Green Chemistry

CRITICAL REVIEW

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2022, **24**, 8606

A review of biodegradable thermoplastic starches, their blends and composites: recent developments and opportunities for single-use plastic packaging alternatives

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Received 8th June 2022,
Accepted 19th August 2022

DOI: 10.1039/d2gc02169b

rsc.li/greenchem

Single-use plastic packaging has become an inevitable part of every aspect of human life. In fact, the increase in the consumption of petroleum-based single-use plastics has resulted in the accumulation of municipal solid wastes which are a leading source of plastic pollution worldwide. Biobased materials are a virtuous replacement for single-use petroleum-based packaging products, when recycling is difficult or not practical, to fulfil environmental and economic demands. Starch is an abundant biobased polymeric material that is sustainable and biodegradable. However, the inefficiency of starch in processability due to the existence of hydrogen bonding interactions and intermolecular forces impedes its applications. An effective solution is plasticization of starch in the presence of heat and shear, and is termed plasticized starch (PS). Although different sources may refer to plasticized starch (PS) as thermoplastic starch (TPS), the plasticization process does not make the starch a thermoplastic material until it is blended with toughened polymer, making the nomenclature counterintuitive. TPS is procured through the process of plasticization of starch with water and plasticizers followed by blending with tougher polymers/biopolymers. This could enhance the flexibility and processability of the blend materials, which are an effective replacement for petroleum-based single-use plastic packaging. In this review the main focus is on analysing the effect of multiple plasticizers and compatibility enhancers such as compatibilizers, coupling agents and essential oils in TPS blends, and starch-based composites' preparation and their effective use in single-use packaging applications. Global production and market analysis of thermoplastic starches and their challenges in real-life packaging applications are also discussed.

1. Introduction

Plastic is an inevitable and pervasive material for packaging. Global plastic production per year is estimated to be above 480 million metric tons, and the packaging sector embraces 40% of the total production.[1] Packaging improves safety, health, and convenience for the manufacturer and consumer during the transportation and storage of a commodity. The diverse uses of packaging materials include consumer goods, food, beverages, cosmetics, and pharmaceuticals.[2] Worldwide marketability and food production trends (fresh, half cooked, fast foods) have changed human perception of food. In their fast-paced life, insufficient time of human demanded more fast-food items, which has driven a novel evolution towards innovative and efficient packaging techniques for food packaging.[3] Thus the polymer food packaging sector dominates the packaging market as it enhances food quality, safety, and shelf-life, and minimizes food waste.

A predominant proportion of packaging materials is developed from fossil hydrocarbons, specifically single-use plastics that account for more than 50% of the packaging sector. Such single-use plastics have a very short life time, ranging from a few hours to weeks, thus creating an alarming environmental waste concern which appears daily in headline news. It is estimated that globally 5 trillion plastic bags are used each year, and recently the COVID-19 pandemic has impacted greatly the rise of production of single-use plastics, especially in take-away packaging from restaurants.[4,5] Polyethylene, polypropylene, polyesters, polystyrene, polyvinyl chloride, and polyamides are the major fossil hydrocarbons used in the single-use plastics packaging industries, since they are cheap and accessible with good mechanical, barrier, and thermal properties.[6] Most of these are non-degradable and non-recyclable, becoming a

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threat to the environment as they accumulate on land and in the oceans after use.[6,7] This has become a great threat affecting the global ecosystem, as it disturbs the life of marine and terrestrial species and leads to the creation of microplastics (<5 mm in size), which have been found across the world's oceans and as far as Mount Everest's snow, and even in human blood. It is believed that a single plastic bag could take up to 1000 years to disintegrate completely.[8] Thus, most countries have taken action against the use of single-use plastics of less than 50 microns, and a few countries have put on a high tax rate on plastic bags.[9,10] Additionally, growing concern about human health and environmental aspects has driven the focus more towards eco-friendly, biodegradable, and sustainable packaging materials.[11] Thus, the development of biobased or biodegradable single-use packaging materials is needed as a replacement for fossil fuel-based materials.

Globally, the production of biobased polymers is 1% of the total polymer production.[12] However, the increasing need for sustainable materials has developed a dynamic rise in bioplastics production in the upcoming years. The study conducted by "European Bioplastics" in 2021 showed a significant rise in the global production capacity of bioplastics from 2021 to 2022, and this is expected to rise to around 7.59 million tonnes (MT) in 2026.[13] Fig. 1(a) shows the production capacity of bioplastics by region, and Fig. 1(b) represents the expected growth of bioplastics production in the period 2020–2026. Furthermore, the ability of bioplastics to replace conventional plastics has diversified the production of bioplastics such as poly(butylene adipate terephthalate) (PBAT), poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), bio polypropylene and bio polyethylene *etc*. Fig. 2 represents the distribution of global bioplastics production capacities from 2020 to 2026. According to the material type, PBAT is expected to have a growth of 30% and starch blends are expected to decrease by 5.2%.[13] The decrease in starch blends may be due to the inability to achieve the desired material properties for the packaging sector. This indicates a requirement for further research and development of starch-based blend materials with enhanced properties for packaging and other sectors.

Biobased polymers are the most promising materials that are partially or completely biodegradable and synthesized from plants or microorganisms through metabolic or biochemical engineering processes.[14] In addition, according to their origin, biobased polymers are classified into 3 types; these are (1) extracted from biomass: (I) Polysaccharides (starch,[15] cellulose,[16] chitosan,[17] carrageenan,[18] pectin,[19] and alginate[20]), (II) Proteins (gelatin,[21] collagen,[22] zein,[23] and keratin[22]) and (III) Lipids[22]; (2) synthesized from biobased

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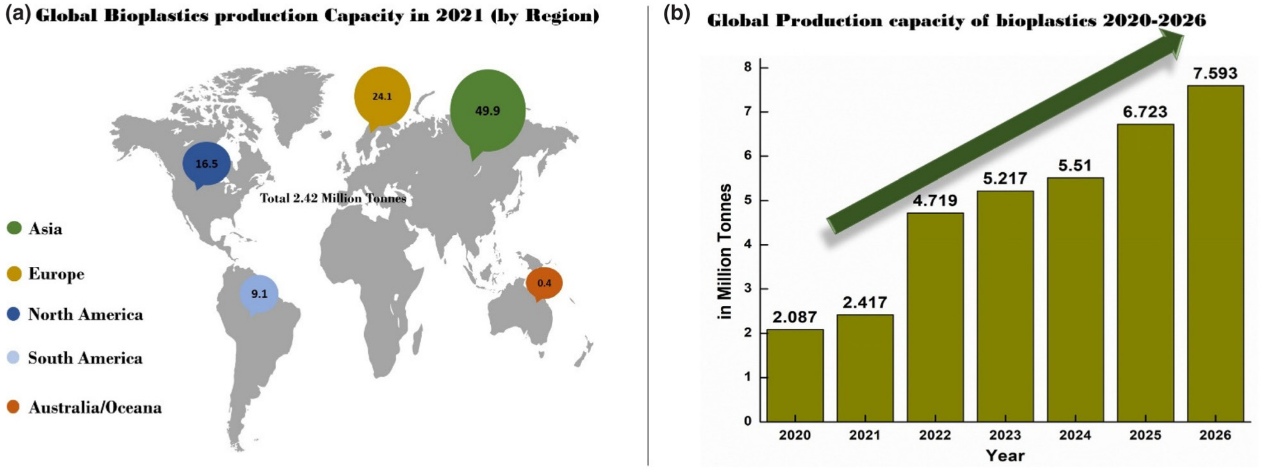

Fig. 1 Dynamic rise in production of bioplastics from 2020 to 2026. (a) Global bioplastic production in 2021 by region, (b) global production capacity of bioplastics 2020–2026 (redrawn from data;[13] accessed the website "European Bioplastics" in January 2022).

monomers (PLA[24] and polyesters); and (3) attained from microorganisms (PHAs[25] and bacterial cellulose).[26] All these materials are abundant, renewable, and ecological. Therefore, biobased packaging materials from these biopolymers can be a sustainable substitute for fossil fuel-based polymers and a solution to the associated waste disposal issues. Notably, polysaccharides are the dominant materials in the biobased packaging market.

