%[c,h]	+125%[c,h]	+155%[c,h]	
Wheat Starch								
33	Wheat (27.4%)/glycerol	2 wt% film-forming solution	0%[g]	0%[g]	0%[g]	REF[d]	ND[b]	(Luchese, Benelli, et al., 2018)
		3 wt% film-forming solution	0%[g]	0%[g]	0%[g]	REF[d]	ND[b]	
		4 wt% film-forming solution	REF[d]	REF[d]	REF[d]	0%[g]	ND[b]	
		5 wt% film-forming solution	0%[g]	0%[g]	0%[g]	0%[g]	ND[b]	
		6 wt% film-forming solution	0%[g]	0%[g]	0%[g]	0%[g]	ND[b]	
34	Nongerminated wheat (34.8%)/glycerol	N/A[a]	REFERENCE MATERIAL[j]				ND[b]	(Baranzelli et al., 2019)
	24 hr germinated wheat (33.6%)/glycerol	N/A[a]	0%[g]	0%[g]	ND[b]	ND[b]	ND[b]	
	48 hr germinated wheat (34.7%)/glycerol	N/A[a]	+80%[c]	+60%[c]	ND[b]	ND[b]	ND[b]	
	72 hr germinated wheat (30.8%)/glycerol	N/A[a]	0%[g]	+110%[c]	ND[b]	ND[b]	ND[b]	
35	Wheat[e]/glycerol	UV-A treatment of film-forming solution (1 hr irradiation)	−30%	+70%	−55%	−30%	ND[b]	(Shahabi-Ghahfarrokhi et al., 2019)
		UV-A treatment of film-forming solution (6 hr irradiation)	−20%	0%[g]	−40%	−25%	ND[b]	
		UV-A treatment of film-forming solution (12 hr irradiation)	0%[g]	0%[g]	−30%	−25%	ND[b]	
		UV-A treatment of film-forming solution (24 hr irradiation)	−30%	+90%	−50%	−20%	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		UV-C treatment of film-forming solution (1 hr irradiation)	−45%	+80%	−70%	0%[g]	ND[b]	
		UV-C treatment of film-forming solution (6 hr irradiation)	−35%	+55%	−55%	−30%	ND[b]	
		UV-C treatment of film-forming solution (12 hr irradiation)	−25%	0%[g]	−40%	−25%	ND[b]	
		UV-C treatment of film-forming solution (24 hr irradiation)	0%[g]	0%[g]	−30%	0%[g]	ND[b]	
36	Wheat (20%)/glycerol	N/A[1]	REFERENCE MATERIAL[j]				ND[b]	(Yousefi et al., 2019)
	STMP/STPP crosslinked wheat[e]/glycerol	N/A[1]	+15%[c]	−10%[c]	+10%[c]	−10%[c]	ND[b]	
37	STMP/STPP crosslinked wheat[e]/glycerol	Montmorillonite (3 wt%)	+80%	—[2]	+55%	−25%	ND[b]	(Yousefi et al., 2019)
		Montmorillonite (5 wt%)	+85%	−25%	+55%	−30%	ND[b]	
		Montmorillonite (7 wt%)	+90%	−35%	+55%	−40%	ND[b]	
		Montmorillonite (5 wt%) + TiO_2 (1 wt%)	+90%	−40%	+55%	−40%	ND[b]	
		Montmorillonite (5 wt%) + TiO_2 (2 wt%)	+80%	−40%	+55%	−50%	ND[b]	
		Montmorillonite (5 wt%) + TiO_2 (4 wt%)	+65%	−45%	+55%	−55%	ND[b]	
Sago Starch								
38	Sago starch[e]/glycerol	N/A[1]	REFERENCE MATERIAL[j]				ND[b]	(Naseri et al., 2019)
	OSA modified sago starch[e]/glycerol	N/A[1]	−55%[c,h]	+40%[c,h]	ND[b]	+50%[c,h]	ND[b]	
	OSA modified sago starch[e]/glycerol	$CaCl_2$ (0.7 wt%)	−20%[7]	+10%[7]	ND[b]	−30%[7]	ND[b]	
		Ferulic acid (0.05 wt%)	−20%[7]	+25%[7]	ND[b]	−40%[7]	ND[b]	
39	Sago (21%)/glycerol	Ultrasonication of film-forming solution (2.5 min)	0%[g]	ND[b]	0%[g]	0%[g]	ND[b]	(Abral et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Ultrasonication of film-forming solution (5 min)	+225%	ND[b]	+195%	0%[g]	ND[b]	
		Ultrasonication of film-forming solution (10 min)	0%[g]	ND[b]	0%[g]	−10%	ND[b]	
Rice Starch								
40	Native rice (20%)/glycerol		REF[d]	REF[d]	ND[b]	0%[g]	ND[b]	(Colussi et al., 2017)
	Acetylated (DS = 0.38) rice (20%)/glycerol	N/A[a]	−70%[c]	+740%[c]	ND[b]	REF[d]	ND[b]	
	Acetylated (DS = 0.45) rice (20%)/glycerol	N/A[a]	−60%[c]	+860%[c]	ND[b]	+80%[c]	ND[b]	
	Acetylated (DS = 0.81) rice (20%)/glycerol	N/A[a]	0%[g]	+630%[c]	ND[b]	+95%[c]	ND[b]	
41	Native rice (32%)/glycerol		REF[d]	REF[d]	ND[b]	0%[g]	ND[b]	(Colussi et al., 2017)
	Acetylated (DS = 0.24) rice (32%)/glycerol	N/A[a]	−65%	+65%	ND[b]	+40%[3]	ND[b]	
	Acetylated (DS = 0.42) rice (32%)/glycerol	N/A[a]	−40%	+65%	ND[b]	REF[d]	ND[b]	
	Acetylated (DS = 0.72) rice (32%)/glycerol	N/A[a]	+30%	+50%	ND[b]	+15%[3]	ND[b]	
Millet Starch								
42	Native millet[e]/glycerol	N/A[a]	REFERENCE MATERIAL[j]				ND[b]	(Shaikh et al., 2019)
	Acetylated (1.12%) millet[e]/glycerol	N/A[1]	0%[g]	+65%	ND[b]	−30%	ND[b]	
	Acetylated (2.44%) millet[e]/glycerol	N/A[1]	0%[g]	0%[g]	ND[b]	−70%	ND[b]	
	Hydroxypropylated (1.65%) millet[e]/glycerol	N/A[1]	0%[g]	+200%	ND[b]	+25%	ND[b]	
	Hydroxypropylated (2.16%) millet[e]/glycerol	N/A[1]	0%[g]	+235%	ND[b]	+35%	ND[b]	
43	Proso millet[e]/glycerol	Curcumin (0.5 wt%)	0%[g]	+80%	ND[b]	0%[g]	ND[b]	(Baek & Song, 2019)
		Curcumin (1 wt%)	0%[g]	+90%	ND[b]	−5%	ND[b]	
		Curcumin (2 wt%)	−25%	+85%	ND[b]	−10%	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Curcumin (3 wt%)	−40%	+100%	ND[b]	−10%	ND[b]	
Tapioca Starch								
44	Tapioca[e]/glycerol	Lime juice (3 wt%)	−40%[h]	+540%[h]	ND[b]	−60%[h]	ND[b]	(Owi et al., 2019)
		Lime juice (5 wt%)	−20%[h]	+400%[h]	ND[b]	−60%[h]	ND[b]	
		Lime juice (10 wt%)	−10%[h]	+390%[h]	ND[b]	−60%[h]	ND[b]	
		Lime juice (15 wt%)	+15%[h]	+135%[h]	ND[b]	−60%[h]	ND[b]	
		Lime juice (20 wt%)	+35%[h]	−30%[h]	ND[b]	−60%[h]	ND[b]	
		Lime juice (10 wt%) + NC (1 wt%)	+60%[h]	+1080%[h]	ND[b]	ND[b]	ND[b]	
		Lime juice (10 wt%) + NC (2 wt%)	−15%[h]	+480%[h]	ND[b]	ND[b]	ND[b]	
		Lime juice (10 wt%) + NC (3 wt%)	−15%[h]	+65%[h]	ND[b]	ND[b]	ND[b]	
		Lime juice (10 wt%) + NC (4 wt%)	−25%[h]	+65%[h]	ND[b]	ND[b]	ND[b]	
		Lime juice (10 wt%) + NC (5 wt%)	−15%[h]	+10%[h]	ND[b]	ND[b]	ND[b]	
45	Tapioca[e]/glycerol	Chitosan (0.5 wt%)	−50%[c,h]	REF[d]	ND[b]	+15%[c,h]	ND[b]	(Pratama et al., 2019)
		Chitosan (0.5 wt%) + palm olein (0.4 wt%)	−45%[c,h]	−70%[c,h]	ND[b]	+15%[c,h]	ND[b]	
		Chitosan (0.5 wt%) + palm olein (0.8 wt%)	−40%[c,h]	−65%[c,h]	ND[b]	REF[d]	ND[b]	
		Chitosan (1 wt%)	−25%[c,h]	−60%[c,h]	ND[b]	+35%[c,h]	ND[b]	
		Chitosan (1 wt%) + palm olein (0.4 wt%)	−20%[c,h]	−55%[c,h]	ND[b]	+15%[c,h]	ND[b]	
		Chitosan (1 wt%) + palm olein (0.8 wt%)	REF[d]	−45%[c,h]	ND[b]	REF[d]	ND[b]	
Miscellaneous Starch Varieties								
46	Banana (50.3%)/glycerol	CNF produced by enzymatic hydrolysis at 15 wt% (4 wt%)	+985%	−40%	+615%	−45%	ND[b]	(Sartori & Menegalli, 2016)
		CNF produced by enzymatic hydrolysis at 35 wt% (4 wt%)	+635%	−35%	+180%	+45%	ND[b]	
47	Babassu mesocarp extracted with acid (21%)/glycerol	N/A[a]	−60%[c]	−20%[c,h]	−55%[c]	+325%[c,h]	ND[b]	(Maniglia et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
	Babassu mesocarp extracted with acid (21%)/sorbitol	N/A[a]	−45%[c,h]	−40%[c,h]	−45%[c,h]	+110%[c,h]	ND[b]	
	Babassu mesocarp extracted with acid (21%)/urea	N/A[a]	−75%[c,h]	−15%[c]	−65%[c,h]	+310%[c,h]	ND[b]	
	Babassu mesocarp extracted with acid (21%)/glucose	N/A[a]	−55%[c,h]	−30%[c,h]	−50%[c,h]	+100%[c]	ND[b]	
	Babassu mesocarp extracted with DI H_2O (37%)/glycerol	N/A[a]	REF[d]	−70%[c,h]	REF[d]	+170%[c]	ND[b]	
	Babassu mesocarp extracted with DI H_2O (37%)/sorbitol	N/A[a]	−70%[c]	−30%[c,h]	−70%[c]	+70%[c]	ND[b]	
	Babassu mesocarp extracted with DI H_2O (37%)/urea	N/A[a]	−60%[c]	−50%[c]	−35%[c]	+215%[c]	ND[b]	
	Babassu mesocarp extracted with DI H_2O (37%)/glucose	N/A[a]	−65%[c]	−40%[c,h]	−60%[c]	REF[d]	ND[b]	
	Babassu mesocarp alkaline extracted (25%)/glycerol	N/A[a]	−70%[c]	REF[d]	−95%[c]	+290%[c,h]	ND[b]	
	Babassu mesocarp alkaline extracted (25%)/sorbitol	N/A[a]	−25%[c,h]	−55%[c]	−30%[c,h]	+185%[c,h]	ND[b]	
	Babassu mesocarp alkaline extracted (25%)/urea	N/A[a]	−75%[c,h]	REF[d]	−70%[c,h]	+285%[c,h]	ND[b]	
	Babassu mesocarp alkaline extracted (25%)/glucose	N/A[a]	−50%[c,h]	−40%[c]	−55%[c,h]	+70%[c]	ND[b]	
48	Bean, common (IPR Uirapuru genotype, 28%)/glycerol	N/A[a]	−10%[c]	−60%[c]	ND[b]	best[d]	ND[b]	(Vanier et al., 2019)
	Bean, common (BRS Pitanga genotype, 33%)/glycerol	N/A[a]	0%[g]	−50%[c]	ND[b]	+40%[c]	ND[b]	
	Bean, common (BRS Pérola genotype, 29%)/glycerol	N/A[a]	REF[d]	−50%[c]	ND[b]	+30%[c]	ND[b]	
	Bean, common (BRS Estilo genotype, 26%)/glycerol	N/A[a]	−35%[c]	REF[d]	ND[b]	+40%[c]	ND[b]	
49	Jicama (11%)/glycerol	CNF (0.05 wt%)	+40%	−30%	0%[g]	0%[g]	ND[b]	(Mahardika et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		CNF (0.10 wt%)	+65%	−50%	+115%	0%[g]	ND[b]	
		CNF (0.15 wt%)	+115%	−75%	+205%	0%[g]	ND[b]	
		CNF (0.20 wt%)	+160%	−80%	+225%	−20%	ND[b]	
50	Lotus rhizome[e]/glycerol	N/A[a]	REFERENCE MATERIAL					(Sukhija et al., 2019)
	Oxidized (0.07% carboxyl content) lotus rhizome[e]/glycerol	N/A[a]	+10%	+5%	ND[b]	−5%	ND[b]	
	Oxidized (0.10% carboxyl content) lotus rhizome[e]/glycerol	N/A[a]	+15%	+5%	ND[b]	+60%	ND[b]	
	Oxidized (0.13% carboxyl content) lotus rhizome[e]/glycerol	N/A[a]	+15%	+5%	ND[b]	+145%	ND[b]	
	Crosslinked (4.3%) lotus rhizome[e]/glycerol	N/A[a]	+20%	0%[g]	ND[b]	−15%	ND[b]	
	Crosslinked (12%) lotus rhizome[e]/glycerol	N/A[a]	+30%	−5%	ND[b]	−20%	ND[b]	
	Crosslinked (18%) lotus rhizome[e]/glycerol	N/A[a]	+35%	−10%	ND[b]	−30%	ND[b]	
	Oxidized (0.15% carboxyl content) and crosslinked (47%) lotus rhizome[e]/glycerol	N/A[a]	+35%	+15%	ND[b]	−20%	ND[b]	
	Oxidized (0.14% carboxyl content) and crosslinked (53%) lotus rhizome[e]/glycerol	N/A[a]	+40%	+10%	ND[b]	−35%	ND[b]	
	Oxidized (0.10% carboxyl content) and crosslinked (58%) lotus rhizome[e]/glycerol	N/A[a]	+45%	−5%	ND[b]	−40%	ND[b]	
51	Pea hydrolyzed with HCl (0.5 hr), (28.6%)/sorbitol	N/A[a]	+5%	−40%	ND[b]	+10%	ND[b]	(Zhang et al., 2019)