Polysaccharides are a widely accepted biobased packaging material for films and coatings, as they provide a good barrier against penetrants like oxygen and carbon dioxide.[27] These materials with varied stereochemistry exhibit a good gas

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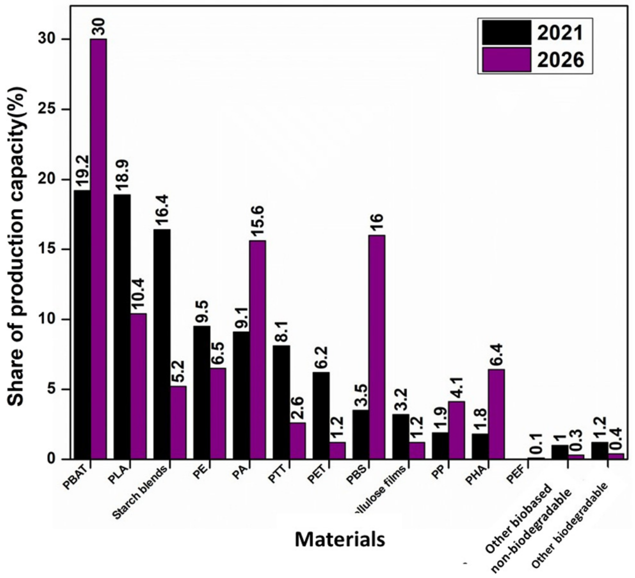


Fig. 2 Distribution of global bioplastics production capacities in 2021 and 2026 according to the material type (redrawn from data;[13] accessed the website "European Bioplastics" in January 2022).

barrier that improves the shelf life of the product by inhibiting the production of anaerobic regions. The film produced from these materials shows functional features; for example, it decelerates the loss of aroma compounds throughout storage time and prevents the penetration of solvent molecules into the packaged content which affect the quality of the products or may even result in toxicity, especially in food packaging.[28] In addition, these films provide a better barrier against fats and oils.[29]

Starch and cellulose are the most abundant polysaccharides available in nature and are widely used for the production of biodegradable polymers for functional applications. They are classified as storage and structural polysaccharides according to their biological functions.[30] Both polysaccharides comprise a glucopyranose unit of different glycosidic linkages, such as α-1,4-glycosidic linkages and β-1,4-glycosidic linkages for starch and cellulose, respectively.[31] Furthermore, starch consists mainly of two types of bio macromolecular components, amylose and amylopectin, whereas cellulose is a linear polysaccharide that depends on the type and treatment of the raw materials, such as wood.[32] Cellulosic polymeric materials are mostly available as bacterial cellulose, microcrystalline cellulose, cellulose nanocrystals or nano whiskers.[33,34] They have good film-forming characteristics, as they are non-toxic and transparent film materials with exceptional mechanical, thermal and barrier properties, specifically for oxygen and oil barriers.[35–37] Modified cellulose and different cellulose derivatives such as cellulose acetate and cellulose esters are predominant materials used in industry for molding, extrusion and film applications.[31] However, their poor solubility and indigestibility have hampered their commercialization in the field of edible films and coatings.[38] Comparing cellulose and other polysaccharides with starch, the diversity in sources of starch with different molecular weights and functional properties, such as the improved processability of starch after plasticization and miscibility with other biopolymers, is important for its market in the biodegradable polymer industries.[39] However, starch has a few disadvantages such as low water resistance, weak mechanical properties and the unstable properties of starch-based plastics due to the diversity in starch molecular structure and properties.[40,41] However, among polysaccharides, starch has been considered as a promising material for biobased packaging owing to its low cost, high film-forming ability, oxygen barrier properties, water solubility and thermo-plasticity.[42,43]

Starch is a polysaccharide obtained from plants that consists of glucan polymers such as amylose and amylopectin.[44] These glucan polymers are found in granular form in different dimensions with systemized semi-crystalline and amorphous homocentric layers.[40] Depending on the starch source, there are disparities in chemical composition and structure which affect the crystallinity and texture of these polymeric materials.[45] However, the higher rate of crystallinity, strong intermolecular forces like hydrogen bonding, and the presence of disordered granules reduce the mechanical properties and reduce the processability of starch as a thermoplastic polymer.[40] Thus, to overcome these issues, starch is plasticized with different plasticizers such as glycerol,[46–49] sorbitol,[50–54] formamide,[55–57] urea,[58,59] citric acid,[60,61] glycerine,[62] polyethylene glycol,[63] amino acids[64] and water,[65] and the resultant destructurized material is termed plasticized starch (PS). Plasticization of starch disrupts the crystallinity of starch material and promotes the processability of starch in the development of thermoplastic polymer.[66]

There are numerous review articles that discuss different biodegradable thermoplastic starch blends and composite systems. However, there are no recent reviews that specifically focus on the effect of different plasticizers in PS and plasticized starch/biodegradable polymer-based blend systems (TPS blends). This article specifically focusses on the effects of compatibility enhancers such as co-plasticizers, compatibilizers, coupling agents, additives, surfactants and epoxidized oils in different biodegradable polymer/PS blends (TPS blends) that improve the mechanical, thermal, surface wettability and barrier properties of the blends for single-use packaging applications. Functional property enhancement of starch by reinforcement with natural fibres/fillers or organic fillers in developing starch-based bio composites and bio nanocomposites is also discussed. In addition, challenges and real-life applications of starch and the global production market of TPS are presented.

2. Starch: chemistry, structure and property co-relationship

Starch is a biodegradable polymer obtained from diverse sources of botanical species including cereal grains (corn, wheat, barley and rice), grain legumes (pea, lentil, chickpea and bean), and root tubers (cassava, taro, *Canna edulis* and potatoes). It is a polysaccharide polymer synthesized in plants and stored as an energy reserve.[67] The purest form of starch is found in white-colored granules without any odour or taste and is unable to dissolve in cold water. The granules of starch are usually found in the diameter range of 2 to 100 μm and with a density of 1.5 g cm^{-3}.[68] Starch comprises two carbohydrate polymers units: amylose segments and amylopectin segments. These carbohydrate polymers are glucose units that are connected through glycosidic linkages. Fig. 3 depicts the chemical structural formula of (a) the amylose moiety, and (b) the amylopectin moiety.

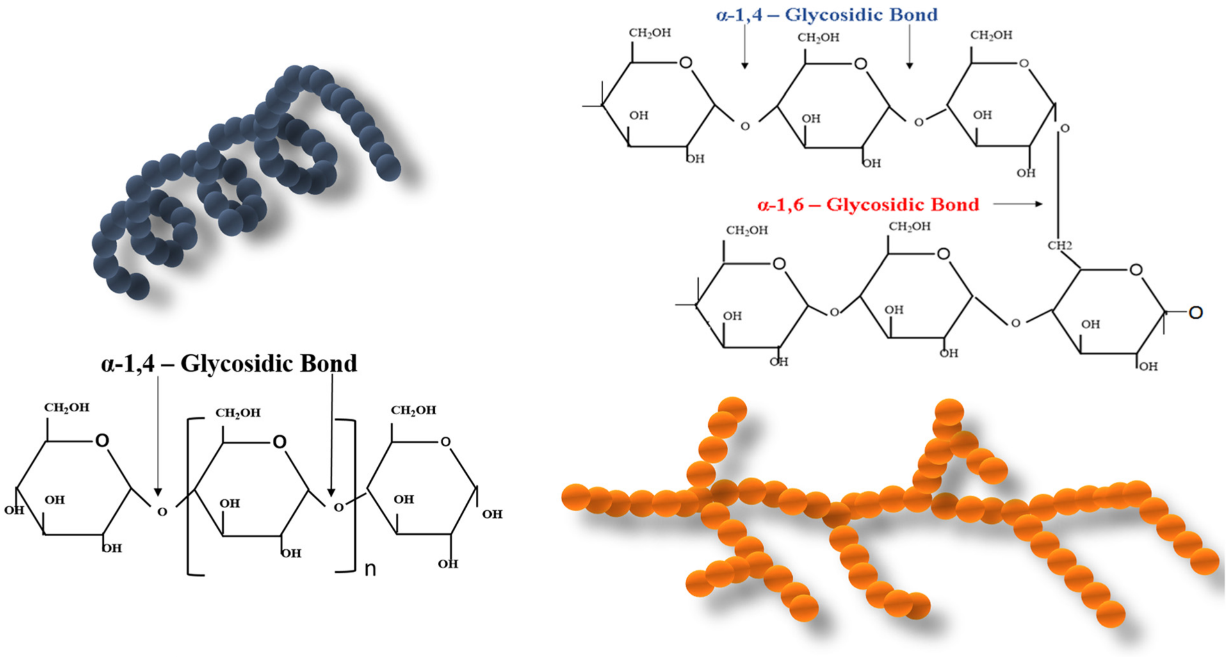
2.1 Biological origin of feedstock

Native starch can be acquired from various botanical sources, specifically from cereals (maize, wheat, rice, and barley) and root vegetables (cassava, tapioca, potato). Starch can also be obtained from agro-waste products and/or byproducts from food processing such as potato and pulse protein extraction. According to geographical and climatic conditions, different plant species produce starch with varying concentrations, molecular sizes and structures of amylose and amylopectin. For example, corn is cultivated in subtropical zones, rice in swamped areas, cassava in tropical regions, and wheat or sweet potatoes in moderately cold climates.[69] Furthermore, the abundance in availability of starch polymer from renewable resources makes it the second most abundant biodegradable polymer in the world after cellulosic polymers. It is predicted that the mass production of starch could reach about 156.3 MT in 2025, irrespective of its use in the alimentary sector or non-alimentary sector.[70] As per the global production rate of starch, corn starch is predominant with 80% of production, followed by other starch sources such as wheat, cassava, and tuber.[71] Conversely, in productivity rate, cassava starch can contribute about two to four times more starch than bean, yam, taro, and around ten times more starch than that of sweet potato.[72] And is estimated that the global starch market of 55.04 billion United States Dollar (USD) in 2020 is expected to rise to around 78 billion USD in the year 2026 with an annual Compound Annual Growth Rate (CAGR) of 5.63%.[73]

2.2 Structure–property relation

Native starch is a semi-crystalline granule made up of two principal types of glucan polymers: amylopectin and amylose. According to the starch source, the weight percentage of amylose components and amylopectin content varies from 20–25% and 75–80%, respectively. Amylose consists of α-(1 → 4)-D-glucopyranosyl moieties in linear or helical forms, whereas in the amylopectin macromolecule, α-(1 → 4)-D-glucopyranosyl moieties are linked with α-(1 → 6)-D-glucopyranosyl moieties at an approximate interval of 20 units, which forms a highly branched and high molecular weight macromolecule.[72]