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
	Pea hydrolyzed with HCl (1 hr), (30.0%)/sorbitol	N/A[a]	+20%	−50%	ND[b]	+15%	ND[b]	
	Pea hydrolyzed with HCl (1.5 hr), (30.8%)/sorbitol	N/A[a]	+30%	−60%	ND[b]	+15%	ND[b]	
	Pea hydrolyzed with HCl (2 hr), (32.6%)/sorbitol	N/A[a]	+35%	−60%	ND[b]	+30%	ND[b]	
	Pea hydrolyzed with HCl (2.5 hr), (33.6%)/sorbitol	N/A[a]	+35%	−55%	ND[b]	+80%	ND[b]	
52	Ulluco (35.3%)/glycerol	2.0 w/v film-forming solution	0%[g]	0%[g]	0%[g]	0%[g]	ND[b]	(Galindez et al., 2019)
		2.5 w/v film-forming solution	−30%[3]	REF[d]	−35%[3]	REF[d]	ND[b]	
		3.0 w/v film-forming solution	REF[d]	0%[g]	REF[d]	0%[g]	ND[b]	
Unspecified Starch Source								
53	Unspecified[e,k]/glycerol	NC prepared from CHPTAC modified MCC by acid hydrolysis (5 wt%)	+50%	−20%	+35%	−15%	ND[b]	(Han et al., 2019)
		NC prepared from CHPTAC modified MCC by high-pressure homogenization (5 wt%)	+85%	−25%	+55%	−20%	ND[b]	
		NC prepared from CHPTAC modified MCC by ultrasonication (5 wt%)	+70%	−25%	+40%	−20%	ND[b]	
54	Unspecified[e,k]/glycerol	Nano-TiO2 (1 wt%)	+15%	0%[g]	ND[b]	−10%	ND[b]	(Li, Zheng et al., 2019)
		Nano-TiO2 (3 wt%)	+20%	−10%	ND[b]	−10%	ND[b]	
		Nano-TiO2 (5 wt%)	+20%	−25%	ND[b]	−15%	ND[b]	
		Nano-TiO2 (7 wt%)	+15%	−40%	ND[b]	−20%	ND[b]	
		Nano-TiO2 (3 wt%) + clove oil (3 wt%)	0%[g]	+15%	ND[b]	−15%	ND[b]	
		Nano-TiO2 (3 wt%) + clove oil (6 wt%)	−5%	+35%	ND[b]	−20%	ND[b]	
		Nano-TiO2 (3 wt%) + clove oil (9 wt%)	−10%	+45%	ND[b]	−20%	ND[b]	

(Continues)

TABLE 2 (Continued)

Entry	Starch (amylose%)/plasticizer	Film additive/procedural difference	TS	EAB	EM	WVP	OP	Ref.
		Nano-TiO2 (3 wt%) + clove oil (12 wt%)	−20%	+25%	ND[b]	−25%	ND[b]	
Various Starch Sources								
55	Waxy corn (0%)/glycerol	N/A[1]	REFERENCE MATERIAL[j]	ND[b]				(Dai et al., 2019)
	Cassava (16%)/glycerol	N/A[1]	+25%[c]	0%[g]	0%[g]	−35%[c]	ND[b]	
	Sweet potato (17%)/glycerol	N/A[1]	−35%[c]	−60%[c]	0%[g]	−25%[c]	ND[b]	
	Potato (22%)/glycerol	N/A[1]	+100%[c]	+45%[c]	+85%[c]	−15%[c]	ND[b]	
	Wheat (27%)/glycerol	N/A[1]	−50%[c]	−55%[c]	−25%[c]	−15%[c]	ND[b]	
	Corn (28%)/glycerol	N/A[1]	+25%[c]	−25%[c]	+65%[c]	−15%[c]	ND[b]	
56	Rice (16.9%)/glycerol	N/A[1]	REFERENCE MATERIAL[j]	ND[b]	ND[b]	(Domene-Lopez et al., 2019)		
	Potato (20.5%)/glycerol	N/A[1]	+45%[c,h]	−10%[c,h]	+55%[c,h]	ND[b]	ND[b]	
	Wheat (24.5%)/glycerol	N/A[1]	+80%[c,h]	−55%[c,h]	+145%[c,h]	ND[b]	ND[b]	
	Corn (24.8%)/glycerol	N/A[1]	+75%[c,h]	−65%[c,h]	+155%[c,h]	ND[b]	ND[b]	
57	Cassava (26.7%)/glycerol	4 wt% film-forming solution	−65%[c]	REF[d]	−95%[c]	REF[d]	ND[b]	(Luchese, Benelli, et al., 2018)
	Wheat (27.4%)/glycerol	4 wt% film-forming solution	−50%[c]	−50%[c]	−55%[c]	+90%[c]	ND[b]	
	Corn (28.5%)/glycerol	4 wt% film-forming solution	REF[d]	−30%[c]	REF[d]	+60%[c]	ND[b]	

Note: In the case that no control film was reported, films are compared to the indicated reference film designated by “REF” or “Reference Material” under the property column. Other acronyms used in the table are as follows: hexamethyldisiloxane (HMDSO), cellulose nanocrystals (CNC), cellulose nanofibers (CNF), (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC), degree of substitution DS, silver nanoparticles (AgNP), sodium trimetaphosphate (STMP) sodium tripolyphosphate (STPP), octenyl succinic anhydride (OSA), nanocellulose (NC), and microcrystalline cellulose (MCC).

[a] No additives or procedural deviation was utilized in the production of the film.

[b] No data were presented in the manuscript.

[c] Percent differences are relative to the “reference” film from the provided reference.

[d] The “REF” material is defined as the material in the series that provided the highest value (for TS, EM, or EAB) or the lowest value (for WVP or OP).

[e] Amylose % was not reported.

[f] No plasticizer other than water was incorporated into the FFS.

[g] No statistically significant difference was observed.

[h] No statistical analysis was performed to determine if difference was statistically significant.

[i] Value was reported as a transmission rate rather than a permeability in the corresponding manuscript.

[j] Material was selected as the reference material to which the rest of the films from the given reference were compared.

[k] Starch source was not provided.

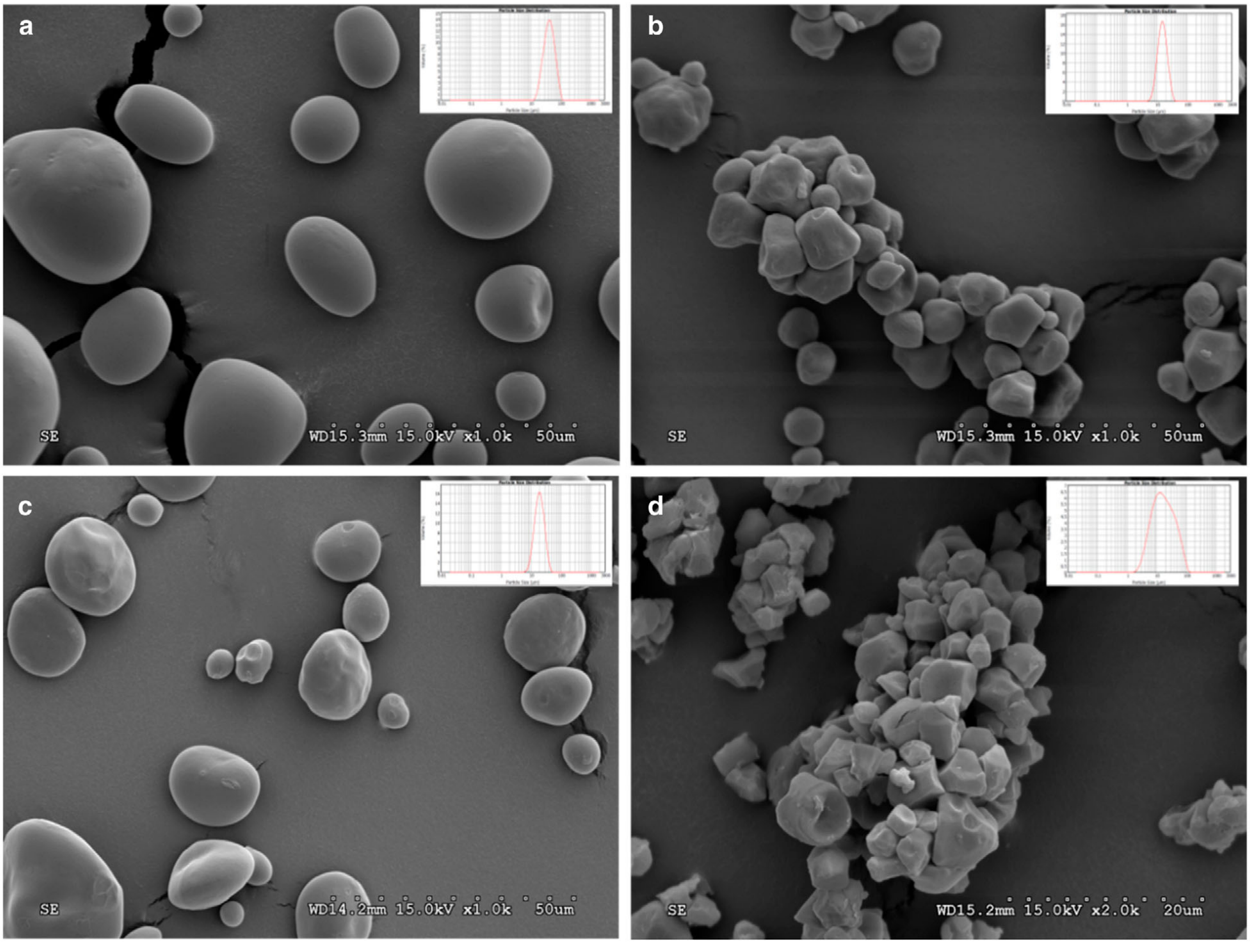

FIGURE 3 SEM micrographs of (a) potato starch, (b) corn starch, (c) wheat starch, and (d) rice starch revealing the difference in granular structures from different starches. Reprinted from Domene-Lopez et al. (2019) under a Creative Commons Attribution license (https://creativecommons.org/licenses/by/4.0/)

& Chiralt, 2014). Higher amylose-content starches also typically exhibit lower WVP and OP due to more effective plasticization. It has also been shown that too low of an amylose percentage disallows the formation of films (Colussi et al., 2017; Luchese, Benelli, et al., 2018). However, to view starch film properties as strictly a result of the ratio of amylose to amylopectin would be a gross simplification; numerous other characteristics impact the resultant film's mechanical properties. Such characteristics include amylose/amylopectin molecular weight, protein content, phosphate monoester content, granular morphology, granule size, and granule size distribution, all of which can vary depending on the starch source (granule size and distributions are highlighted in Figure 3). Even seemingly minute details, such as different cultivars of the same species or when in the plant's lifecycle the starch was extracted, can have consequential impacts on film properties (Baranzelli et al., 2019; Colussi et al., 2017; Dai et al., 2019; Domene-Lopez et al., 2019; Pajak et al., 2019; Vanier et al., 2019).

The science of producing films is also quite complex. Chemical or physical modification of starch provides an avenue for altering film properties. Films are strongly affected by the choice and amount of plasticizer included in the film formulation. A key focus of this review is to delineate the extent to which additives impact film mechanical/barrier properties. Finally, the method of film synthesis (Table 2, entry 20) and conditioning humidity and time (Table 2, entry 23) can have a drastic impact on the films' properties (Andretta, Luchese, Tessaro, & Spada, 2019; Galindez, Daza, Homez-Jara, Eim, & Vaquiro, 2019; Luchese, Abdalla, Spada, & Tessaro, 2018; Sapper, Talens, & Chiralt, 2019; Tavares, de Campos, Mitsuyuki, Luchesi, & Marconcini, 2019). Computational techniques like principal component analysis (PCA) or central composite design and response surface methodology have been implemented to rapidly deduce the impact of multiple independent variables. The predictive power of these techniques has been quite promising and will likely continue to see widespread use in this field for developing models that allow for the determination of formulations producing target film properties (Luchese, Benelli, et al., 2018; Navia Porras, Gordillo Suarez, Hernandez Umana, & Poveda Perdomo, 2019; Silva et al., 2019). Delving into the fundamental physical phenomena that give rise to differences in mechanical properties (Table 2, entry 56) also offers valuable insight and has been the subject of numerous recent works (Dai et al., 2019; Domene-Lopez et al., 2019; Gutierrez et al., 2019; Luchese, Benelli, et al., 2018; Maniglia et al., 2019).

An often-overlooked property of starch films is their potential to undergo retrogradation. Retrogradation occurs when the amylose in plasticized starch begins to realign as a result of molecular motion to reestablish H-bonding between starch molecules with concomitant extrusion of plasticizer from the matrix. Retrogradation can lead to significant decreases in both mechanical and barrier properties over time. The most common approach to attenuating retrogradation-induced film failure is to add plasticizer in excess or utilize other additives like carbohydrates, proteins, and salts. These approaches, however, may result in reduced mechanical properties as well as increased costs of film production (Cheng et al., 2019; van Soest & Vliegenthart, 1997; Wang, Li, Copeland, Niu, & Wang, 2015). A few researchers have tried to develop new plasticizers or investigated the impact of mixed plasticization systems in order to inhibit retrogradation, but the field would benefit from more cognizance of retrogradation and more research toward understanding the change in mechanical properties of films over time when exposed to a variety of conditions (Esmaeili, Pircheraghi, & Bagheri, 2017; Krogars et al., 2003; Zhang, et al., 2020).

2.2 | Hurdles to commercialization of starch films for packaging applications

Plastics have been extensively utilized in packaging applications as they are lightweight, cheap, and easy to process on a commercial scale. Most commonly, plastic films are thermally processed by extrusion technologies (Emblem & Emblem, 2012). Contrarily, mechanical and thermal processing of starch films is more complicated due to the requirement of large excesses of processing solvents and the propensity for starch to degrade under mechanical and thermal stressors. While this precludes the potential of starch-only films to be processed in this manner, commercial successes have been seen with starch-containing resin formulations, such as BioBag®, a fully compostable bag made from plant- and oil-derived starting materials as well as synthetic, compostable polymers. Like any initial commercialization of sustainable technologies, there exist numerous avenues of improvement to elevate the properties of these sustainable surrogates to posses attributes on par with their petroleum-derived counterparts while simultaneously developing technologies that are increasingly sustainable (Janik, Sienkiewicz, Wawrowska, Wiecierzycka, & Przybytek, 2017). This review seeks to systematically analyze single variables to provide insight on potential methods for improving more complex resin and film formulations as well as to assess the potential of various additives to produce antioxidant and antibacterial functional films or spoilage-indicating films.

3 | EXTRACTION METHODS

Extraction methods vary depending on the starch source (Table 1). The difference in protein–starch interaction and protein type are the predominant factors for consideration when designing an optimal extraction process and necessitates the development of source-specific extraction methods. El Halal et al. (2019) provide an insightful review of starch extraction from various cereal grains. In general, the most common methods for isolating starch from cereal grains include soaking the grain to soften it followed by milling, several steps of washing with water, and/or dilute alkaline solutions and centrifugation (Bergthaller, 2004; Gani et al., 2017; Gous & Fox, 2017; Van Hung, Chau, & Phi, 2016; Verwimp, Vandeputte, Marrant, & Delcour, 2004; Ziegler et al., 2017). Commercially, potato, corn, and tapioca root starches are prepared by mechanical milling of the material with water to separate the starch from the plant fiber followed by a dewatering process that typically involves centrifugal separation followed by flash drying (Sanchez, Silva, Kalid, Cohim, & Torres, 2017; Whistler & BeMiller, 2009). The method of extraction unequivocally impacts the properties of the starch as well as the properties of the resultant film so that this aspect must be carefully considered in film design (Maniglia et al., 2019).

4 | MODIFICATION STRATEGIES

Once starch has been successfully extracted from its source, it can be plasticized as-is for a variety of applications or it may be chemically modified before plasticization. One of the most common chemical modifications of starch is the formation of esters by its reaction with octenyl succinic anhydride (OSA, Figure 4a). This modification was originally patented in 1953 but continues to be a promising route to develop sustainable materials as it changes the physical properties while endowing the starch granules with negative surface charge and available olefin functionalities for further modification (Caldwell & Wurzburg, 1953). The typical synthesis of OSA-starch

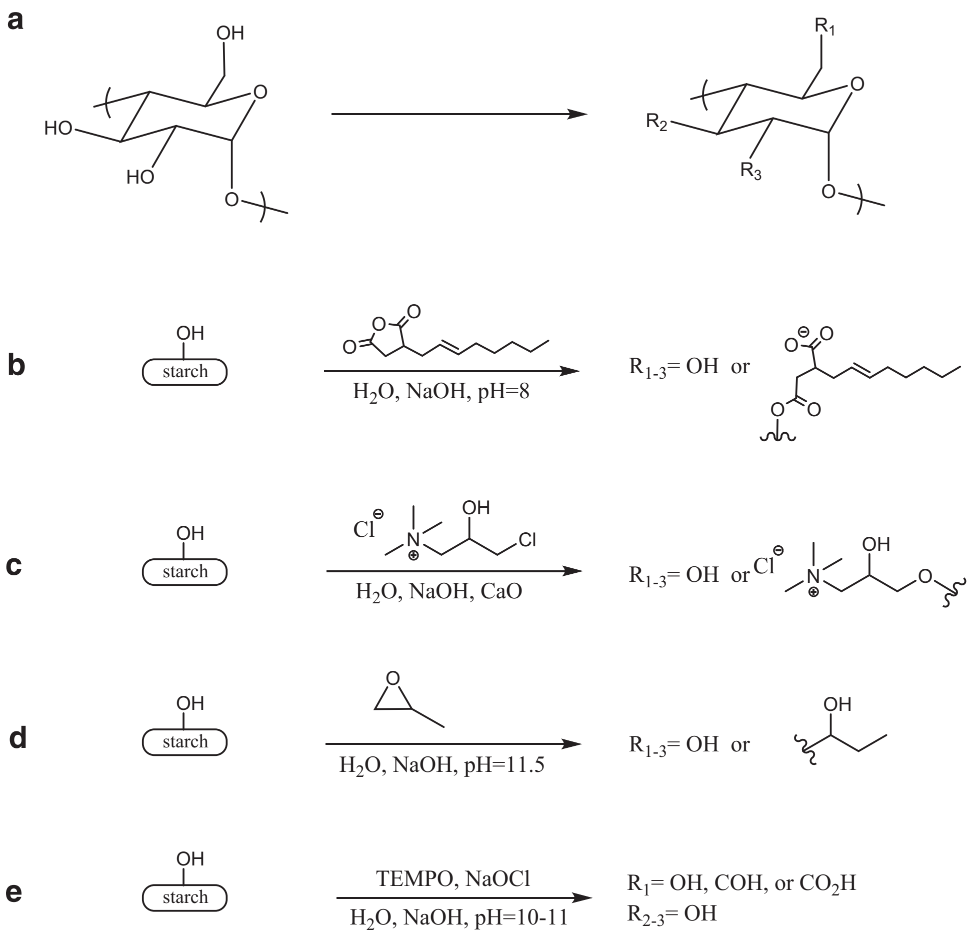

FIGURE 4 Common reactions for the modification of starch showing (a) the general reaction scheme, (b) the reaction of starch with octenylsuccinic anhydride (OSA) to make anionic OSA-starch, (c) the reaction of starch with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) to make cationic starch, (d) the reaction of starch with propylene oxide to make hydroxypropylated starch, and (e) the reaction of starch with (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and bleach to make oxidized starch

is exceptionally straightforward and typically proceeds through the gradual addition of OSA to an aqueous suspension of starch while maintaining the pH of the slurry at 8 by the addition of NaOH. A recent review details the many uses of OSA-modified starch (Altuna, Herrera, & Foresti, 2018).

Although OSA-modified starch features negative functionalities, cationic starch can also be prepared via etherification by several methods. One common method involves the use of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) (Figure 4b) (Bayat Tork, Khalilzadeh, & Kouchakzadeh, 2017; Butrim, Bil'dyukevich, Butrim, & Yurkshtovich, 2016; Huang et al., 2019). Some other strategies that have been commonly applied to cellulose have also been applied to starch, to include carboxymethylation (Cai et al., 2019; Jiang et al., 2019; Li, Wu et al., 2019; Zhang, Pan et al., 2017; Zhang, Chi et al., 2017; Zhang, Tao, Niu, Li, & Chen, 2017), hydroxypropylation (Fang, Fu, Tao, Liu, & Cui, 2020; Fu, Zhang, Ren, & BeMiller, 2019; Hu, Jia, Zhi, Jin, & Miao, 2019; Shaikh, Ali Tahira, Hasnain, & Haider, 2019) (Figure 4c), and oxidation (Li et al., 2020; Wang et al., 2015; Zhang, Ding, Gu, Tan, & Zhu, 2015; Zhao et al., 2015). Oxidation of C6 hydroxyl groups with catalytic TEMPO and bleach can be accomplished in a facile and environmentally friendly route in aqueous media (Figure 4d). Other transformations include etherification to make neutral starches (Misman, Azura, & Hamid, 2015), and ozone treatment, which is both a chemical and physical modification method (Castanha, Santos, Cunha, & Augusto, 2019; Klein et al., 2014). Morphological modification is also a common strategy that is utilized to change starches' functional properties to give porous starch or starch nanoparticles (NPs) (Li, Zhao et al., 2018; Oliyaei, Moosavi-Nasab, Tamaddon, & Fazaeli, 2020; Xiang et al., 2016; Yang et al., 2017). Enzymatic modification by pullulanase, an enzyme that cleaves (1,6)-α-D glycosidic linkages, can also effectively change the amylopectin to amylose ratio (Abidin et al., 2018; Hu et al., 2019; Huang, Li, Chen, & Li, 2017; Lu et al., 2019; Yang et al., 2017).

Although most of these modification strategies involve fairly simple synthetic reaction steps, much attention has recently been focused on developing and optimizing processes for reactive extrusion of starch, opening the door for further commercialization of starch-based products (Fitch-Vargas et al., 2019; Fonseca-Florido et al., 2019; Jebalia et al., 2019; Kaisangsri, Kowalski, Kerdchoechuen, Laohakunjit, & Ganjyal, 2019; Liu et al., 2019; Milotskyi, Bliard, Tusseau, & Benoit, 2018; Nessi et al., 2019; Siyamak, Laycock, & Luckman, 2020; Tian, Zhang, Sun, Jin, & Wu, 2015; Ye et al., 2019). Although chemical modification of starch typically diminishes the mechanical properties of the resultant films by causing less efficient polymer packing and subsequent decreases in film crystallinity, modified films can exhibit some improvements in some mechanical properties (Table 2, entries 40 and 41) as well as oftentimes leading to better barrier properties or increased compatibilization with additives that can offset the decrease in properties (Table 2, entries 10 and 38) or can endow the film with additional function while decreasing the potential for retrogradation (Colussi et al., 2017; Fu et al., 2019). Outcomes largely depend on the modification type, the extent of modification (which also depends on the starch type as amylose is more reactive to most modification strategies compared to amylopectin), and other components in the film formulation.

5 | FILMS WITH ENHANCED MECHANICAL AND BARRIER PROPERTIES

Although films prepared from plasticized starch can display reasonable mechanical and barrier properties, they are still inferior to widely used petrochemical polymer films. With the goal of supplanting current technologies with more sustainable ones, improving the properties of starch-based films is imperative. In this vein, various starch sources and modifications, additives, procedural modifications, or curing procedures have been pursued in the last several years, as enumerated in Table 2.

One of the problems facing researchers across the field (and indeed in much of materials science) when attempting to compare results from different studies is the variability of formulations, procedures, environmental factors, batch variation, and so on (Figure 1b). *In an effort to screen out these effects, the data in* Table 2 *are reported as changes in a given property*–TS, EAB, EM, WVP, and OP–induced by a procedural change or additive *within one research report* compared to a control in which the designated procedural change or additive is not employed. In the case that no control film was reported, films are compared to the indicated reference film designated by "REF" or "Reference Material" under the property column. Such a presentation of the data provides a meaningful reference guide for predicting the direction and relative magnitude of change that could be induced in other starch films prepared using the same procedural modifications or additives. It is worth noting that, in general, increasing values (i.e., "+") are desirable for TS, EAB, and EM, while decreasing values (i.e., "−") are desirable for OP and WVP. The table is organized by starch type studied in each report, from most references in the last 5 years (corn) to least. Studies in which multiple starch types are compared are at the end of the table.

5.1 | Starch sources

Although the field of starch films has grown significantly over the past decade, it is still a widely held belief that mechanical properties of films follow directly from the amylose content such that higher amylose content leads to greater strength and stiffness as denoted by TS and EM. While this can be true, the following examples highlight the potential for deviations from this "rule" and reflect the reality that the impact of the starch source is multivariate.

In a work by Luchese et al. (2018) (Table 2, entry 57), films composed of potato (10 wt% amylose), cassava (26.7 wt% amylose), wheat (27.4 wt% amylose), and corn (28.5 wt% amylose) were each made from several concentrations of film-forming solutions (FFS). The exceptionally low amylose content of potato starch led to cracked films upon drying at all concentrations, while the other three starches formed structurally sound films resulting in the inability to acquire mechanical or barrier data for potato starch films. Comparing films cast from 4 wt% starch solutions, corn proved to have the highest TS and EM, those properties decreasing with decreasing amylose content. EAB followed the opposite trend, however, with cassava starch exhibiting the highest values followed by wheat and finally corn. Interestingly, there was no trend relating WVP to amylose content. All films were additionally shown to be biodegradable. Due to the large number of films produced, PCA was performed and with only a couple of outliers, each grouping included only starches of the same type. In general, the cassava starch films produced higher EAB and lower WVP, a result of them having more hydrophobic surfaces, the corn starch films had higher TS and EM values, a property potentially related to their high amylose content, and the wheat starch films exhibited higher WVP and worse mechanical properties.

Another study revealed similar results when starch films made from rice (16.9% amylose), potato (20.5% amylose), wheat (24.5% amylose), and corn (24.8% amylose) were analyzed (Domene-Lopez et al., 2019). All the prepared films were similar thicknesses but exhibited very different opacities. Corn was the opaquest followed by wheat and rice, with the potato starch film being the most transparent. The rice starch film was plasticized most effectively, as diagnosed by the broadening and intensity of peaks in the powder X-ray diffraction analysis. Films made from rice starch exhibited the highest EAB, and EAB once again decreased with increasing amylose content. Films made from corn starch showed the highest EM and EM decreased with decreasing amylose content. TS followed a similar relationship as EM although wheat exhibited a slightly higher value than corn.

Work by Dai et al. (Table 2, entry 55) further highlights that the properties of films are more than a product of the amylose content (Dai et al., 2019). Six films were produced from starch derived from either waxy corn (0% amylose), cassava (16% amylose), sweet potato (17% amylose), potato (22% amylose), wheat (27% amylose), or corn (28% amylose). As was previously shown, corn starch produced a less transparent film but was followed closely by waxy corn starch although the amylose content is significantly different. Cassava, sweet potato, and potato starch films showed the lowest surface roughness by atomic force microscopy. Most interestingly, the authors found that for all tested mechanical properties (TS, EAB, and EM), potato starch outperformed every other starch, and there was no apparent trend in the properties relating these metrics to amylose content. A trend was observed for WVP, where cassava starch had the lowest value, and WVP increased with increasing amylose concentration to a point where it remained unchanged. A related study similarly compared films prepared from cassava (18% amylose) and corn (28% amylose) starches and likewise found that cassava produced superior films in terms of TS, EAB, and WVP, while EM measurements were comparable (Tavares et al., 2019).

5.2 | Starch modification

Various avenues for starch modification have proven valuable for influencing the properties of resulting starch films. Work by Vanier et al. (2019) showed that common bean starch of different genotypes, although grown in the same location and harvested at the same moisture content, would produce films with different properties. It was found that *BRS Pitanga* and *BRS Pérola*, for example, exhibited the highest TS, while *BRS Estilo* had the highest EAB and *IPR Uirapuru* had the smallest WVP (Table 2, entry 48). These results were especially surprising considering the very similar moisture and amylose contents of the extracted starches. Most notably, *IPR Uirapuru* starch exhibited a polyhedral granular structure, a very unusual morphology for a common bean starch. It also exhibited a gelatinization enthalpy approximately six times higher than the other three genotypes, highlighting the potential for enormous differences between starches produced by the same plant species and containing similar amylose contents. Germination progression of wheat was also shown to impact the properties of the films produced from its starch (Baranzelli et al., 2019). Although most of the mechanical properties of wheat starch films differing only in the germination stage of the wheat from which starch was isolated were relatively similar, films comprising starch from wheat that had germinated for 48 hr exhibited > 50% higher TS and EAB than did the other films (Table 2, entry 34).