The higher molecular weight of starch in comparison with synthetic polymers, which affects the molecular mobility of molecules, is one of the reasons that make the processing of starch more difficult by conventional methods. Typically, the average molecular weight of amylose molecules is found in the range of 0.2–2 million Da, and amylopectin is 100–400 million Da.[74] The branch chains of amylopectin components with helical structure contribute to the crystalline region of starch, and the degree of crystallinity of starch granules usually ranges



(a) Amylose

(b) Amylopectin

Fig. 3 The chemical structural formula of (a) amylose moiety, and (b) amylopectin moiety (molecular structures drawn by author using ChemDraw).

from 15–45%.[74] Additionally, in starch granules, amylose molecules are mostly found in the amorphous section, while individual amylose molecules are dispersed in both crystalline and amorphous phases of amylopectin clusters and in proximity with one another.[75]

Different studies have been conducted on starch granules to explore their molecular arrangement, internal structure, and physical and chemical properties.[76,77] The chemical and physical properties of starches from different botanical sources are shown in Table 1. In the starch granule, the quantity of amylose content has a significant effect in achieving desired physical, chemical and functional properties.[78] The starch source, degree of polymerization, lipids, proteins, and inorganic components are the significant aspects influencing the starch granule morphology and other functional properties.[69] The complex morphological structure of starch granules can be analyzed by various characterization techniques such as scanning electron microscopy (SEM), light microscopy, atomic force microscopy (AFM) and neutron and X-ray scattering (XRS).[79]

Crystallization of amylopectin forms polymorphic structures and has been studied through wide-angle X-ray diffraction (WXRD). From WXRD analysis, starch granules exhibit three main types of polymorphic pattern: A-type, B-type and C-type.[65] A- and B-type patterns are the common configurations found in cereals and tuber starches, respectively, while pattern C is the combination of A and B forms that is also produced naturally in pea or bean starches.[76]

According to the model proposed by Imberty *et al.*,[80] A-type pattern (Fig. 4A(a)) is packed with monoclinic unit cells and four H_2O molecules/unit cell, whereas in the B-type pattern (Fig. 4A(b)) water molecules are present in the center of a six double helix structure (a hexagonal unit with 36 H_2O molecules/unit cell). Although amylose is not a crystalline material it can recrystallize into another pattern called V-type by complexing with guest molecules like iodine, fatty acid, emulsifiers, or butanol.[81] The association of amylose with guest molecules forms a helical structure in antiparallel direction. The outer surface of the helical structure will be hydrophilic, and the inner part will be hydrophobic as it is accommodated with guest molecules, and this association is termed intrahelical association. The resultant crystal structure is termed V-hydrate (V_h) or V-anhydrous (V_a), where V_a is formed by shrinking V_h on losing water molecules from the unit cell. The crystalline morphologies of these starch polymorphs are usually analysed by XRD, Fourier transform infrared spectroscopy (FTIR) and electron diffraction techniques. The XDR patterns in Fig. 4B represent intensity peaks of A type starch, B-type starch and V_h and V_a-type amylose.[81] Fig. 4C depicts the cluster model of amylopectin classified according to the branch chain type and length.

3. Starch as a packaging material

For the past decades, starch has been gaining great prominence in the biodegradable polymer packaging industries owing to its film-forming ability, renewability, recyclability, and low cost.[42,100] Furthermore, starch is valued as the best alternative for petroleum-based single-use plastic and as a blending partner for expensive commercial biopolymers for attaining better processability, production cost, heat resistance and oxygen barrier properties.[101,102] Starch-based films and their coatings are optimal for food product packaging industries because of their transparency and good barrier properties (CO_2 and O_2 barrier).[103,104] Lourdin *et al.*[105] found that for unplasticized starch films, an increase in amylose concentration increased the elongation and tensile strength of the films. Furthermore, Forssell *et al.*[106] analysed the effect of relative humidity on the oxygen permeability of amylose and amylopectin films prepared by the solution casting technique. The prepared film showed an oxygen barrier similar to that of commercial ethylene-vinyl alcohol (EVOH) film at ambient humidity, and on increasing the humidity above 70% RH, amylose had a better oxygen barrier than amylopectin.

Corn starch that contains higher amylose content is used in the production of edible films and coatings in the food packaging sector.[102] In addition, pea and rice starch with high amylose content have shown better oxygen barriers than protein-based polymers.[107] However, the hydrophilic nature of

Table 1 Chemical and physical properties of starches from different botanical sources

Starch source	Corn	Cassava	Wheat	Rice	Tapioca	Potato	Sago	Ref.
Starch granule diameter (μm)	5.2	5–25	12.37	<20	6.97	7.14	6.9	82 and 83
Carbohydrates (%)	99.38	87.8	99.56	—	99.21	99.39	99.29	82
Amylose content (%)	28	16–21	18.10	22	17	27	30	82, 84 and 85
Amylopectin content (%)	78	76–84	72	77	75	74	77	82, 84 and 85
Protein (%)	0.27	1.35	0.20	0.33	0.11	4.54	0.19	82, 84, 86 and 87
Fat (%)	0.29	1.0	0.27	0.34	0.64	0.16	0.10	67, 82, 87 and 88
Ash content (%)	0.06	0.02	0.17	0.17	0.044	0.29	0.06	82, 84, 86 and 87
Density (g cm^{-3})	1.4	1.5	1.11	1.282	—	—	0.76	67 and 89–93
Moisture content (%)	10.45	8–10	9.70	11.24	8–12	15.6	13.9	67, 89, 91 and 93–96
Crystallinity (%)	43–48	13	36–39	38	35–38	23–53	23.09	43, 97 and 98
Crystalline type	A	B	A	A	C	B	C	68 and 78
Shape	Polyhedric	Semi-spherical	Polyhedric, lenticular	Polyhedric	—	Ellipsoidal	—	99

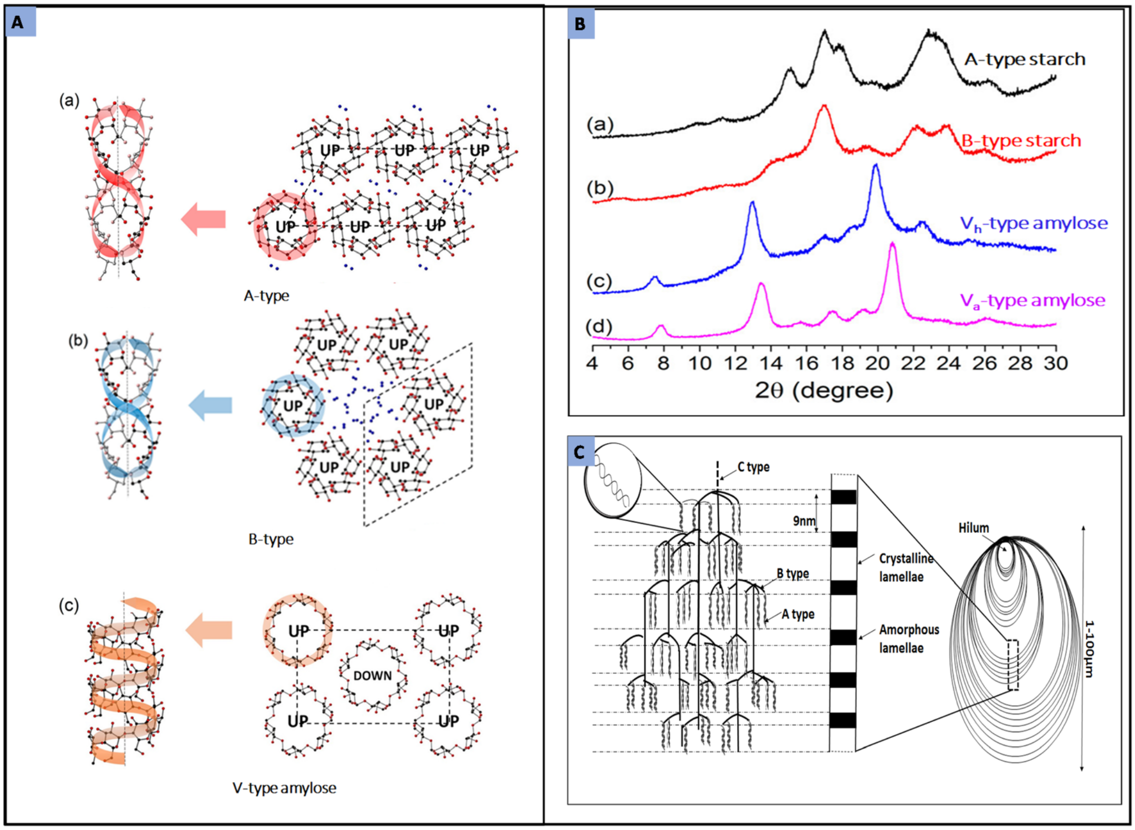


Fig. 4 (A) Shows the helical structure and (right) unit cell projection in the *c*-axis of A-type, B-type and V-type amylose. The 'UP' and 'DOWN' in the unit cells represent the direction of the reducing end of the helical structure moving up and down, respectively. Blue colour dots represent the water molecules. (B) The XDR patterns in Fig. 4B have been produced by (a) A-type starch is from acid-hydrolysed and annealed pea starch, (b) B-type starch is from acid-hydrolysed and annealed Hylon starch, (c) V_h-type amylose from amylose crystallised with palmitic acid as guest molecule and (d) V_a-type amylose pattern from crystallisation of amylose lacking guest. (Figure A and B reproduced from ref. 81 with permission from the American Chemical Society, Copyright 2014.) (C) Shows the cluster model of amylopectin where the terms A, B, and C are related to the chain type and length of amylopectin (drawn by author).