Physical modifications of starch are also effective ways to drastically change starch film properties. The extraction of babassu mesocarp starch was conducted under acidic, neutral, or alkaline conditions (Maniglia et al., 2019). While the yields, unsurprisingly, were affected by the extraction conditions, so were the physical properties of the starch including the crystal structure. Films produced from starch extracted under acidic conditions produced predominantly "B-type" crystal structures, whereas starch extracted under neutral or alkaline conditions led to more "A-type" structure (Table 2, entry 47). Ultimately, the starch exhibiting "A-type" structure resulted in more compact films with better mechanical properties. In a similar vein, Zhang, Hou, et al. (2019) hydrolyzed pea starch with hydrochloric acid for varying amounts of time to elucidate the impact on the starch film properties. At longer hydrolysis times, the starch granules were visibly degraded and began to agglomerate as amylopectin was broken down with concomitantly higher amylose percentage and crystallinity (Table 2, entry 51). The mechanical properties followed as TS increased with increasing hydrolysis time. WVP was significantly increased with increasing hydrolysis time, whereas the impact on EAB was less significant. This modification strategy proved to be an effective way to improve film mechanical and barrier properties with a relatively simple pretreatment process.

Acetylation is commonly implemented to improve starch film degradability despite the drawback that it is typically accompanied by diminished mechanical properties (Colussi et al., 2017). Millet starch, however, can be acetylated to 1.12% or 2.44% with little change in mechanical properties (Shaikh et al., 2019). At 1.12% acetylation, EAB was improved relative to native starch, whereas at 2.44% it was unchanged (Table 2, entry 42). Low-level acetylation effectively improved WVP with lower WVP at a higher degree of acetylation. No change in TS was observed with acetylation in this work. Another study was done to elucidate the impact of degree of acetylation for both low (20%) and high (32%) amylose rice starch (Colussi et al., 2017). Contrary to the work with millet starch, the WVP for low amylose corn starch increased with increasing degree of acetylation, whereas the high amylose starch exhibited an optimal WVP at an intermediate degree of substitution (Table 2, entries 40 and 41). In general, acetylation increased the EAB, especially for the low amylose starch, while decreasing TS.

Crosslinking is an effective method for improving the strength properties of nearly any polymeric material and has, therefore, been extended to starch film chemistry. Wheat starch can be crosslinked with sodium trimetaphosphate (STMP) and sodium tripolyphosphate, for example (Table 2, entry 36). These crosslinked films exhibited slightly improved TS, EAB, and WVP with a subsequent decrease in EAB (Yousefi, Savadkoohi, Zahedi, Hatami, & Ako, 2019). Sukhija, Singh, and Riar (2019) observed more substantial improvements in strength by crosslinking lotus rhizome starch with STMP at various concentrations. Increasing crosslinking led to an increase in TS with a slight decrease in EAB and WVP (Table 2, entry 50). Crosslinked films exhibited, unsurprisingly, much lower water contents and solubilities. In the same body of work, the effect of starch oxidation was also studied. Oxidation was found to increase moisture content and solubility with a corresponding increase in WVP. There were, however, slight improvements to TS and EAB of the oxidized films relative to the control film. The oxidized films could also attain higher degrees of crosslinking upon reaction with STMP, leading to films with improved TS and WVP relative to STMP-crosslinked starch films. The synergy of a dual modification strategy was also observed by Zhengyu et al., who found that debranching corn starch led to improvements in TS, WVP, and OP but decreased EAB, while hydroxypropylation of starch was deleterious to TS and barrier properties, albeit with improved EAB. Dual modification resulted in films with improved TS, EAB, WVP, and OP relative to control films.

Dai et al. (2019) looked at the impact of three different modification strategies on cassava starch, including esterification, crosslinking, and oxidation. Surprisingly, they found that all modifications improved nearly all mechanical and water vapor barrier properties. Crosslinked cassava starch was the standout, as its film exhibited the highest TS and EAB with the lowest WVP and slightly increased EM relative to the uncrosslinked control (Table 2, entry 22).

5.3 | Starch as an additive

Reinforcing starch with starch has also proven to be an effective way to improve film properties. Most notably, starch nanocrystals or starch NPs act as reinforcing agents to generate nanocomposites with improved TS, EM, and WVP. Starch NPs generated by debranching and crosslinking waxy corn starch (Table 2, entry 5) were dispersed in corn starch and were found to be effective at slightly improving EAB (Lu et al., 2019), whereas incorporation of starch nanocrystals into an oxidized cassava network (Table 2, entry 19) led to significantly decreased EAB (Dai, Zhang, & Cheng, 2020).

Fang et al. (2020) synthesized NPs from waxy corn starch and κ-carrageenan to endow starch films with antimicrobial properties while improving the mechanical properties of hydroxypropyl cassava starch films (Table 2, entry 18). Although EAB was reduced, TS was significantly improved. Incorporation of NPs generally improved WVP relative to the control film but was optimized at an intermediate concentration of 3 wt% incorporation. Cassava starch films were also prepared by incorporating some oxidized cassava starch into the formulation with good results. Although surface roughness was increased with increasing incorporation of oxidized starch, the moisture and solubility of the films were decreased and all mechanical properties were improved (TS, EAB, and EM). Based on these results, the analysis of WVP would likely demonstrate significant barrier properties relative to the control films.

5.4 | Cellulose as an additive

Cellulose, especially nanocellulose (NC), has gained much attention in the past decade for the ability to improve the mechanical properties of nanocomposite materials. As a natural extension, they have also been incorporated into starch-based films with good results. Several fundamental studies analyzing the change in properties with varying wt% of cellulose nanofibers (CNFs) have been performed and are largely consistent with one another for different starch films. Zhao, Huerta, and Saldana (2019) varied the wt% of CNFs produced from canola straw (Table 2, entry 16) and incorporated them into cassava starch films (2.5 to 10 wt%). With increasing incorporation of CNFs, TS increased by 7 to 11 times the TS of the control film with a smaller but consistent decrease in EAB. WVP was decreased for all films with CNFs relative to the control films but reached the maximum value at an incorporation of 7.5 wt%. When CNFs were incorporated from 5 to 20 wt% into corn starch films (Li et al., 2018), all films exhibited improved TS, EAB, EM, and WVP relative to reference films but 15 wt% proved to be the optimal incorporation for all metrics incorporated (Table 2, entry 6). At higher wt% incorporation of CNFs, problems begin to emerge with agglomeration of CNFs leading to a reduction in film properties. Work by Mahardika et al. (2019) (Table 2, entry 49) revealed that incorporating 0.05 to 0.2 wt% CNFs into jicama starch films led to improvement in TS, EM, and WVP with increasing incorporation of CNFs, although

EAB decreased significantly over the series as well. Tavares et al. (2019) found that incorporation of carboxymethyl cellulose led to drastic improvements in the TS and EAB of corn starch films (+90% and 850%, respectively; Table 2, entry 15) with no statistically significant change to any of the mechanical properties of cassava starch films, highlighting the inherent variability in mechanical properties of quite similar film formulations.

More in-depth studies on NCs have revealed that the source and preparation method are paramount in determining the mechanical properties. Chen, Liu, and Chen (2019) found that in general, incorporation of various concentrations of cellulose nanocrystals (CNCs) into corn starch films increased TS and decreased EAB while also improving OP and WVP (Table 2, entry 7). The source of CNCs (bamboo, cotton linter, or sisal), however, also drastically impacted the magnitude of these changes as well as the concentration, which provided the optimal improvements in mechanical properties. Sartori and Menegalli (2016) determined that producing CNFs from banana peels at lower reaction concentrations resulted in better reinforcing of banana starch films (Table 2, entry 46) and therefore, better mechanical and barrier properties. Han et al. (2019) examined the effect of NCs made from CHPTAC-modified microcrystalline cellulose. In this study, three standard methods of NC production were screened–acid hydrolysis, ultrasonication, or high-pressure homogenization–to determine which method produced NCs capable of reinforcing starch films the most effectively. Incorporating NCs produced by acid hydrolysis resulted in some agglomeration in the films, while the incorporation of NCs produced by the other methods led to even dispersion and low surface roughness. It was found that high-pressure homogenization led to more crystalline NC, therefore, optimizing TS and EM (Table 2, entry 53).

5.5 | Other additives

Plant-derived additives are attractive due to their renewable nature as well as their biological compatibility, a chief concern when designing films for food packaging applications. One interesting strategy is to utilize small organic diacids, which can interact with the hydroxyl groups of starch to act as a plasticizer and a crosslinking agent. One commonly utilized diacid for this purpose is citric acid (CA). CA was incorporated into potato starch and chitosan films from 5 to 20 wt% (Wu et al., 2019). Increasing incorporation of CA led to increasing surface roughness with decreased moisture content and water solubility up to 15 wt%. Relative to the control film in which no CA was incorporated, TS, EAB, and WVP were improved with the 15 wt% film having the best TS and WVP, while the 20 wt% film had the highest EAB (Table 2, entry 27). These results are consistent with CA acting as a plasticizer by increasing the elasticity while also acting as a crosslinker to improve the strength and decrease permeability. Owi et al. (2019) did similar work in which they utilized CA-containing lime juice (3 to 20 wt%) as a crosslinking plasticizer for tapioca starch. This process also involved a second heating step after gelatinization to ensure effective crosslinking. When films were heated to 105 °C for 15 min, an interesting trend emerged. With increasing incorporation of lime juice, the TS increased although improvements relative to the control film were not seen until at least 15 wt% of lime juice had been incorporated (Table 2, entry 44). EAB was increased more than five-fold with the addition of 3 wt% lime juice but dropped off steadily with increasing incorporation. As crosslinking reduces the number of free hydroxyl groups, the addition of lime juice resulted in a decreased WVP relative to the control film although there was no correlation between lime juice concentration and WVP. Another plant-derived additive that has been utilized in starch films is curcumin. Although this system was primarily designed to provide films with some antioxidant capacity, varying the incorporation from 0.5 to 3 wt% in proso millet starch films showed consistent improvements in EAB reaching a 100% improvement relative to the control film at 3 wt% incorporation (Baek & Song, 2019). WVP was also improved with increasing incorporation due to an increase in hydrophobicity with a concomitant decrease in TS (Table 2, entry 43).

Various plant extracts have also been explored as potential additives for films, largely for their potential to contribute antioxidant properties. These antioxidant species are often hydrophobic organic compounds that can disrupt polymer packing or form aggregates, worsening the mechanical properties. In some cases, however, improvements are observed due to hydrogen-bond formation (like in the case of various phenolic compounds) or the encapsulation of the active species in a hydrophilic species, leading to uniform additive dispersion. Orange peel oil and zein, a protein found in corn, were used to form microcapsules and were incorporated into corn starch films at 11, 43, or 100 wt% (Wang, Kang, Yu, Liu, & Cui, 2019). Small improvements to TS and EAB were observed due to a plasticizing effect of the microcapsules, while significant improvements to OP and WVP were also observed due to the hydrophobicity contributed by the orange peel oil (Table 2, entry 12). Green tea extracts (GTEs) were incorporated into potato starch films (Table 2, entry 28) at 5 wt% and were found to slightly improve TS, EM, and WVP with small decreases in EAB (Nisa et al., 2015). Extracts from rice straws (RSE) were substituted into potato starch formulations for an equal amount of plasticizer at 5, 7.5, and 10 wt% (Menzel, Gonzalez-Martinez, Chiralt, & Vilaplana, 2019). Large improvements to TS and EM were observed at 5 and 7.5 wt% incorporation; however, incorporation of more RSE led to mechanical properties on par with the control film, likely due to the large decrease in plasticizer concentration. Optimal WVP and OP were obtained at 7.5 and 10 wt%, respectively (Table 2, entry 29). More niche plant extracts, such as extracts from Chinese bayberry (CBE), have produced some interesting results (Yun et al., 2019). Incorporation of just 1 wt% CBE into cassava starch films (Table 2, entry 25) led to a 40% increase in TS and a 10% reduction of WVP. With the incorporation of more extract, the improvements to TS were less significant but EAB was improved relative to the control film when at least 3 wt% was incorporated. WVP was optimized at the highest concentration of 4 wt%. The incorporation of *Lycium ruthenicum* anthocyanins (LRA; Table 2, entry 24) had a very similar outcome (Qin et al., 2019). Although initial incorporation of LRA saw an increase in TS, increasing the concentration above 1 wt% resulted in a decrease in TS, likely due to the formation of LRA agglomerates observed by SEM. With the addition of LRA, WVP decreased, further decreasing with increasing LRA concentration. It was hypothesized that this was the result of LRA hydrogen bonding with the starch, decreasing starch's potential to hydrogen bond with water thereby decreasing WVP. The primary difference between the films' properties was that an increase in LRA led to a slight decrease in EAB.

Chitosan has recently been gaining attention due to its antimicrobial properties as well as its ability to provide strength to composite materials (Table 2, entries 14 and 17) and being biocompatible and environmentally benign (Kumar, Mukherjee, & Dutta, 2020; Nunes, Coimbra, & Ferreira, 2018; Sharma, Rokana, Panwar, & Dhiman, 2017). Chitosan is produced through the deacetylation of a waste product of the seafood industry making it a sustainable additive although potentially limiting its accepted use due to being predominantly animal derived. Bof, Bordagaray, Locaso, and Garcia (2015) investigated the impact of chitosan molecular weight (M_n) on corn starch films' properties. Unsurprisingly, they found that high molecular weight provided a stronger, more rigid film with improved WVP (Table 2, entry 14). Low and mid M_n chitosan had little impact on the barrier properties relative to the control film. Utilizing low M_n chitosan improved the TS by two-fold but had a similarly drastic negative impact on EM. Mid M_n chitosan provided a much more stretchable film although the strength was ultimately decreased compared to a starch film not containing chitosan. Dang and Yoksan (2015) incorporated chitosan at relatively low concentrations (0.37 to 1.45 wt%) into cassava starch films (Table 2, entry 17) and found that at the upper end, the TS increased by 100%, while the EM increased by 150% although the EAB did decrease (~70%) due to the increase in rigidity resulting from the incorporation of chitosan. The incorporation of chitosan at 0.5 or 1 wt% into tapioca films (Table 2, entry 45) was also conducted though there was no control film produced for means of comparison (Pratama, Abduh, Legowo, & Hintono, 2019). Between the two films, increased incorporation of chitosan led to higher TS but worsened EAB and WVP. The authors also prepared chitosan and palm olein emulsions and saw negligible changes in the TS and small improvements in WVP of the films in which the emulsions were incorporated. EAB was improved with incorporation of palm olein to the film containing 1 wt% chitosan but was decreased by addition to the film containing 0.5 wt% chitosan.