starch-based films and coatings has resulted in high water solubility and poor water resistance.[104] Similarly, the brittleness, retrogradation and thermal degradation of starch during melt processing can affect the mechanical integrity of the films and limits their industrial applications.[101] Thus, starch modification is desirable to amplify the processability and functional properties. The physical and mechanical properties of the starch film can be improved by physical and chemical modification techniques, namely plasticization, derivatization, blending and graft polymerisation.[60,108–113]

4. Plasticization of starch

Native starch lacks the ability to act as a plastic owing to the presence of strong inter and intra-molecular H-bonding formed by the amylose and amylopectin of starch.[55] Hence, plasticization is used to change the molecular structure of starch in the presence of plasticizer, under elevated temperature and shear.[114] There is plenty of research that has been conducted on the plasticization of starch with different low molecular weight molecules (water, glycerol, sorbitol *etc.*) to enhance the processability of starch.[47,51,54,55,115,116] The process of plasticization of starch involves different chemical and/or physical interactions such as water diffusion, and starch granules' expansion, gelatinization, and polymer melting.[114,117] Gelatinization is one of the processes that can augment starch granule disintegration and decrease the intermolecular affinity.[118] However, the presence of plasticizer in the starch formulation destroys the inter and intra molecular hydrogen bonding of the starch granule, partially depolymerizing the starch backbone and further leading to the decrease in melt temperature of starch below degradation temperature.[119] Thus, plasticization overcomes the brittleness of native starch by increasing the macromolecular chain mobility and enhances the processability of starch at low temperatures.

To achieve efficient plasticization, the type and concentration of plasticizers play important roles.[120] An efficient plasticizer would be a hydrophilic polar molecule that has high compatibility with the starch molecule, and that has a boiling point higher than that of the polymer processing temperature. Rodriguez *et al.*[47] found that the optimum concentration of glycerol as plasticizer is 20 wt% of starch content, and further increase in plasticizer leads to phase separation and leaching out from the film.

The efficiency of the plasticizer also depends on the amylose and amylopectin content, which varies with the starch source. The study conducted by van Soest *et al.*[121] on PS prepared by plasticizers such as glycerol and sugars showed the tendency to form retrogradation after cooling and storage, which caused brittleness to the plasticized material. Retrogradation is the process of recrystallisation of linear chains of amylose and amylopectin moieties that results in a more ordered structure during the process of storage after gelatinization.[122,123] Amylose and amylopectin are the responsible components for retrogradation in starch. During cooling and storage of gelatinized starch, amylose moieties reassemble to form double helix structures and amylopectin branches form a partially ordered crystal structure.[124] In this process, at the beginning of storage, amylose forms aggregates and with increasing storage time amylopectin cause crystallization that affects the deterioration of plasticized starch.

High amylose content starch forms a tough and flexible polymer because of its amorphous structure. However, on plasticization with glycerol, high amylose starch undergoes retrogradation over time and its crystallinity increases, which affects the functional properties of PS. It is important for an efficient plasticizer to have the ability to suppress retrogradation during aging, and it should enhance the flexibility. The study conducted by Ma and Yu[55] found that the use of amide-based plasticizers like urea, formamide, and ethanolamine could suppress the retrogradation process and enhance the mechanical properties of PS. Urea was more effective, as the double amide group in urea could form stable hydrogen bonds with starch, resulting in an amorphous structure. This was confirmed by XRD analysis, where the crystalline peaks of starch were not visible as compared with native starch. However, urea is a small molecule with lower internal flexibility. Thus, urea-plasticized starch forms a rigid and brittle material rather than a tough thermoplastic material. Hence to rectify this issue, multiple plasticizers were introduced during plasticization of starch. The use of multiple plasticizers could enhance the plasticization efficiency and could prevent the retrogradation process.

Analysing the effect of hybrid (multiple or co-plasticization) plasticization of starch with urea and ethanolamine, Ma *et al.*[108] demonstrated better thermal and mechanical properties as stronger bonds were formed with the hydroxyl group of starch than glycerol. In addition, this combination could effectively avoid the retrogradation process. An analysis of the mechanical properties of starch from various sources in different compositions of plasticizers is shown in Table 2. It is evident from the table that the type of starch, concentration and combination of plasticizer, relative humidity and storage time have an effect in achieving variable mechanical properties in plasticized starch. Furthermore, it shows that multiple plas-

Table 2 Mechanical properties of various starch sources in different compositions of plasticizers

PS formulations	Relative humidity (%) and storage time	Tensile strength (MPa)	Young's modulus (MPa)	Percentage elongation (%)	Breaking energy (N m)	Ref.
Corn starch plasticized with glycerol	50, 14 days	5.5	38.1	7	1.9	116
Corn starch plasticized with ethanolamine	50, 14 days	6.0	75.3	14	2.3	116
Corn starch plasticized with sorbitol (30%)	7 days	13.62	500	50	—	51
Corn starch plasticizes with sorbitol and glycerol	7 days	6	<100	50	—	51
Corn starch with glycerol : xylitol (1 : 1)	—	2.56	—	62.94	—	125
Corn starch plasticized with urea (30 wt%)	33, 7 days	12.5	1664	5.7	0.32	108
Corn starch plasticized with ethanolamine (30 wt%)	33, 7 days	3.1	61.6	57	0.75	108
Corn starch plasticized with urea/ethanolamine (15/15 (wt%))	33, 7 days	9.0	236	34.4	1.34	108
Corn starch plasticized with thymol	52, 1 day	27.51	1488	2.22		126
Corn starch plasticized with glycerol and thymol	52, 1 day	1.52	73	66.85	—	126
Corn starch plasticized with 1-ethyl-3-methylimidazolium acetate (1.5 wt%) and water	50, 7 days	4.25	75	68	—	127
Potato starch plasticized with glycerol	53, 7 days	6.56	5.33	5.67	—	128
Potato starch plasticized with sorbitol (10–50%)	52, 4 days	4.95–9.37	—	1.84–9.00	—	50
Potato starch plasticized with 1-ethyl-3-methylimidazolium acetate (1.5 wt%) and water	50, 7 days	2.43	14.65	38	—	127
Wheat starch plasticized with glycerol	53, 7 days	3.29	0.12	15.21	—	128
Wheat starch plasticized with 1-ethyl-3-methylimidazolium acetate (1.5 wt%) and water	50, 7 days	4.99	87.64	75.59	—	127
Rice starch plasticized with glycerol (30%)	63, 1 day	2.0	—	19.5	—	129
Rice starch plasticized with sorbitol (40%)	63, 1 day	3.25	—	23.7	—	129
Mango kernel starch plasticized with glycerol (40%)	58, 2 days	3.57	50.07	17.78	—	130
Mango kernel starch plasticized with sorbitol (40%)	58, 2 days	25.06	959	4.02	—	130
Mango kernel starch plasticized with glycerol : sorbitol (1 : 1)	58, 2 days	5.73	96.25	26.13	—	130

ticizers are depicting more percentage elongation at break (EB) than single plasticizer.

Huneault and Li[131] investigated the effect of glycerol, sorbitol, and glycerol/sorbitol mixture as a plasticizer in PS/PLA blend on achieving better morphology and mechanical strength. The processes were conducted in a series of steps such as starch plasticization, water devolatilization and PLA addition using a twin-screw extruder, where the first half was devoted to starch gelatinization followed by free water removal in the devolatilization zone, and in the second zone PLA was introduced and mixed with PS. In this study, when sorbitol was compared with glycerol, an improvement in mechanical and thermal properties was obtained for the sorbitol-plasticized starch/PLA blend because of the low rise in vapour pressure of sorbitol at higher temperature and low volatility that restricts the loss of plasticizer during melt blending. Furthermore, plasticizing starch with sorbitol could reduce the recrystallisation rate and plasticizer migration, but an increase in sorbitol content could reduce the tensile modulus (TM) of the PS/PLA blend. In contrast, the use of glycerol as a single plasticizer improves the flexibility of the starch material but decreases the thermal resistance, TM, and resistance to retrogradation. This may be due to the higher vapour pressure and weak interaction of small glycerol molecules with starch. Thus, co-plasticization is an effective method to attain a balanced thermomechanical property and retrogradation resistance in starch. This has been further proved by the study conducted by Esmaeili *et al.*[132] on the co-plasticization effect of glycerol and sorbitol in different ratios and concentrations of plasticizers; they have shown that the mixture of plasticizer concentration raised the thermomechanical properties of the plasticized starch by providing a reasonable TS, TM, and elongation with a glass transition temperature (T_g) below room temperature (RT) (Fig. 5). Fig. 6 shows the schematic representation of hydrogen bonds formed during the plasticization of starch with glycerol, sorbitol, or glycerol/sorbitol after melting blending.[132]

Recently, Kahvand and Fasihi[63] investigated the effect of citric acid as co-plasticizer for starch by plasticizing starch with water/glycerol/citric acid. The terms CAPS (citric acid-plasticized starch) and PS represent water/glycerol/citric acid and water/glycerol as plasticizers, respectively. The addition of citric acid as co-plasticizer led to the development of stronger and stable hydrogen bonds with starch, and was confirmed by