Sodium montmorillonite (MMT), a group of phyllosilicate minerals, has also gained quite a bit of attention recently as a potential additive for starch films (Giannakas & Leontiou, 2018; Guo, Aryana, Han, & Jiao, 2018). The incorporation of MMT generally improves mechanical and barrier properties although it also typically increases film opacity, potentially limiting its use in commercial films for food packaging. By incorporating 3 or 5 wt% MMT into corn starch films (Table 2, entry 9), small improvements in TS and EM were observed that increased with larger incorporation of MMT (Li et al., 2019). EAB was also increased relative to the control film but was optimized at a lower wt% incorporation. Light transmittance at 600 nm was quite low at 15% although it was on par with the control corn film. The contact angle increased with increasing MMT incorporation indicating that the films may have improved barrier properties although WVP was not directly quantified in this study. Similarly, when MMT was incorporated at 3, 5, or 7 wt% in modified wheat starch films (Table 2, entry 37), TS and WVP increased with increasing incorporation of MMT, while EAB decreased slightly and EM was maintained throughout the series despite some MMT agglomeration at higher concentrations (Yousefi et al., 2019). Transmittance through these films at 600 nm was significantly improved relative to the corn starch films (~90%T). The films also showed good UV absorption throughout the range with efficacy dropping off at longer wavelengths. Wang et al. (2018) incorporated MMT as well as organic modified montmorillonite (*o*-MMT) into CHPTAC modified corn starch films with varying degrees of substitution. In general, MMT outperformed *o*-MMT and incorporation of MMT led to improved TS, decreased EAB, and small changes in WVP, both positive and negative (Table 2, entry 19).

Metal NPs have also been implemented in film formulations due to their antibacterial and reinforcing properties (Huang, Mei, Chen, & Wang, 2018; Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012; Sharma et al., 2017).

Antibacterial corn starch films were prepared by incorporating 143 ppm silver nanoparticles (Ag NPs) into films prepared with different starch concentrations in the FFS (Ortega, Garcia, & Arce, 2019). The impact of incorporating AgNPs was most significant with the 3 wt% film, where incorporation had significantly improved TS and EM with no change in EAB and a large increase in WVP. Incorporation into other FFS showed similar trends but with less significant changes. Incorporation of AgNPs also increased film opacity. Nano-titanium dioxide (nano-TiO_2) has also been of great interest as an additive in starch films due to its potential for protecting food from UV damage. Dash, Ali, Das, and Mohanta (2019) incorporated varying concentrations of nano-TiO_2 (0.5 to 4 wt%) into sweet potato starch films (Table 2, entry 30) and found that with increasing concentration of nano-TiO_2, there was some agglomeration of nano-TiO_2 and increased surface roughness, contrary to improvements in TS, EM, and WVP, with a concomitant decrease in EAB. In this system, films containing nano-TiO_2 were more transparent than the reference film although they possessed higher whiteness indices and significantly larger UV absorption. When TiO_2 was incorporated into modified wheat starch films containing MMT, increasing incorporation of MMT saw a negative effect on TS and EAB while not affecting EM (Yousefi et al., 2019). Opacity increased significantly with increasing incorporation of TiO_2; however, WVP was improved and transmittance was reduced across the entire UV region to less than 3.5%. In other starch films, incorporation of nano-TiO_2 slightly improved TS (Table 2, entry 54) although the increase was not concentration dependent (Li, Zheng et al., 2019). EAB and WVP both decreased with increasing incorporation of nano-TiO_2. Incorporating clove oil into these films negated the positive impact of nano-TiO2 on TS but significantly improved EAB and further improved WVP.

Other additives that have been implemented include $CaCl_2$ and ferulic acid, which were incorporated into modified sago starch (0.7 and 0.05 wt%, respectively) due to their ability to plasticize starch (Naseri et al., 2019). As plasticizers, these agents caused a slight reduction in TS and an increase in EAB (Table 2, entry 38). Most notably, $CaCl_2$ and ferulic acid significantly improved WVP. Due to the small amounts required to produce these changes as well as their ubiquitous nature, low cost, and biocompatibility, these additives should be further explored with other starch films. Oxidized sucrose, which can effectively crosslink starch, was also explored as an additive for corn starch films (Balakrishnan et al., 2019). Oxidized sucrose was incorporated at 1, 2, and 3 wt%. At 1 wt%, the change in mechanical properties was negligible; however, at 2 and 3 wt%, there were significant improvements in TS and WVP with only slight decreases in EAB (Table 2, entry 8). This may be explained by the ability of oxidized sucrose to act as both a crosslinker and a plasticizer as seen with previous work with CA (Wu et al., 2019). Fabra, Martinez-Sanz, Gomez-Mascaraque, Gavara, and Lopez-Rubio (2018) incorporated various strains of microalgae into corn starch films. They found that while the algae negligibly affected the mechanical properties, incorporation of *Nanochloropsis gaditana* significantly improved both the WVP and OP (Table 2, entry 11). The primary drawback of these films was their dark green to black color and low transmittance across visible wavelengths.

5.6 | Manipulations to FFS

Although the commercialization of starch films precludes their preparation through FFS, the manipulations that can be performed can provide information on the fundamental physical phenomena that result in a change in film properties. One of the most straightforward manipulations is simply to change the concentration of starch in the solution (Table 2, entries 20 and 33). Luchese, Benelli, et al. (2018) studied how the concentration of starch in the FFS affected the film properties for multiple different starch sources. Upon analyzing cassava starch, it was found that 4 wt% of starch formed films with optimal EAB and WVP, while the film formed with 5 wt% of starch had the highest TS and EM (Table 2, entry 57). Analysis of wheat starch showed that regardless of the concentration (2 to 6 wt%), all films performed identically within statistical significance. Analysis of corn starch films revealed that 4 wt% was optimal for TS, EAB, EM, and WVP. Work done by Ortega et al. (2019) showed slightly different results for corn starch films when analyzing 1, 3, and 5 wt% films. It was determined that TS was maximized at 3 wt%, EAB was maximized at 5 wt%, and EM was optimized at both 3 and 5 wt% (Table 2, entry 13). Most interestingly, they found that optimal WVP was obtained at 1 wt%. Analysis of 2, 2.5, and 3 wt% ulluco starch films found that changing the concentration within this range did not change WVP, while TS and EAB were maximized at 2 or 3 wt% with decreased properties at the intermediate concentration, 2.5 wt%.

The concentration and identity of the plasticizer are also very impactful in establishing film metrics. Cheng et al. (2019) analyzed the effect of the change in concentration of glycerol or D-sorbitol on the film properties of Chinese yam and found that for both plasticizers, TS and EM were maximized at 2.4 wt% plasticizer, while EAB, OP, and WVP were optimized at 4.0 wt%, the highest concentration implemented in this study but much lower than is implemented in many systems (Table 2, entries 31 and 32). At 4 wt% starch in the FFS, D-sorbitol significantly outperformed glycerol in all aspects except EAB where they produced similar results. When the identity of plasticizer was varied in babassu mesocarp starch films, a general trend emerged where glycerol and sorbitol led to the best mechanical properties, whereas glucose was most effective at improving WVP.

Other modifications can still be envisioned. Sakkara et al. (2020) found that by varying the pH of the FFSs in the absence of plasticizer, corn starch film properties could be altered. At a pH of 5, TS and EM were optimized, while EAB was optimized at a pH of 11 (Table 2, entry 2). It would, however, be prudent to investigate the change in pH with plasticizer to see if such drastic film property changes are still observed. Treatment of FFSs with UV-A and UV-C for various amounts of time was also undertaken to develop UV-resistant food packaging films (Table 2, entry 35) although a deleterious impact was observed for almost all mechanical properties due to decomposition of polymer structure (Shahabi-Ghahfarrokhi, Goudarzi, & Babaei-Ghazvini, 2019). WVP did improve slightly for most of the treated films and some of the films also saw improvements in EAB although there was no obvious trend. Ultrasonication of FFS for 2.5, 5, or 10 min revealed surprisingly large improvements in TS and EM (Table 2, entry 39) for the sago starch systems ultrasonicated for 5 min (Abral et al., 2019). Other treatment times saw no change in mechanical properties except for a small decrease in WVP for the FFS treated for 10 min. Due to the large improvement in mechanical properties with a simple, time, and cost-effective 5-min ultrasonication treatment, this avenue should be explored for other starch films.

5.7 | Surface optimization

Surface optimization is an effective strategy to analyze the impact of several variables on a single system. This process involves first using a well-understood composite as a starting point for designing additional film formulations. These additional formulations are then prepared, and results are collected. Surface optimization is then performed to determine an optimal formulation depending on experimental results and desired outcomes. This recursive feedback process has been successfully applied to various systems, with the experimental results that are quite close to the predicted values. This method proved useful for determining the optimal amount of nanofillers, nanostarch, and NCs (Silva et al., 2019). The optimized conditions produced a film that was, within standard deviation, identical to the predicted results for TS, EAB, and EM. Surface optimization was also successfully performed to determine the optimal starch, rosemary oil, and emulsifier concentration in the FFS while also considering optimal film thickness of the resultant cassava starch-based film (Navia Porras et al., 2019). The film that was produced was quite close to the predicted values for TS, EM, EAB, and water vapor transmission although some values were slightly outside of the standard deviation. Errors were +6.27%, −3.37%, +10.61%, and +4.35% for TS, EM, EAB, and water vapor transmission rate, respectively. This technique was also used to determine optimal concentrations of *S. platensis*, gelatin, and cassava bagasse in a cassava starch film. Unlike the other examples, the goal, in this case, was to create a predictive model so that, depending on the application, an optimal formulation could be produced (Cardoso, Esmerino, Bolanho, Demiate, & Danesi, 2019).

6 | ANTIOXIDANT FILMS

The global food market dictates that foods, both processed and natural, have a shelf life longer than has been necessary in the past. For fresh produce, protection from oxidation is important to maintain nutrient quality, whereas processed foods and fresh meat are high in fatty acids, requiring protection from oxidation to preserve quality and flavor (Menzel et al., 2019). Numerous technologies have been developed in which antioxidant species are incorporated into starch films. Although antioxidants are important constituents of food packaging to extend shelf life, the potential of the antioxidants to enter the food must be quantified, as some of them are not meant for consumption (Yang, Yang, Liu, Zhao, & Lun, 2012). To circumvent this issue, researchers are proposing the use of compounds that are naturally occurring in foods and are therefore thought to be safe for consumption (Ahmad, Gokulakrishnan, Giriprasad, & Yatoo, 2015). One salient consideration is that these additives should ideally come from waste products to reduce the cost of the films as well as being cognizant of the ecological impacts of large-scale film production.

6.1 | Quantitating antioxidant capacity

There are many methods to measure and report antioxidant capacities, highlighting the need for agreement on standard methods and reporting protocols. The most common method is the DPPH (2,2-diphenyl-1-picrylhydrazyl) assay (Figure 5a, Table 3). DPPH forms stable radicals and exhibits a strong absorption at ~515 nm in its radical form so that reaction of antioxidant species with the DPPH radical produces a decrease in absorbance (Blois, 1958; Bonilla, Atares, Vargas, & Chiralt, 2012; Brand-Williams, Cuvelier, & Berset, 1995; Erkan, Ayranci, & Ayranci,

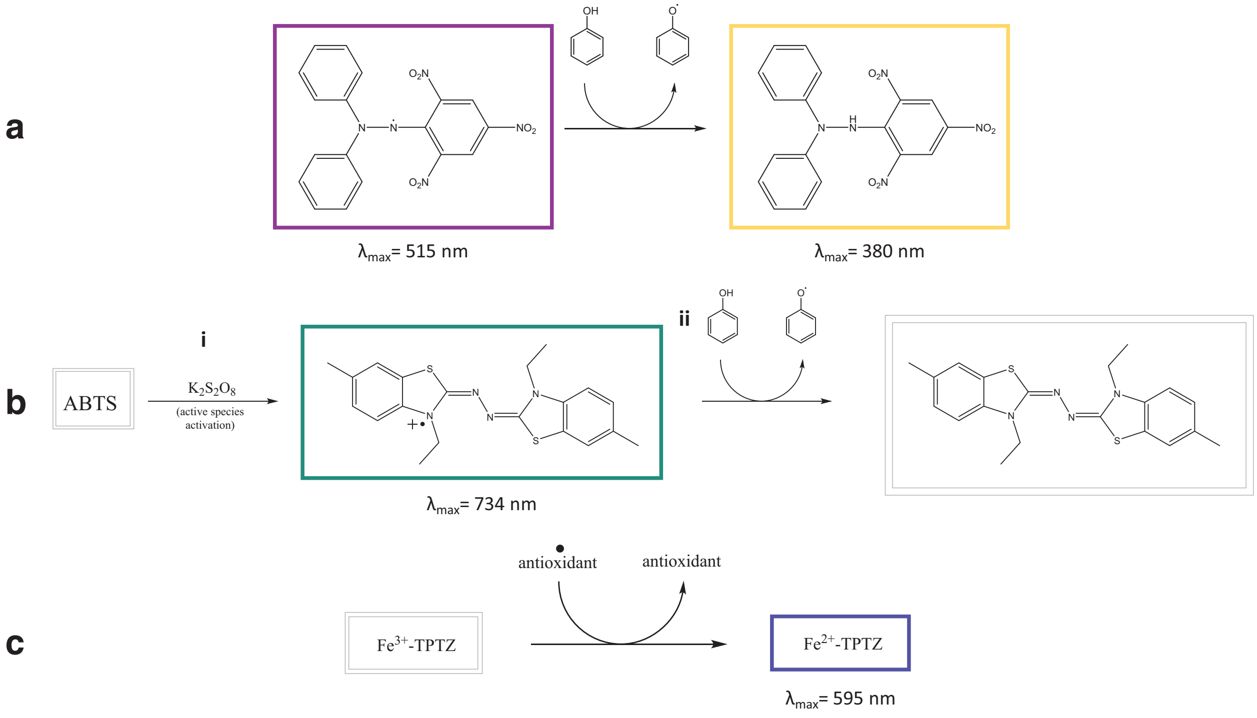

FIGURE 5 Common assays for determining antioxidant capacities include (a) DPPH, (b) ABTS, and (c) FRAP