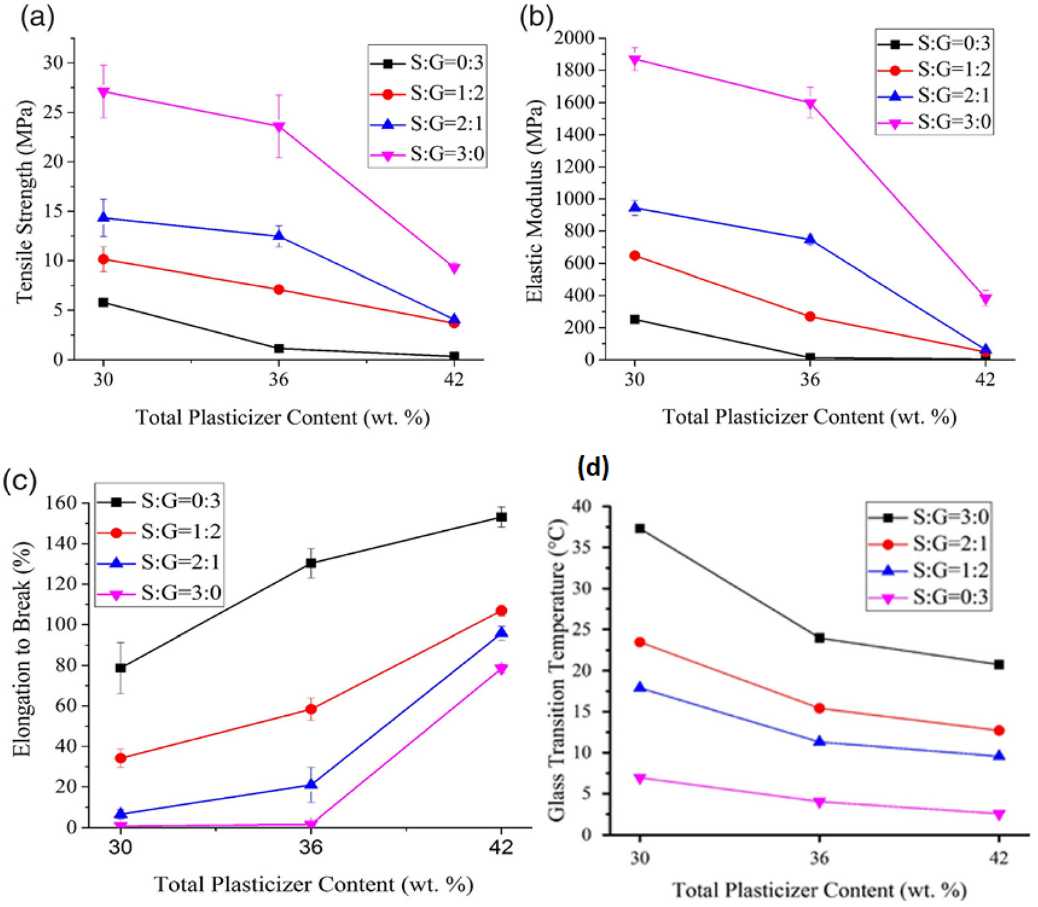


Fig. 5 The variation in thermomechanical properties of sorbitol/glycerol co-plasticized starch at different weight ratio and total plasticizer content. (a) Tensile strength (b) elastic modulus (c) elongation at break and (d) glass transition temperature. Reproduced from ref. 132 with permission from John Wiley and Sons, copyright 2017.

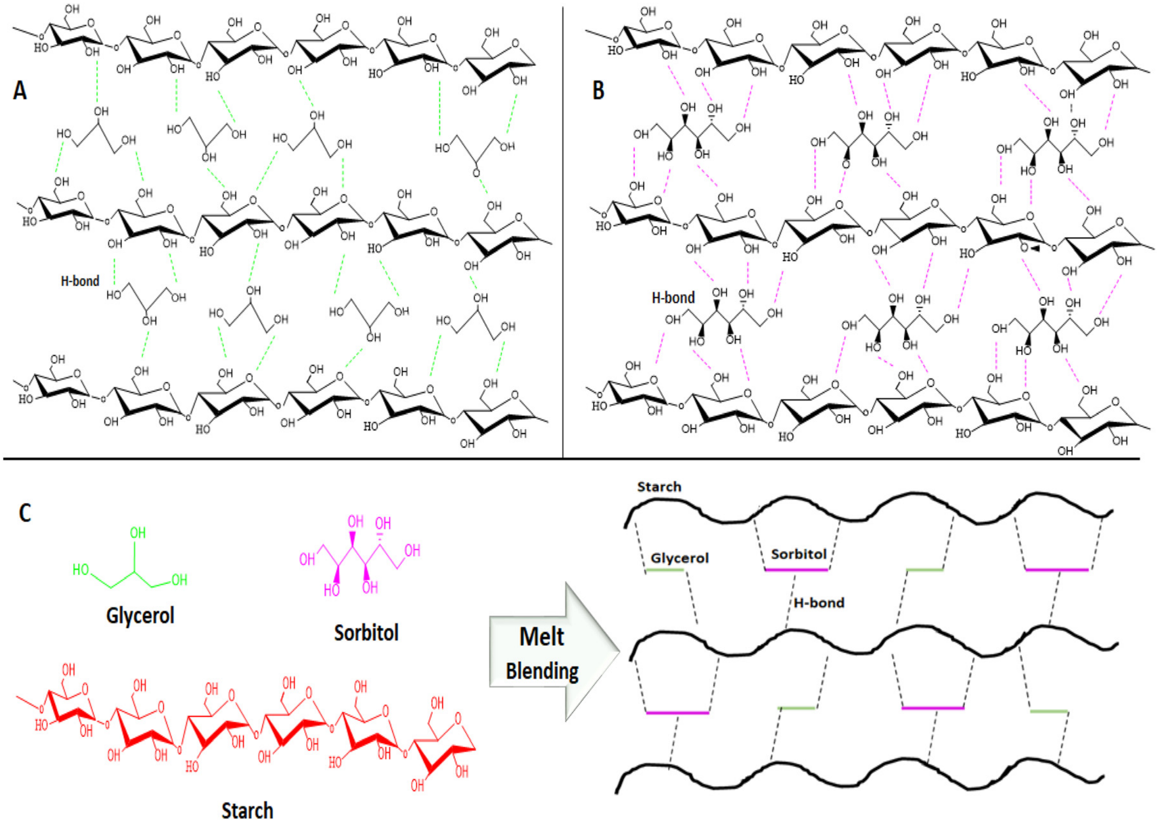


Fig. 6 Shows the schematic representation of hydrogen bonds formed during the plasticization of starch with (A) glycerol, (B) sorbitol and (C) glycerol/sorbitol after melt blending (molecular structures drawn by author using ChemDraw).[132]

SEM, FTIR (Fourier transform infrared spectrometer) and XRD analysis (Fig. 7). The FTIR analysis of starch, PS, and CAPS confirmed the formation of new hydrogen bonds in starch with plasticizers by attenuating the intermolecular hydrogen bonds of starch. This was confirmed by the formation of characteristic dual peaks at 992 cm^{-1} and 1024 cm^{-1} for plasticized starch instead of a single peak of 994 cm^{-1} for pure starch. The intensity of these dual peaks was higher in the presence of citric acid, which represents the ability of the carboxyl group of citric acid to form stronger hydrogen bonds with the C═O group of starch. Furthermore, the formation of a characteristic peak at 1737 cm^{-1} in CAPS confirmed the formation of partial ester linkages in starch that enhanced the thermal resistance of starch and decreased its rate of retrogradation. Additionally, the XRD analysis of CAPS confirmed the elimination of the A-type crystal structure of starch with the formation of V-type crystal structure in CAPS, indicating the formation of a homogeneous structure without unmelted components, confirmed by SEM images.

5. Thermoplastic starch blends

Native starch is a semi-crystalline hydrophilic material with brittle characteristics which limit its application especially in the packaging sector, such as in plastic bags, mulch film, edible coatings on fruits, meats and vegetables, and food packaging. The brittleness of native starch is due to the relatively high glass transition temperature and the absence of sub T_g (β-transition).[133] In addition, brittleness can increase with time through the retrogradation process.[55] Furthermore, the higher melting point and lower thermal degradation temperature of starch have resulted in poor melt processability.[114] However, to enhance the processability and functional properties of starch, it is converted into thermoplastic by the incorporation of one or more plasticizers followed by blending with polymer or biopolymers at elevated temperature and shear force; these are called TPS blend systems.[112] In most articles the term plasticized starch refers to thermoplastic starch and is abbreviated to TPS, making the nomenclature counterintuitive. The process of plasticization of starch does not make starch a thermoplastic material until it is blended with a toughened polymer or biopolymer material. Furthermore, the lower mechanical properties and hydrophilicity of plasticized starch reduces its application in industrial use. Irrespective of the use of the term thermoplastic starch, plasticized starch cannot be remolded or reused once it is processed. Thus, for commercialization and industrial use, TPS blend systems are preferred.