2008; Kedare & Singh, 2011). Another common method is the ABTS (2,2′-azino-bis(3-ethylbenzthiazoline-t-sulfonic acid) assay, which works by similar principles (Figure 5b, Table 4). ABTS assay starts with the conversion of ABTS to a radical cation, typically by using potassium persulfate. This step is necessary because ABTS is a less stable radical than DPPH, providing a clear explanation for the common discrepancy in results between ABTS and DPPH assays. In its radical cation form, ABTS absorbs strongly at 734 nm so that antioxidant capacity can be quantified by measuring the change in absorbance upon interaction with the antioxidant species (Bonilla et al., 2012; Re et al., 1999). Another less common method is the ferric-reducing antioxidant power (FRAP) assay (Figure 5c). The FRAP process relies on the antioxidant's ability to reduce an Fe^{3+} complex to an Fe^{2+} complex that absorbs at 595 nm in acidic solution (Benzie & Strain, 1996; Nogueira, Soares, Cavasini, Fakhouri, & de Oliveira, 2019). A drawback of such antioxidant measurement methods is that the film first is placed in a solvent for hours to entire days. Not only is this process very time-consuming, but it also does not testify to the mobility of the antioxidant species. Furthermore, aqueous dissolution is an unrealistic condition for most food packaging needs. More cautious work is needed in which a variety of film dissolution conditions are employed to mimic real foods that are hydrophilic, hydrophobic, or acidic (Food and Drug Administration, 2007; Colin-Chavez, Soto-Valdez, Peralta, Lizardi-Mendoza, & Balandran-Quintana, 2013; Estevez-Areco, Guz, Fama, Candal, & Goyanes, 2019; Ju & Song, 2019).

$$\textit{radical scavenging activity}\ (\%) = \frac{A_{blank} - A_{sample}}{A_{blank}} * 100 \quad (1)$$

Both DPPH and ABTS are typically reported as % radical scavenging ability (Eq. 1), which has the benefit of being very straightforward to calculate but has the primary drawback of not taking reagent or solution concentrations into account. Another method for reporting antioxidant capacity is with EC_{50} or the effective concentration required to react with 50% of the radical species. Because this is normalized to concentrations, it is a more universal method for reporting but also requires numerous dilution and measurement steps. Yet, another common way to report antioxidant capacities is with the Trolox equivalent antioxidant capacity. Trolox is a water-soluble compound with known antioxidant capacities and, as such, is used as a reference compound by acquiring absorbance values for standard Trolox solutions and preparing a calibration curve to determine the mM or μM concentration of Trolox required to produce the same signal as a 1 mM test solution. Like EC_{50}, units of Trolox equivalents can be normalized to concentration to afford a more universal value, but using the Trolox assay has the disadvantage of requiring standard sample preparation and a calibration curve (Estevez-Areco et al., 2019; Re et al., 1999).

TABLE 3 Results from DPPH* assays of antioxidant films

Starch (amylose%)/plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Conc. active additive	DPPH assay results (%)[a]	Ref.
Acidic extracted babassu (21%)/none	Solution cast	N/A	Phenolics	Methanol	N/A	72	(Maniglia et al., 2019)
Acidic extracted babassu (21%)/mixed[b]						70	
Neutral extracted babassu (37%)/none						67	
Neutral extracted babassu (37%)/mixed[b]						63	
Alkaline extracted babassu (25%)/none						69	
Alkaline extracted babassu (25%)/mixed[b]						65	
Job's tears (3.8)/sorbitol	Solution cast	N/A	N/A	Water	0 wt%	1	(Kang & Song, 2019)
		Clove bud essential oil	Phenolics		0.25 wt%	17.5	
					0.50 wt%	59	
					0.75 wt%	72	
Unspecified[c, d]/glycerol	Solution cast	3 wt% TiO_2	N/A	Water	0% (w/v)	1.78	(Li, Zheng et al., 2019)
		Clove oil + 3 wt% TiO_2	Phenolics (~75% eugenol)[e]		3% (w/v)	23.5	
					6% (w/v)	28.6	
					9% (w/v)	45.3	
					12% (w/v)	52.2	
Teff (17%)/sorbitol	Solution cast	Camu-camu extract	Phenolics	Water	0.3% (w/v)	42.6 ± 2.4	(Ju & Song, 2019)
					0.6% (w/v)	72.2 ± 3.2	
					1.0% (w/v)	87.3 ± 0.6	
					2.0% (w/v)	89.2 ± 0.4	

(Continues)

TABLE 3 (Continued)

Starch (amylose%)/plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Conc. active additive	DPPH assay results (%)[a]	Ref.
Cassava[d]/glycerol	Solution cast	N/A	N/A	50% (v/v) aqueous ethanol	0	1.0	(Knapp et al., 2019)
		Yerba mate extract	Chlorophylls, carotenoids, phenolics		5 wt%	8.7	
					10 wt%	24.5	
					15 wt%	29.0	
					20 wt%	39.5	
Rye (19.2%)/sorbitol	Solution cast	Rosehip extract	Ascorbic acid, carotenoids, phenolics	Water	13 wt%	55.0 ± 1.8	(Go & Song, 2019)
					23 wt%	70.3 ± 1.5	
					33 wt%	80.2 ± 0.3	
Potato[d]/glycerol	Solution cast	N/A	N/A	Water	0 wt%	5.5[f]	(Nisa et al., 2015)
				10% aq. ethanol		13[f]	
				95% aq. ethanol		15[f]	
		Green tea extract	Polyphenols	Water	5 wt%	13[f]	
				10% aq. ethanol		52[f]	
				95% aq. ethanol		48[f]	
		BHT	Phenolic	Water	5 wt%	7.5[f]	
				10% aq. ethanol		26[f]	
				95% aq. ethanol		48[f]	
Millet, proso[d]/glycerol	Solution cast	Curcumin	Polyphenol (curcumin)	Water	0.5 wt%	11.8 ± 0.2	(Baek & Song, 2019)
					1.0 wt%	15.5 ± 0.7	
					2.0 wt%	30.2 ± 0.5	
					3.0 wt%	43.0 ± 0.4	
Corn[d]/glycerol	Solution cast	N/A	N/A	Ethanol	0 wt%	2.5	(Wang et al., 2019)
		Orange peel oil/zein nanocapsules	Terpenes (~80% limonene)[e]		11 wt%	7.0	
					43 wt%	28.5	
					100 wt%	30.8	

(Continues)

TABLE 3 (Continued)

Starch (amylose%)/plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Conc. active additive	DPPH assay results (%)[a]	Ref.
Potato (27%)/glycerol	Solution cast	Sunflower hull extracts	Phenolics	Water	1 wt%	318 ± 1[g]	(Menzel et al., 2019)
					2 wt%	211 ± 1[g]	
					4 wt%	122 ± 10[g]	
					6 wt%	71.3 ± 3.1[g]	
Potato (27%)/glycerol	Melt blending and compression molding	Rice straw extracts	Phenolics (ferulic acid, p-coumaric acid, protocatechuic acid)	Water	5 wt%	119 ± 14[g]	(Menzel et al., 2019)
					7.5 wt%	105 ± 5[g]	
					10 wt%	72 ± 4[g]	
Corn[d]/glycerol	Solution cast	Eugenol	Phenolic, eugenol	Methanol	4.0 wt%	117± 12[g]	(Talon et al., 2019)
		Eugenol encapsulated in whey protein isolate			4.0 wt%	87 ± 4[g]	
		Eugenol encapsulated in whey protein isolate and oleic acid			3.4 wt%	41 ± 1[g]	
		Eugenol encapsulated in lecithin			4.0 wt%	74 ± 2[g]	
		Eugenol encapsulated in oleic acid and lecithin			3.6 wt%	34 ± 4[g]	

(Continues)

TABLE 3 (Continued)

Starch (amylose%)/plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Conc. active additive	DPPH assay results (%)[a]	Ref.
Cassava (18%)/glycerol	Extrusion of fibers and thermocompression to generate films	Rosemary extract	Polyphenols	10% aq. ethanol	2.5 wt%	33.6 ± 2.7[h]	(Estevez-Areco et al., 2019)
				50% aq. ethanol		64.8 ± 3.4[h]	
				3% aq. acetic acid		123.1 ± 8.0[h]	
				10% aq. ethanol	5 wt%	36.4 ± 3.5[h]	
				50% aq. ethanol		81.4 ± 6.2[h]	
				3% aq. acetic acid		140.9 ± 8.8[h]	
				10% aq. ethanol	10 wt%	29.5 ± 2.3[h]	
				50% aq. ethanol		60.9 ± 5.8[h]	
				3% aq. acetic acid		134 ± 13[h]	

[a] % scavenging as defined by Eq. 1.

[b] Multiple plasticizers were tested and it was found that there was no statistically significant difference in DPPH assay results.

[c] The starch source was not specified in the manuscript.

[d] No amylose % was given in the manuscript.

[e] Information is general knowledge and was not measured in the manuscript.

[f] Results are for the addition of 0.1 mL of the prepared film solution.

[g] Results are reported as EC_{50} given in units of g film/g DPPH.

[h] Results are reported as Trolox equivalents in units of μmol TE/g film.

TABLE 4 Results from ABTS assays of antioxidant films

Starch (amylose%) /plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Formulation	ABTS assay results (%)	Reference
Unspecified[b,c] /glycerol	Solution cast	3 wt% TiO_2	N/A	Water	0% w/v	16.5	(Li et al., 2019)
		Clove oil + 3 wt% TiO_2	Phenolics (~75% eugenol)[d]		3% w/v	21.6	
					6% w/v	28.3	
					9% w/v	39.5	
					12% w/v	44.7	
Teff (17%)/sorbitol	Solution cast	Camu-camu extract	Phenolics	Water	0.3% w/v	49.8 ± 0.6	(Ju & Song, 2019)
					0.6% w/v	87.3 ± 1.1	
					1.0% w/v	100.0 ± 0.0	
					2.0% w/v	100.0 ± 0.0	
Job's tears (3.8)/sorbitol	Solution cast	N/A	N/A	Water	0 wt%	1	(Kang & Song, 2019)
		Clove bud essential oil	Phenolics		0.25 wt%	32	
					0.50 wt%	95	
					0.75 wt%	98.5	
Rye (19.2%)/sorbitol	Solution cast	Rosehip extract	Ascorbic acid, carotenoids, phenolics	Water	13 wt%	84.1 ± 1.2	(Go & Song, 2019)
					23 wt%	96.0 ± 0.4	
					33 wt%	96.9 ± 0.2	
Millet, proso[c] /glycerol	Solution cast	Curcumin	Polyphenol (curcumin)	Water	0.5 wt%	29.2 ± 0.3	(Baek & Song, 2019)
					1.0 wt%	52.4 ± 0.2	
					2.0 wt%	97.2 ± 0.1	
					3.0 wt%	100.0 ± 0.0	
Arrowroot (35.2%)/glycerol	Solution cast	N/A	N/A	50% aq. methanol followed by 70% aq. acetone	0 wt%	9.2 ± 6.5[e]	(Nogueira et al., 2019)

(Continues)

TABLE 4 (Continued)

Starch (amylose%) /plasticizer	Film synthesis method	Additive	Active species in additive	Assay extraction solvent	Formulation	ABTS assay results (%)	Reference
	Solution cast, active species in FFS	Blackberry pulp, freeze-dried	Anthocyanins		20 wt%	162.0 ± 10.5[e]	
					30 wt%	180.7 ± 22.5[e]	
					40 wt%	174.2 ± 51.7[e]	
	Solution cast, active species sprinkled on top				20 wt%	253.6 ± 24.7[e]	
					30 wt%	368.3 ± 37.0[e]	
					40 wt%	408.2 ± 32.0[e]	
	Solution cast, active species in FFS	Microencapsulated blackberry pulp, freeze-dried			20 wt%	272.6 ± 73.0[e]	
					30 wt%	274.6 ± 46.7[e]	
					40 wt%	278.9 ± 8.3[e]	
	Solution cast, active species sprinkled on top				20 wt%	385.6 ± 18.5[e]	
					30 wt%	436.8 ± 24.5[e]	
					40 wt%	446.8 ± 39.7[e]	
Arrowroot (35.2%)/glycerol	Solution cast, active species in FFS	Blackberry pulp, spray-dried	Anthocyanins	50% aq. methanol followed by 70% aq. acetone	20 wt%	475.4 ± 8.4[e]	(Nogueira et al., 2019)
					30 wt%	384.2 ± 4.1[e]	
					40 wt%	416.2 ± 44.6[e]	
	Solution cast, active species sprinkled on top				20 wt%	455.6 ± 40.9[e]	
					30 wt%	541.1 ± 46.2[e]	
					40 wt%	449.5 ± 67.8[e]	

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[a] % scavenging as defined by Eq. 1.

[b] The starch source was not specified in the manuscript.

[c] No amylose % was given in the manuscript.

[d] Information is general knowledge and was not measured in the manuscript.

[e] Results are reported as Trolox equivalents in units of μmol TE/g blackberry solids.

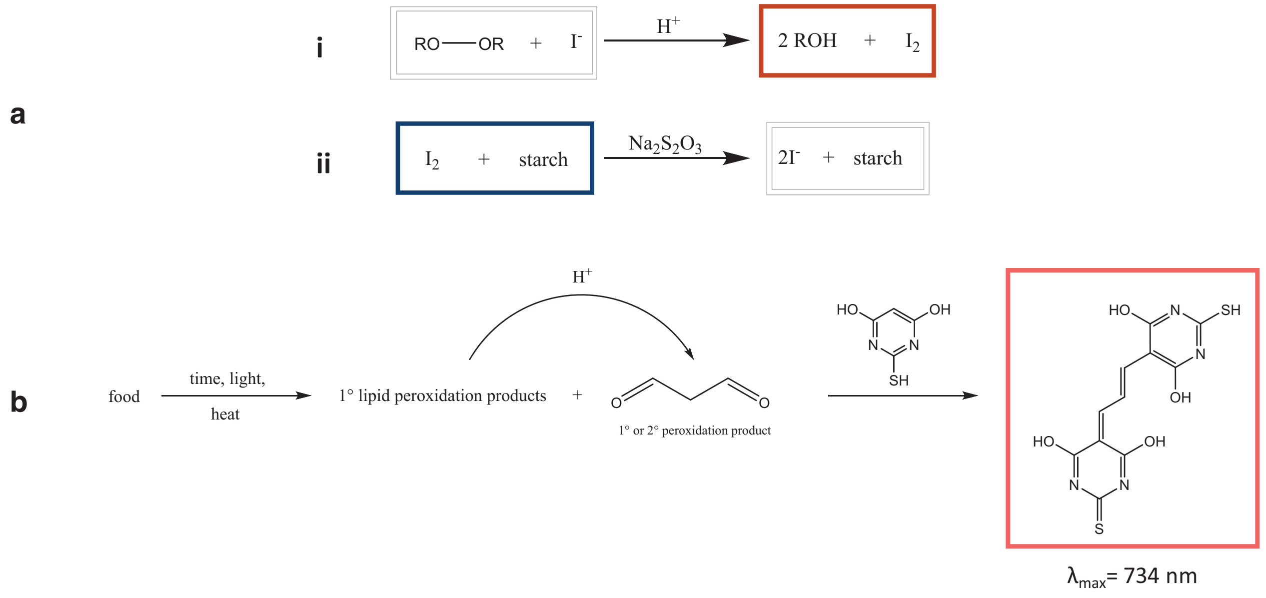


FIGURE 6 Reaction schemes for the determination of (a) peroxide value and (b) TBARS

It is worth noting that while larger radical scavenging percentages and Trolox equivalents indicate more effective antioxidants, lower EC_{50} values indicate more potent antioxidants.

Other methods have also been developed to determine the oxidation of real food samples. For determining the efficacy of a film in preventing oxidation, food is wrapped in the film and analyzed at various points over a specified timeline. The most common method of analysis is with the peroxide value (POV) assay (Figure 6a). This method tests peroxides that form in real food samples as a result of oxidation. The assay works by providing an excess of iodide (I^-), which can react with peroxides to form iodine (I_2), which can subsequently be titrated with sodium thiosulfate ($Na_2S_2O_3$), utilizing starch as an indicator. Like the other methods, this is not a perfect indicator of food spoilage as not all decomposition pathways produce peroxides. Another common method for detecting food spoilage is the thiobarbituric acid reactive substances (TBARS) assay (Figure 6b). This assay relies on the reaction of food decomposition products with thiobarbituric acid (TBA) to produce malondialdehyde (MDA), which absorbs at 539 nm and can, therefore, be determined photospectrometically. Like the POV assay, not all decomposition products react to form substances that are TBA reactive and not all decomposition products react with TBA to form MDA.

6.2 | Solution-based analysis of film antioxidant capacity

The first test that should be performed on a potentially antioxidant film is one of the previously mentioned analyses in which the film is dissolved or suspended into solution and the supernatant is analyzed. After promising initial results, it would be prudent to undertake dissolution in multiple food simulants or perform some other form of antioxidant *migration* analysis.

Various additives containing phenolic species have been incorporated into films due to their ability to lose a hydrogen atom to form a stable phenoxy radical. Phenolic species are naturally abundant in a multitude of agricultural products providing a diverse scope of potential materials for incorporation into starch-based films. Maniglia et al. (2019) made the interesting observation that starch extracted from babassu mesocarp naturally contained phenolic compounds and that the antioxidant capacities depend on the extraction method. They also determined that the addition of plasticizers had a slightly detrimental impact on antioxidant capacity although all plasticizers produced nearly identical antioxidant capacities via DPPH assay. Assay results showed 63% to 72% antioxidant capacity.

Another source of phenolic compounds that has been incorporated into films is clove oil, which contains predominantly eugenol. Films of starch derived from job's tears seeds with less than 1% clove bud essential oil were found to have antioxidant capacities up to 72% by DPPH assay and 98.5% by ABTS assay (Kang & Song, 2019). Other work with clove oil showed less promising results (Li, Zheng et al., 2019) when TiO_2 and 12 wt% clove oil (over an order of magnitude higher than in the aforementioned study) were incorporated into starch films, the highest antioxidant capacity of only 52.2%. In the same vein, eugenol was incorporated into films through direct addition to FFS or by fist encapsulating eugenol in a variety of systems (Talon, Vargas, Chiralt, &

Gonzalez-Martinez, 2019). All encapsulation systems outperformed neat eugenol with the best results coming from an encapsulation strategy employing oleic acid, lecithin, and maltodextrin, from which an EC_{50} of as low as 34 (mg film/mg DPPH) was achieved. Although good results were obtained utilizing clove oil, further work utilizing this additive should be headed with caution as a recent sensory analysis report concluded that eugenol-containing films present an unpleasant aroma, potentially limiting the scope of their use (Osorio et al., 2019). Camu-camu extracts were prepared by an ethanolic extraction and incorporated into teff starch films with good results. At just 0.6% (w/v), antioxidant capacities of 72% and 87% were achieved by DPPH and ABTS assays, respectively and with 1.0% (w/v), capacities of 87% and 100% were achieved.

Plant extracts frequently contain phenolics with other antioxidant compounds. Rosehip extract (RHE), which contains various phenolics as well as carotenoids and ascorbic acid, was also successfully incorporated into starch films although the amount incorporated was quite large. At the highest concentration incorporated of 33 wt%, antioxidant capacities were 80 and 97 for DPPH and ABTS assays, respectively. Knapp et al. incorporated yerba mate extracts containing chlorophylls, carotenoids, and phenolic compounds with decent results. At the highest concentration of 20 wt%, an antioxidant capacity of 40% was achieved.

Optimally, antioxidant phenolics as film additives would be obtained from waste products produced by agriculture. Rice straws, which are typically burned or used as animal feed post rice harvest, were treated by multiple solvent systems to determine that water provided the largest extraction of phenolics (Menzel et al., 2019). These extracts were successfully incorporated into potato starch films providing EC_{50} values of 72 (g film/g DPPH) at 10 wt% incorporation. Other work by the same group optimized the extraction of phenolics from sunflower hulls, another waste product. Utilizing either aqueous methanolic or ethanolic solutions (80%), phenolics could be effectively extracted. A similar EC_{50} value of 71 was obtained when only 6 wt% of the extract was incorporated into a potato starch film (Menzel et al., 2019).

Polyphenols can also be incorporated into films as antioxidant additives, reducing radical species in an analogous mechanism to phenolic compounds. Polyphenol-containing GTE was incorporated into potato starch films (5 wt%) and dissolved in water as well as hydrophilic and hydrophobic food simulants, 10% aq. ethanol and 95% ethanol, for antioxidant capacity analysis by DPPH assay (Nisa et al., 2015). GTE showed the best performance of 52% in the hydrophilic food simulant followed closely by 48% in the hydrophobic food stimulant indicating good performance under a range of conditions. As a standard of comparison, antioxidant BHT (butylated hydroxytoluene, a common food additive) was also incorporated into potato starch films and was found to have a similar performance in hydrophobic food simulants but a much weaker activity in hydrophilic food simulants of 26%. Both additives performed poorly in water giving values of 13% and 7.5% for GTE and BHT, respectively. Baek and Song (2019) incorporated curcumin into millet starch films and found good results. At just 2 wt% incorporation of curcumin, values of 30% and 97% were recorded for DPPH and ABTS assays, respectively. Polyphenol containing rosemary oil was incorporated at varying concentrations into cassava starch films. DPPH assays were conducted by making solutions with hydrophilic, hydrophobic, and acidic food simulants. In all cases, antioxidant activity was significantly higher in the acidic food simulants than either other food simulants. Interestingly, antioxidant performance was diminished when more than 5 wt% of rosemary extract was incorporated into the film.

Work incorporating blackberry pulp into films was performed by Nogueira et al. through several methods (Nogueira et al., 2019; Nogueira, Fakhouri, & Augustus de Oliveira, 2019; Nogueira, Fakhouri, Velasco, & de Oliveira, 2019). Blackberry pulp was either used as pulp, freeze-dried, or spray-dried. After obtaining freeze-dried or spray-dried powders, they were either incorporated directly into FFS or sprinkled on top of the solutions after casting. Sprinkling the powder on top of the film led to significantly higher antioxidant capacities, likely due to more effective diffusion into the solution. Optimal results were obtained by spray drying the blackberry pulp and then sprinkling it on top of the cast solution at 30 wt%.

6.3 | Application-based analysis

The oxidation of a eugenol system that was previously described was analyzed for its ability to prevent oxidation of sunflower oil over 18 days by measurement of the POV (Talon et al., 2019). The films containing eugenol encapsulated by oleic acid, lecithin, and maltodextrin were selected for analysis as a result of its performance in the preliminary tests. It was compared to a starch film with no additives, PE, and a sample with no covering. After just 4 days, there were two groups that emerged with different values. The starch film and the starch film with encapsulated eugenol were virtually unchanged, whereas both the open control and PE coverings led to significantly higher POVs. After 11 days, the sample covered with the starch film had oxidized enough to be statistically different from the initial value. After 18 days, the sample covered with the encapsulated eugenol impregnated film was still statistically indistinguishable from the POV on the first day. A similar study was conducted with films containing lycopene or lycopene nanocapsules where references were LDPE, uncovered, and a closed pot. After just 3 days, the POV for all the references had increased significantly. The closed pot performed the best of all the references but after just 3 days had produced a POV larger than the nanoencapsulated lycopene starch film did after 30 days.

Films with RHE (1 wt%) were analyzed for their potential to prevent oxidation in chicken breast (Go & Song, 2019). POV revealed no significant change in the POV of the film containing RHE after 6 days, whereas the control film not containing RHE produced a POV more than twice as high after just 3 days. TBARS revealed that while some oxidation did occur to the sample wrapped in a film containing RHE, the TBARS value remained about half of the film not containing RHE over the 9-day period.

Films containing GTE or BHT were analyzed for their ability to prevent oxidation of chicken breast samples (Nisa et al., 2015). BHT doped films were more effective at preventing oxidation than all other films. GTE films were more effective at preventing oxidation at room temperature but proved less effective at preventing oxidation under refrigeration conditions than undoped control films by TBARS analysis. Interestingly though, upon analysis of metmyoglobin, a byproduct of myoglobin oxidation, films doped with GTE outperformed all other films so much so that meat stored at room temperature wrapped in GTE doped films produced lower values than the meat wrapped in BHT doped or undoped films stored under refrigeration conditions.

Oxidation of ground beef was prevented by wrapping it in films containing various systems involving Zataria multiflora essential oil (ZMEO) and cinnamaldehyde (Amiri, Aminzare, Azar, & Mehrasbi, 2019). The best results were obtained with films containing nano emulsions of ZMEO in terms of both TBARS and POV analysis. Compared to the control film not containing any additives, the POV after 20 days was more than 50% less and the TBARS value was approximately 40% less.

7 | ANTIBACTERIAL/ANTIFUNGAL FILMS

Due to the length of time between harvest and consumption of food in modern society, antibacterial films are advantageous to prevent food spoilage, especially in highly sensitive foods like grape tomatoes, berries, and meat. One challenge in comparing antibacterial films is the reliance on qualitative agar disc diffusion assay for reporting antibacterial efficacy. A more useful yet infrequent method of reporting antibacterial efficacy is through the calculation of inhibition zones, which quantitatively expresses the degree of inhibition a certain additive provides (Acosta et al., 2016; Arezoo et al., 2020; Li, Zheng et al., 2019). Like antioxidant additives, care should be taken to address the diffusion of additives through the polymer matrix to various food stimulants to optimize efficacy/cost analysis (Ke et al., 2019).

Some of the most antibacterial films published to date incorporate Ag NPs though the toxicity of Ag NPs could preclude their use in packaging in which the films are in direct contact with food. Additionally, the addition of Ag NPs tends to reduce film transparency, further limiting their scope of use in food packaging. In one study, Ag NPs were used in varying concentrations from 14.3 to 143 ppm, a range thought to be below the threshold for cytotoxicity (Ortega, Giannuzzi, Arce, & Garcia, 2017). These NPs were synthesized *in situ* using a green synthesis in which maltose acted as the reductant and starch as the end-capping functionality to control Ag NP size. The antibacterial efficacy of these films was tested by agar disc diffusion method with *Salmonella spp.*, *E. coli ATCC*, *Penicillium spp.*, *and S. aureus*. At concentrations as low as 28.6 ppm, inhibition of the growth of *Salmonella spp.* was observed. At 71.5 ppm, films could additionally inhibit the growth of *E. coli ATCC*. Unsurprisingly, the most effective film was the film containing 143 ppm Ag NPs, which could additionally inhibit the growth of *Penicillium spp.* and slightly inhibit the growth of *S. aureus*. Quantitative analysis of the antimicrobial efficacy of the film containing 143 ppm Ag NPs was done by using it to package a soft cheese. It was found that the Ag NP containing film had a shelf life (as defined by the production of 10^6 CFU/g) 50% longer than that of the control film. Another study by the same group analyzed the impact of varying FFS concentrations (1, 3, and 5) and incorporating 143 ppm Ag NPs (Ortega et al., 2019). The film prepared from an FFS of 1 wt% potato starch was the most bacterially inhibitive with inhibition decreasing as film thickness increased due to poor diffusion of the active species revealing an inverse relationship between mechanical properties and antibacterial efficacy. The film prepared from an FFS of 1 wt% starch showed contact inhibition for *E. coli ATCC* and *Salmonella spp.*, while a 2.0 mm inhibition halo was observed *for S. aureus ATCC* and *Penicillium spp.* showed no growth for this film. The analogous control film containing no Ag NPs saw no inhibition for *E. coli ATCC*, *Salmonella spp.*, or *S. aureus ATCC*, and growth was observed for *Penicillium spp.* Abreu et al. (2015) prepared films with quaternary ammonium modified MMT, called Cloisite®, films with Ag NP, and films that contained both Cloisite and Ag NP. Cloisite® was selected due to the known efficacy of quaternary ammonium functionalities inhibiting bacterial growth paired with the reported enhancements in film properties upon the incorporation of MMT to starch films. The

Cloisite®-only film could inhibit the growth of *S. aureus* and *E. coli*, while the addition of Ag NP increased the film's efficacy to additionally inhibit the growth of yeast, *C. albicans*.

Essential oils are growing in popularity as film additives due to their antibacterial efficacy, biological compatibility, and generally pleasant sensory properties. The antifungal properties of cinnamon, clove, and oregano EOs were determined in starch/gelatin blended films (Acosta et al., 2016). Oregano EO was found to be the least effective film for the two bacterial species tested, *Fusarium oxysporuum* (FOG) and *Colletotrichum aloeosporiodes* (CG). The cinnamon EO containing film was the most effective at inhibiting the growth of FOG, while the film containing clove EO was the most effective at inhibiting the growth of CG after 72 hr. As mentioned previously, eugenol is the primary constituent of clove oil and as such, has also been incorporated independently into films (Osorio et al., 2019). In films prepared with 1 to 5 wt% eugenol, antibacterial efficacy was found to increase with increasing eugenol concentration (Cheng et al., 2019). The film containing 5 wt% eugenol inhibited bacterial growth of *E. coli, S. aureus*, and *L. monocytogenes*, 88%, 71%, and 65% better than undoped films, respectively. For all concentrations, eugenol doped films showed superior antibacterial activity against *E. coli* compared to the other strains. This film containing 3 wt% of eugenol was also found to preserve the shelf life of pork by at least 50%.