Thermoplastic starch-based blend systems have properties comparable with conventional polymers, and could act as an alternative for certain synthetic thermoplastic polymers. Since

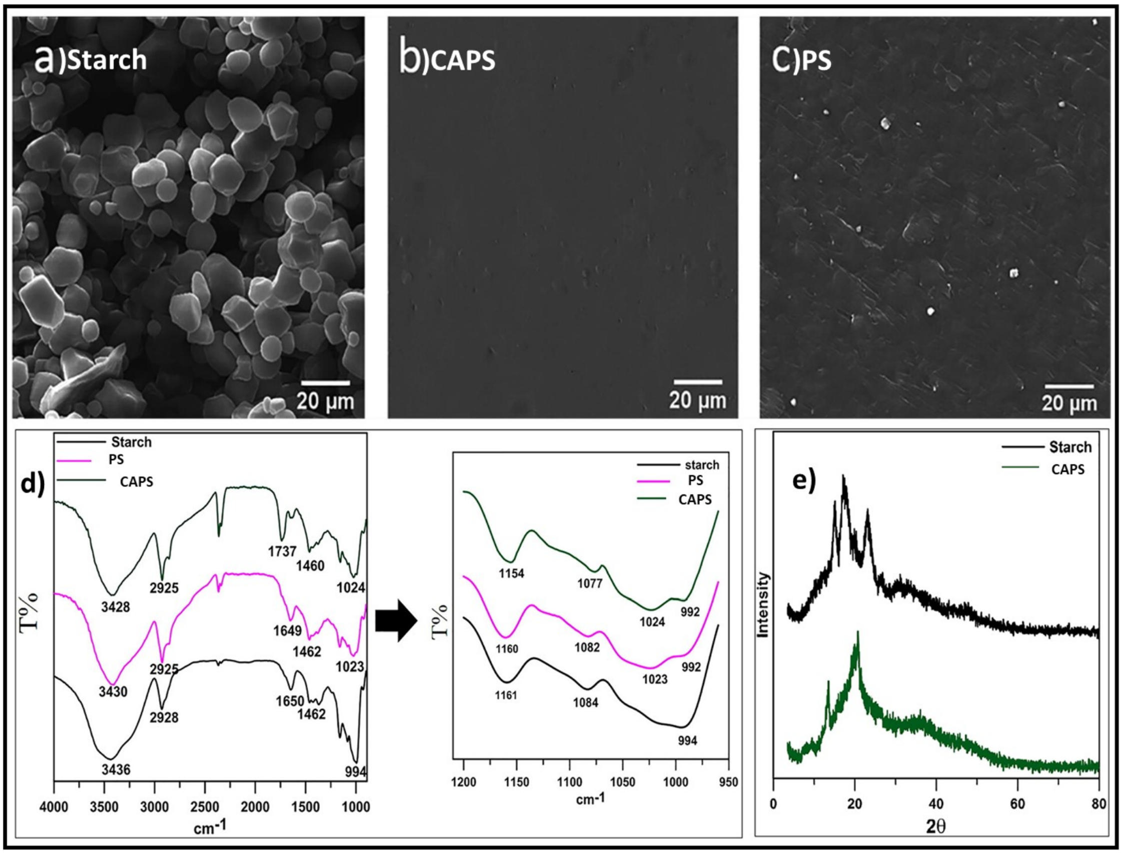


Fig. 7 (a) SEM micrograph of starch, (b) SEM micrograph of CAPS, (c) SEM micrograph of PS, (d) FTIR spectroscopy of starch, CAPS and PS, (e) XRD of starch and CAPS. Reproduced from ref. 63 with permission from Elsevier, copyright 2019.

starch is an abundant biodegradable polymer, the TPS blend system for packaging applications will be cost-effective and environmentally friendly. There are many types of research on the development of thermoplastic starch blend systems with the incorporation of biodegradable and non-biodegradable thermoplastic polymers. However, interest in biodegradable and biobased systems has increased the development of TPS blends from biobased thermoplastic polymers and plasticized starch systems. They are prepared by thermochemical processing techniques like kneading, casting, melt blending, and compression molding.[74] The processing technology, which determines the possible physical and chemical interactions, is an important aspect in achieving the blend properties.

5.1 Processing techniques

Different processing techniques have been utilized for preparation of PS and TPS blends and composite systems. In most research, the TPS blends are prepared by the solution casting technique. This is a wet process usually done at laboratory scale to analyse the plasticization, gelatinisation, and retrogradation mechanisms of starch. The ability to achieve uniform thickness distribution, dimensional stability, low haze, and optical purity are the key factors of this technology.[134] However, for industrial applications extrusion techniques are preferred, as this is a reliable and continuous process. During extrusion, polymer melt is forced through a desired shaped die and formed into profiles like sheets, tubes, films *etc*. It is a fast and reliable technology used to manufacture thermoplastic starch-based products for commercial applications.

5.1.1 Extrusion. Extrusion is a core processing technology conducted before other processing technologies such as injection moulding, blown film moulding, cast film and compression moulding. The hot melt extrudate obtained from the extruder die is immediately formed into blown films or cast films by secondary shaping operations. Secondary shaping is the process of mechanical stretching of a cylinder or sheet in the machine and in transverse directions.[135] In extrusion-cast film, the melt is passed through the slit die followed by polished chill rolls, where it is rapidly quenched to maintain the mechanical property and clarity of the films. It travels further through another series of rollers such as chill rollers and nip rollers to draw the film into the desired thickness. In the blown film extrusion technique, the molten polymer material is forced through an annular die and formed into a thin tube. The tube is then drawn and inflated until it reaches the freezing line beyond which stretching is negligible. In addition, this technology is used for the preparation of self-supporting plastic films.[136]

Extrusion technology is a widely accepted thermal processing technology used to prepare PS, thermoplastic starch blends and related films and composites owing to its ability to withstand higher viscosity, and its operational flexibility in a wide range of processing conditions.[43] TPS blends and composites are prepared by a two-step extrusion process such as primary and secondary extrusion. Primary extrusion is plasticization of starch to develop PS. In PS extrusion processes, the starch granules or pellets in the presence of plasticizer and/or additives are fed into a screw through the hopper and subjected to high-temperature shear mixing in different heating zones. During this process, the presence of water and plasticizer destroys the crystallites of starch which undergoes fragmentation that eases PS melting and flowability. In the secondary extrusion process, the resultant PS is blended with toughened polymer and/or reinforced with fillers or fibres to develop TPS blends and composites, and the subsequent extrudate from the die can be injection moulded into products of the desired shape, or films can be cast or blown according to the application of the final product (Fig. 8A).

5.1.2 Compression moulding. In compression moulding technology the materials are heated at elevated temperature and pressure with low moisture and low dwell time, resulting in the viscoelastic melt, which on cooling forms assorted products such as packaging sheets or containers (Fig. 8B).[137] Conversion of native starch to plasticized starch-based blends and composites through elevated temperature techniques such as compression moulding and blown film extrusion resulted in degradation of high molecular weight amylose and amylopectin molecular structure compared with low-temperature processing solution cast films.[138]

Altskär *et al.*[138] scrutinized the effect of different processing techniques such as compression molding, blown film extrusion and solution-cast film of PS obtained from glycerol and water plasticization of hydroxy propylated and oxidised potato starch (HONPS). The results showed that the composition of TPS and processing conditions affect the morphological and structural properties of the films. Furthermore, the transmission electron microscope (TEM) analyses of HONPS films from different processing techniques are shown in Fig. 9. The morphological analysis of all these processing techniques has shown phase separation according to the presence of plasticizer-rich and plasticizer-poor regions. However, the higher moisture content and molecular mobility of cast films, and recrystallisation on cooling of compression films have shown the presence of a network structure in morphology, whereas this was not found in blown film owing to its low moisture content.

5.1.3 Casting. The casting of starch-based films is a common and mature fabrication technology used for the

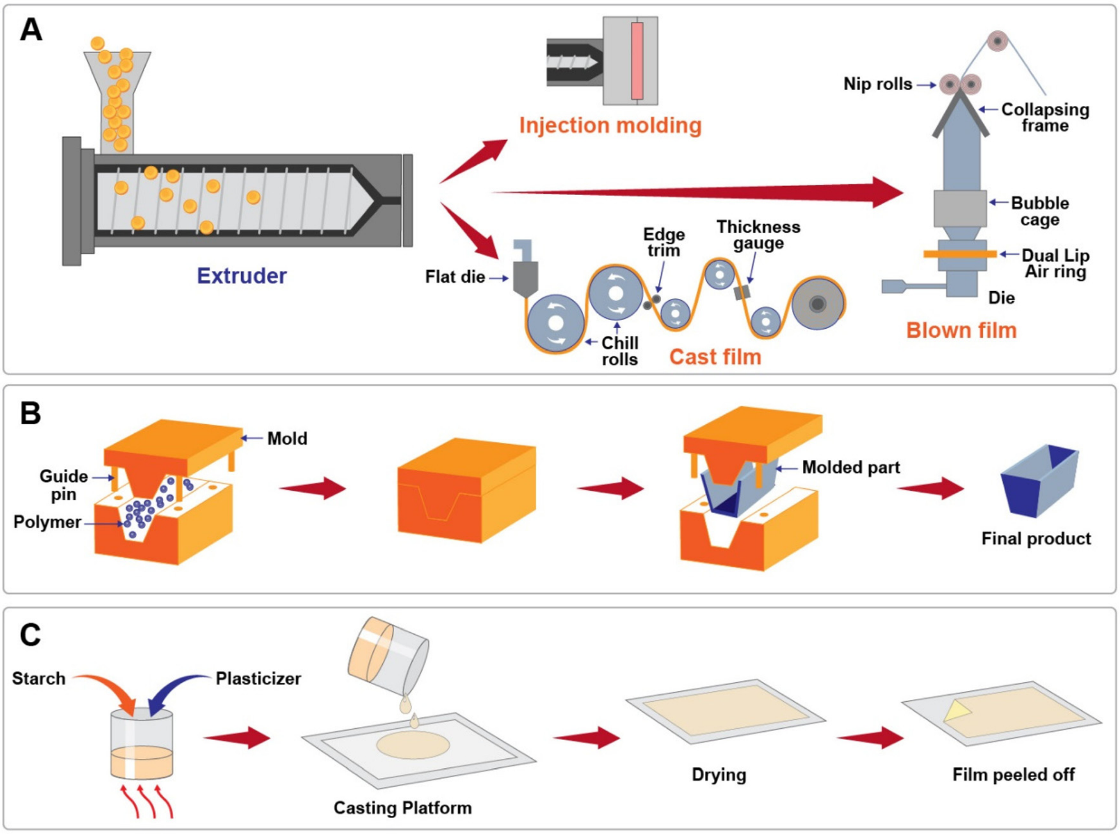


Fig. 8 Processing techniques (A) extrusion technique (B) compression moulding and (C) solution casting followed by injection for rigid-type applications and blown film or cast film for flexible packaging type applications (drawn by author).