TiO_2 is another common additive that contributes to antibacterial activity, while maintaining film color though film transparency is frequently reduced. Arezoo et al. (2020) incorporated cinnamon essential oil (CEO) and nano-TiO_2 into sago starch films at various concentrations to determine their antibacterial efficacy against *S. aureus, E. coli, and S. typhi*. All the tested films were most effective at inhibiting growth of *S. aureus* and least effective at inhibiting *S. typhi*. Inclusion of CEO alone improved inhibition relative to the neat starch film but incorporation of 3 or 5 wt% TiO_2 dramatically increased the inhibition of all tested strains. Similarly, Li, Zheng et al. (2019) prepared films from various concentrations of nano-TiO2 (1, 3, 5, or 7 wt%) or 3 wt% nano-TiO_2 with 3, 6, 9, or 12 wt% clove oil. The films showed better antibacterial inhibition for *S. aureus* compared to *E. coli*. With increasing incorporation of nano-TiO_2, films showed better inhibition. The addition of clove oil showed increased inhibition although less significant than the increase endowed by nano-TiO_2.

Chitosan nanoparticles (CNPs) were incorporated into tapioca starch films at 5, 10, 15, and 20 wt% concentrations (Shapi'i, Othman, Nordin, Kadir Basha, & Nazli Naim, 2020). By disc diffusion assay, it was determined that increasing concentration of CNP led to higher antibacterial activity. Gram-positive bacteria (*B. cereus* and *B. aureus*) could be inhibited at 15 and 20 wt% CNP, while inhibition was not observed for gram-negative bacteria (*E. coli* and *S. typhi*) for any of the produced films. The 15 wt% CNP film was also tested for bacterial inhibition on cherry tomatoes. After 10 days of cold storage, a neat starch film showed a 5.3 times lower bacterial growth than uncovered tomatoes, whereas the film containing CNP showed a 16 times lower bacterial growth than uncovered tomatoes.

In the process of trying to optimize the mechanical properties of starch films, mild, wide-spectrum antibacterial properties were acquired when researchers crosslinked films with oxidized sucrose and added CNFs to some film formulations to improve mechanical properties (Balakrishnan et al., 2019). Compared to the control film, all films containing oxidized sucrose or oxidized sucrose and CNFs had ~40% decreased minimum inhibitory concentrations (MICs) although all film formulations had quite similar MICs to one another. The film with 3 wt% oxidized sucrose and 5 wt% of CNF was found to have the best mechanical and barrier property improvements while decreasing the MICs for *E. coli*, *S. typhimurium*, *St. aureus*, and *B. cereus* by 40%, 40%, 45%, and 40%, respectively, compared to undoped films. Wu et al. (2019) prepared films from potato starch and chitosan (8:3 ratio by weight, respectively) by CA crosslinking. Due to the presence of chitosan, films without CA were found to inhibit the growth of *E. coli* and *S. aureus*. Increasing CA content from 5 to 20 wt% showed only slight improvement in the film antimicrobial properties. Interestingly, antibacterial activity was similar for gram-positive and negative bacteria for all films.

8 | SENSING FILMS

Research in the area of "smart films" for the detection of food spoilage has recently gained a bit of traction. These films are prepared with an additive that exhibits a physical change upon interaction with an analyte or with a change in pH, allowing for the visual detection of food spoilage as a quality control measure. These indicators should be edible so as not to endanger the food it is in contact with. Due to the cost, limited scalability, and poor mechanical/barrier properties of these films, they may find use in conjunction with another primary packaging that provides the requisite mechanical and barrier function.

Anthocyanins and polyphenols have found use in these applications due to their biocompatibility and their pH-responsive color-changing properties. These compounds are also capable of hydrogen bonding so that they may be stabilized within the network, thereby maintaining mechanical integrity as well as preventing leaching into

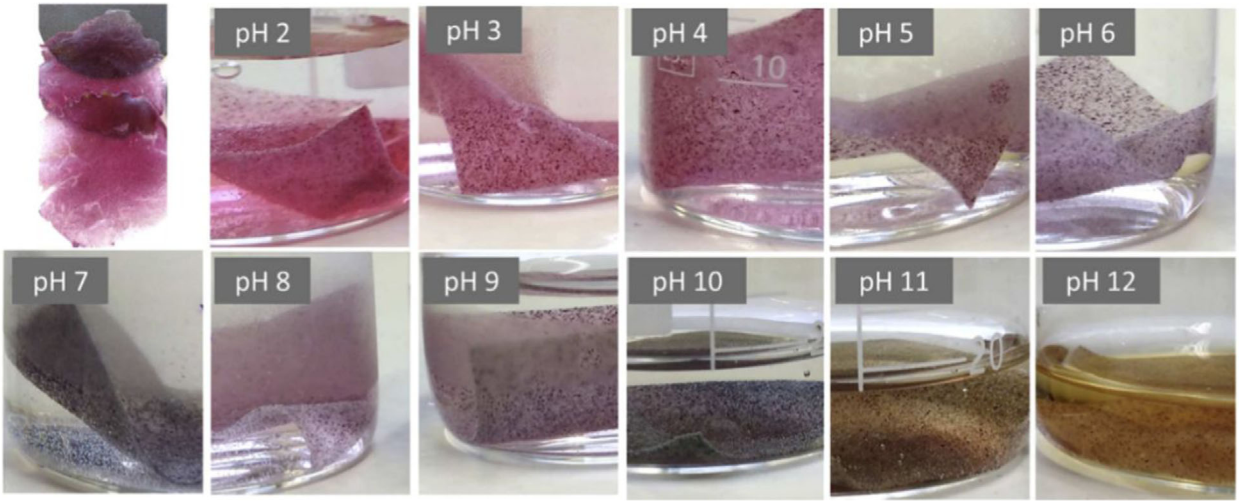


FIGURE 7 Sensing film prepared with blueberry residue powder in air and buffer solutions of pH = 2 to 12. Reprinted with permission from Andretta et al. (2019)

the food product. One important consideration when identifying potential anthocyanins or polyphenols for incorporation into smart films is that they need not be competitive with food resources due to concerns about food scarcity as well as being economically prohibitive.

Blueberry residue powder contains anthocyanins and is considered to be a waste product from the production of blueberry juice. Blueberry residue powder of two different particle sizes—one with large particle size and one with small particle size (149 µm cutoff) was prepared and incorporated into starch-based films (Luchese, Abdalla et al., 2018). Although the pH-responsive changes in color were only subtle, this work inspired further research in which similarly formulated films were prepared by thermocompression (Andretta et al., 2019). These films showed excellent pH sensitivity and could reveal pH changes from 2 to 12 with 1 pH unit sensitivity (Figure 7). Due to the hydrophilicity of the blueberry residue, barrier properties were significantly worsened with an OP ~7 orders of magnitude larger than the control film.

Blackberry pulp was also tested for its pH indicating ability as it also contains anthocyanins; however, unlike blueberry residue powder, the blackberry pulp used in this study was made from whole blackberries, directly competing with food sources and providing economic obstacles to scalability (Nogueira et al., 2019). The color changes were slight across the pH range of 3 to 10 but could be accurately quantified with color parameters for the film which incorporated 20 wt % blackberry pulp.

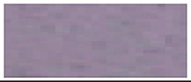
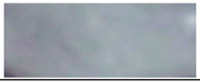
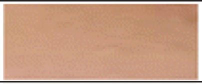
Starch was treated with TMP and films were prepared with CMC and purple sweet potato anthocyanins (Jiang et al., 2020). The films were found to be colorimetrically pH-responsive with significant differences between color parameters over the range 2 to 12. The films were stable for 20 days of storage and were found to be sensitive to total volatile basic nitrogen (TVB-N), a by-product of the decomposition of fish and pork that also produces a local alkaline pH change.

Yun et al. (2019) utilized anthocyanin containing CBE, an edible red fruit, to incorporate into starch films at varying concentrations. At the lowest concentration of 1 wt%, the film was able to clearly resolve differences in volatile nitrogen compounds indicating food spoilage by measurement of color parameters although the differences were harder to resolve with the naked eye. Additionally, films placed in the headspace of pork samples aged at room temperature showed changes in color that correlated with the production of TVB-N (Table 5).

Cassava starch films were prepared and anthocyanin containing Lycium ruthenicum fruit extracts (1, 2, and 4 wt%) were incorporated (Qin et al., 2019). All films exhibited strong color changes over the pH range of 2 to 13 with the 4 wt% film allowing for the easiest distinction between pH units and these films were similarly able to show changes in TVB-N when placed in the headspace of pork samples although the resolution during the early stages of decomposition was less impressive than the films containing CBE extracts.

Green tea or basil extracts were incorporated into films as they contain polyphenols, which may act as antioxidants as well as containing chlorophyll and carotenoids, which can facilitate the indication of pH changes (Medina-Jaramillo, Ochoa-Yepes, Bernal, & Fama, 2017). The films exhibited a slight color difference at low (3) compared to high (11) pH but no exhaustive pH study was performed. Because the color differences were only slight, it is not likely that these films would be useful for detecting the slight pH changes that typically accompany food spoilage

TABLE 5 The measured change in total volatile basic nitrogen (TVB-N) developed in the headspace of a pork sample and the resultant change on the film appearance

Time (h)	TVB-N levels (mg/100 g)	Color response of starch–BBE I film
0	8.35 ± 0.61f	
8	8.77 ± 0.78f	
16	10.35 ± 0.21e	
24	17.16 ± 1.15d	
32	22.10 ± 0.70c	
40	28.01 ± 1.59b	
48	34.28 ± 1.17a	

Note: Reprinted from Yun et al. (2019) under a Creative Commons Attribution license (https://creativecommons.org/licenses/by/4.0/).

(Yun et al., 2019). The films additionally exhibited fast degradation, degrading to near completion in 2 weeks' time. More work should be done on this system to determine its efficacy to be implemented in food packaging systems.

9 | CONCLUSIONS

Starch films have shown recent promise in supplanting petroleum-based polymers for use as food packaging materials given the drastic improvements in mechanical and barrier properties revealed by the large body of recent work on this subject. Although films produced through FFS do not provide a drop-in replacement for currently implemented packaging materials, the research presented here shows potential directions for improving film formulations while considering consumer safety and sustainability. Many procedural modifications and additives have proved successful in producing films with properties on par to traditional packaging materials while remaining biodegradable or compostable. Previously held notions that amylose/amylopectin ratios alone are responsible for property outcomes have been disproven repeatedly and the plethora of nuances in the preparation of starch films are gradually being teased out. Emphasis must continue be placed on the sensitivity of the conflicting variables and researchers must remain diligent in recording and reporting all aspects of starch cultivation and extraction and film formulations and design.

Simple processing treatments, such as germination of grains preharvest or acid hydrolysis postharvest, have shown to be effective methods for improving starch film properties and should be continued to be explored as effective, scalable, and inexpensive methods for improving film properties. Various methods of crosslinking have also proven to be effective in increasing the strength and oftentimes the barrier properties of starch films while frequently showing synergistic improvements when paired with other modification methods. Good compatibility of starch or cellulose NPs allows for the production of a nanoreinforced composite material while maintaining good dispersivity resulting in the improvement of film strength and barrier properties. The addition of hydrophobic antioxidant species to films can be done without compromising mechanical properties and while improving barrier properties so long as they are well dispersed throughout the film matrix, requiring effective hydrogen-bonding with starch or by encapsulation in a more hydrophilic species. Chitosan has proven to be a reasonable additive for enhancing strength characteristics as well as acting as a bio-derived emulsifier for hydrophobic additives, thereby improving barrier properties. Although there has been a plethora of work showing the benefits to mechanical properties of the incorporation of metal NPs (principally titania and silver) into film formulations, there should be a thorough cost analysis as well as more in-depth analysis on the potential safety concerns of this strategy. Although there are undeniable benefits to the mechanical and barrier properties upon the incorporation of MMT clays into film formulations, the natural variability of chemical composition should be considered before this additive could be implemented in a commercialized product.

While inherently unscalable, systematically altering FFS either chemically or mechanically has proved an effective way to positively impact film mechanical properties. Most notably, simple ultrasonication of FFS proved effective at producing more compact films with improved mechanical properties providing a simple, low-cost technique that could be implemented with many scalable technologies as a pretreatment method before introduction into a more complex resin formulation.

Central composite design paired with predictive tools like surface optimization has proved useful in developing optimal formulas for certain applications, while PCA has shown useful in determining the parameters responsible for differentiation in films with differing mechanical and barrier properties. Numerous recent works have additionally focused on making functional films, increasing their appeal and ability to supplant petroleum-derived plastics for food packaging applications.

Numerous additives have shown great promise toward developing antioxidant films; however, there remain two critical concerns for researchers in this field. First, differences in assessing and reporting antioxidant capacity should be reduced to help standardize results. Second, when assessing antioxidant capacity, numerous realistic considerations must be taken into account, such as the use of "food simulant" solvents rather than strictly utilizing water as well as assessing diffusion of antioxidant species through the film matrix so that they may act as sacrificial radical scavengers. Natural phenolic compounds, such as polyphenols and anthocyanins, especially those extracted from waste streams like sunflower hull or rice straw extracts, show great potential to be utilized on a commercial scale. Research on the extraction of polyphenols from lignocellulosic waste should continue to be explored. Antibacterial films will remain a worthwhile pursuit; however, given the potential for cytotoxicity of metal-based additives and the high cost and low potential for scalability of implementing plant essential oils, the most promising routes for developing antibacterial films remain through the addition of chitosan or cellulose NPs. These additives should continue to be explored to parse out the effects of characteristics, such as polymer molecular weight, particle size, and crystallinity. The field of sensing films has quite a bit of potential although to date, it is underdeveloped and would benefit from the implementation of more economically and environmentally friendly alternatives compared to the current methods that directly compete with food resources. This fundamental research may, however, provide insight into the types of compounds that can act as good food spoilage indicators.

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AUTHOR CONTRIBUTIONS

M. K. Lauer gathered and interpreted background literature and led the writing process. R. C. Smith provided funding and contributed to the writing process.

CONFLICTS OF INTEREST

There are none to declare.

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