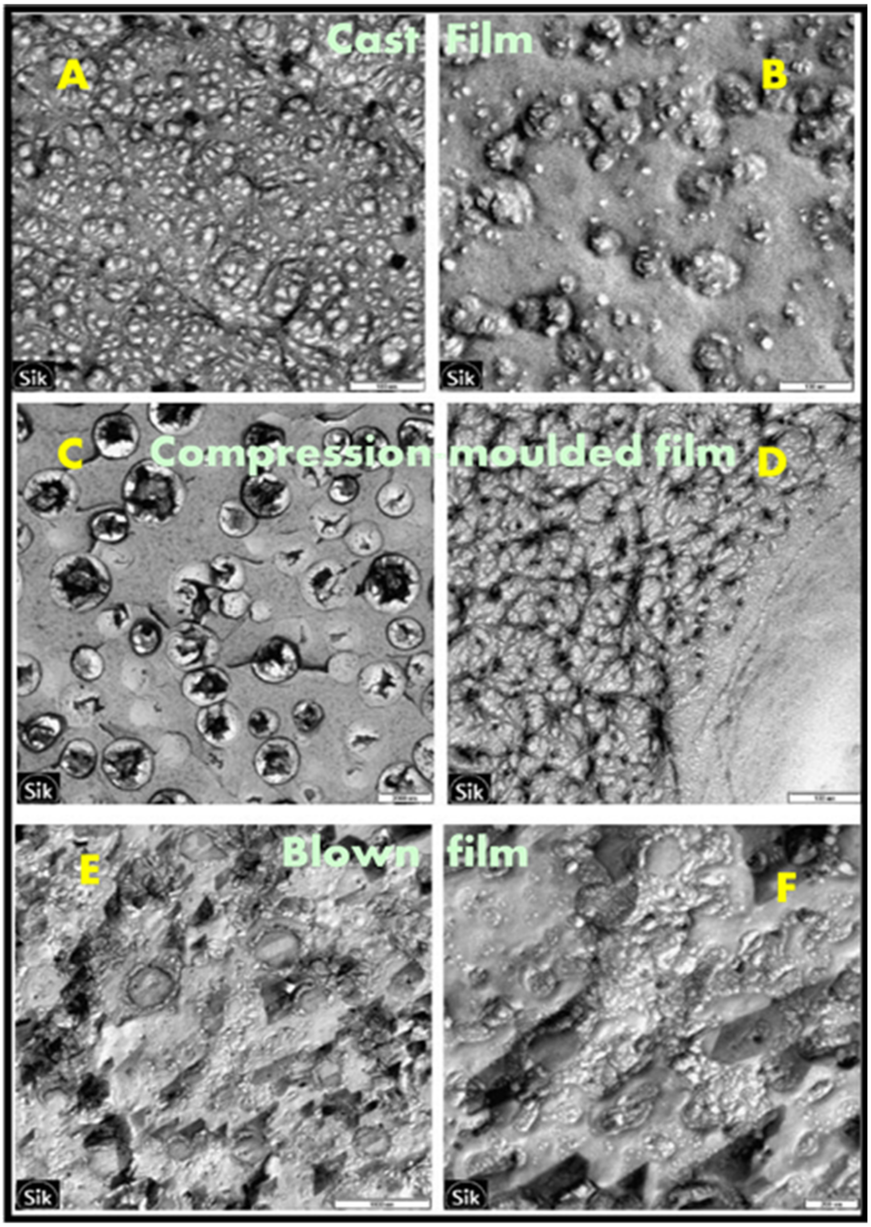


Fig. 9 TEM micrograph of cast, compression moulded and blown HONPS films. (A) and (B) shows two different structures in cast HONPS with scale bars 100 nm, (C) and (D) shows compression moulded (HONPS) with scale bars 2000 and 100 nm, (E) and (F) shows blown HONPS films with scale bars of 1000 nm and 200 nm respectively. Reproduced from ref. 138 with permission from Elsevier, copyright 2008.

preparation of high-quality films. On casting starch films, high-amylose starch forms more flexible films than amylopectin does, due to the linear and highly entangled structure of amylose resulting in high tensile strength.[139] However, on casting plasticized starch, up to 40% amylose content shows higher plasticization efficiency, and a further increase in amylose content reduces the mechanical properties by increasing the T_g above room temperature.[140] Furthermore, in another study, Koch *et al.*[141] evaluated the effect of higher temperature and long heating time on solution-cast PS films of high amylose and amylopectin content. The results showed that the increase in time and temperature negatively affected the cohesiveness of the film but had no effect on tensile properties.

In most of the studies, PS, TPS blends and composites systems were fabricated by the casting technique where the films were fabricated either from film-forming dispersion, or from an emulsion with higher percentage of water content. The process of solution casting involves mainly 3 steps: gelatinisation/plasticization or homogenisation (in the case of mixtures or emulsions), casting and drying (Fig. 8C).[142] The optimization of processing temperature and gelatinisation/plasticization time depends on the starch source and plasticizer content, as the granule structure of starch varies with source.

In the casting process, when starch is hydrated by being dissolved in hot water, the crystalline components of amylose and amylopectin are lost, and while forming film, the macromolecules and linear components of amylose and amylopectin rearrange and reassociate by hydrogen bonding. Thus, the resultant crystallinity of starch-based films depends on plasticizer content, and temperature and humidity conditions during drying and storage.[142]

6. Recent progress in TPS-based biodegradable blends

As there is much research going in the field of TPS-based biodegradable blends, the following sections separately discuss the different biodegradable polymer and starch blend systems that have been developed in the last two decades. The sections mainly focus on the different strategies that have been carried out during the processing of TPS blends to enhance the compatibility between starch and other biodegradable polymers such as PLA, PCL, poly(propylene carbonate) (PPC), PHA, poly (vinyl alcohol) (PVA), and poly(butylene succinate) (PBS). Fig. 10 shows the chemical structure of different fully biodegradable or compostable polymers.

6.1 Poly(lactic acid)/PS blends

PLA is an aliphatic polyester fabricated from renewable sources (such as starch, sugar, corn, *etc.*).[143,144] The excellent mechanical properties and easy processability of PLA to form flexible films have shown potential applications in the field of packaging industries.[145,146] However, the high cost and inherent brittleness of PLA has reduced its wide spectrum of applications.[144] Thus, blending of PLA with polymers such as PCL, starch and polyethylene is cost effective and could improve the toughness of the material.[147–149] Since starch is an abundant biodegradable polymer, blending of starch with PLA could result in a cost-effective blend.[150] However, the lack of interfacial adhesion between hydrophilic starch and hydrophobic PLA reduces the mechanical strength of resultant blends.[151] Hence, numerous studies have been performed aiming to achieve efficient compatibility in PLA/starch blend by incorporating several types and concentrations of compatibilizers, organic acids, natural oils and crosslinkers.[132,152–154]

Initially, Zhang *et al.*[155] studied the effect of one-step and two-step extrusion on the preparation of a PLA and starch powder (55/45) blend system with maleic anhydride (MA) as a compatibilizer and 2,5-bis(*tert*-butylperoxy)-2,5 dimethyl hexane (L101) as initiator. In the one-step approach, MA and L101 were added into the PLA/starch system and extruded, whereas in the two-step approach, PLA-*g*-MA (1% MA and 10% L101 (MA basis)) was prepared initially and blended with PLA/starch blend system. The obtained mechanical properties such as TS and EB showed that, irrespective of one-step or two-step processing, the addition of MA in the presence of initiator markedly improved the mechanical properties of the blend, and showed similar mechanical strength of that of neat PLA. Fig. 11 shows the SEM images of the PLA/starch blend system obtained through the one-step process, where PLA/starch with MA and initiator indicates better compatibility between PLA and starch.

In later studies, utilization of PS was analysed as it enhances the properties of PLA/PS blends and additionally it could increase the starch content in blend systems, which could reduce the cost. The process of plasticization can overcome the strong intermolecular and intramolecular hydrogen bonding of starch and improve the compatibility with the blending polymer. Wang *et al.*[156] studied the effect of different plasticizers such as glycerol and formamide in the presence

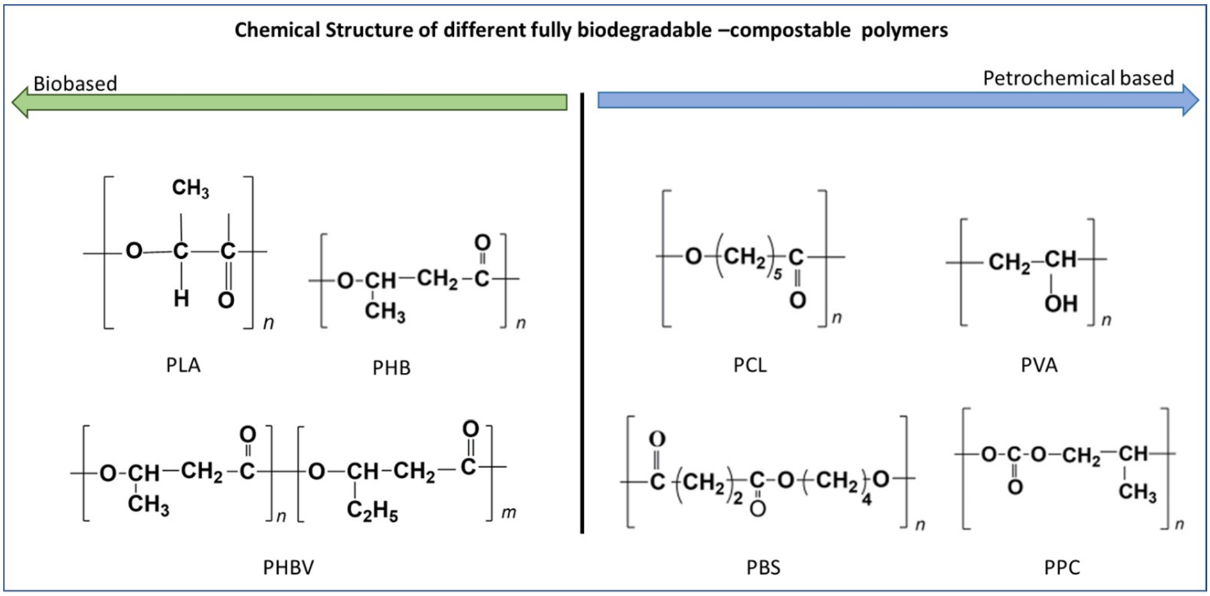


Fig. 10 Chemical structure of different fully biodegradable and compostable polymers (drawn by author).

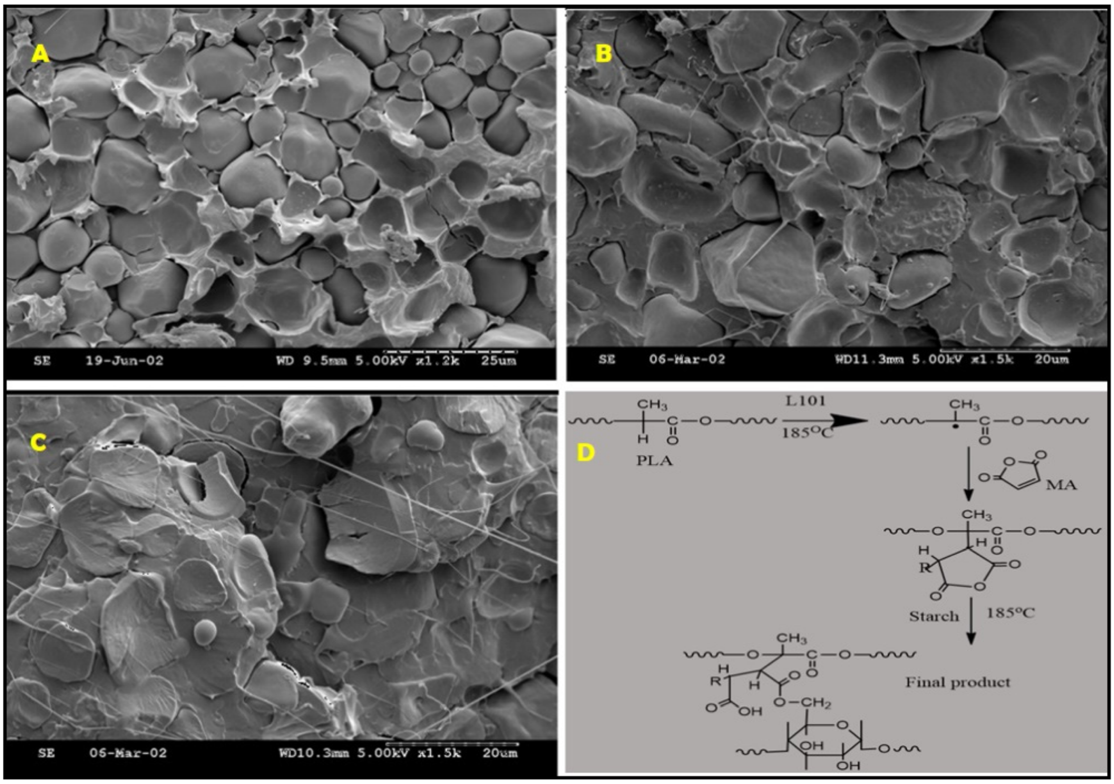


Fig. 11 (A) Shows an immiscible PLA/starch blend without MA and initiator where PLA is the continuous phase and starch is the dispersed phase, (B) PLA/starch blend with MA and without initiator shows similar behaviour as of PLA/starch blend (without MA and initiator) with some visible cavities, (C) PLA/starch blend with MA and initiator shows uniform dispersion of starch in PLA (figure A, B, C reprinted and figure D is redrawn from ref. 155 with permission from the American Chemical Society, Copyright 2004).

and absence of water in enhancing the dispersion and interfacial adhesion of the PS/PLA blend, and the results showed that replacing glycerol with formamide in the presence of water is an efficient plasticizer PS/PLA blend system. The formamide–water plasticizer is better than the glycerol–water plasticizer system, as formamide improved the dispersion and compatibility between the polymers, evident from TGA analysis where higher $T_{\max}$ (temperature at the maximum rate of weight loss) and AED (activation energy of decomposition) were obtained. Furthermore, amide group-containing plasticizers such as urea, acetamide, and formamide can reduce the retrogradation and structural changes of starch and are excellent as plasticizers, but the toxicity of these materials limits their applications in the biomedical, pharmaceutical and food packaging fields.[132]

On using glycerol alone as plasticizer for starch, the flexibility of the PS/PLA blend material improves, but it reduces the TM, thermal resistance and retrogradation resistance. The reduction in these properties is mainly due to the higher vapour pressure of glycerol that causes loss of plasticizer during processing, and the low molecular interaction of the small molecules of glycerol with starch molecules. Conversely, on using sorbitol as a plasticizer for starch in PS/PLA blend exhibits higher retrogradation resistance but lower flexibility. Thus, the issues of starch retrogradation, brittleness and migration of plasticizers during plasticization of starch were avoided by utilizing a mixture of plasticizers (hybrid plasticization or co-plasticization) such as formamide/urea, ethylenebisformamide/sorbitol, sorbitol/glycerol, and glycerol/maltose.[15,115,157,158] According to studies conducted by Esmaeili *et al.* and Huneault and Li,[131,159] the combination of sorbitol and glycerol as co-plasticizers for PS/PLA blend improved the mechanical property and exhibited fine morphology compared with glycerol alone as plasticizer. This is due to the similarity in solubility parameters of PLA and plasticizers, that caused the plasticizers, specifically glycerol, to migrate to the PLA phase, decrease the storage modulus and complex viscosity of the blend systems, and thus improve the processability of the melt.

Another approach stated by Yokesahachart and Yoksan *et al.*[160] is to use amphiphilic molecules such as Tween 60 (polyethylene glycol sorbitan monostearate or polysorbate), linoleic acid, and zein as an additive for thermoplastic starch blends prepared with glycerol as a plasticizer and followed by PS/PLA blend preparation. Amphiphilic molecules are compounds having two sets of hydrophobic hydrocarbon parts and polar hydrophilic parts like carboxylates, sulphates, sulfonates, and amine groups. The incorporation of these amphiphilic molecules resulted in a drastic improvement in elongational property and enhanced processability of plasticized starch and the consequent PS/PLA blend due to the decrease in T_g and T_m without affecting the thermal stability of the TPS blend systems.

In earlier studies, the use of reactive compatibilizers or coupling agents (such as acrylic acid, methylene-diphenyldiisocyanate (MDI), poly(hydroxyester ether) (PHEE), poly(vinyl alcohol) (PVA) and MA) was one of the methods introduced to improve the interaction between PLA and starch-based blends.[71,155,161,162] Other than that, Akrami *et al.*[152] developed a new compatibilizer of maleic anhydride-grafted polyethylene glycol-grafted starch to modify the compatibility of PLA/PS blend. This newly developed compatibilizer significantly enhanced the interfacial adhesion and ductility of the blend because of interaction between the active groups of PLAs and PS and carboxylic acid end groups of the compatibilizer. However, most of these compatibilizers are noxious and injurious for health.

To replace harmful compatibilizers and plasticizers, the use of non-toxic, renewable, and abundant epoxidized vegetable oils would be an effective solution.[154,163,164] There is much research on epoxidized oil as an effective component in reducing the brittleness and enhancing the interaction of the blends. Ortega-Toro *et al.*[165] assayed the efficiency of epoxidized sesame oil as a compatibilizing and plasticizing agent for PLA/starch blend films obtained from melt extrusion followed by compression moulding. The incorporation of epoxidized sesame oil increased the flexibility and thermal stability by providing a plasticization effect to PLA, and it acted as a coupling agent that augmented the interfacial adhesion of the blend (Fig. 12). In Fig. 12, PS is referred to as TPS.

Fig. 13 shows different compatibility enhancers for PLA and starch-based blends, where co-plasticization is an effective technique to improve the thermal stability during processing and could reduce the plasticizer migration during blending of PLA and starch, whereas the addition of additives or epoxidized oils could further improve the extensivity of the blends. Replacing amide-based plasticizers such as urea and formamide with citric acid or other organic acids (acetic acid, maleic anhydride, linoleic acid and oleic acid) could be an effective option for food-contact packaging applications and prevent the retrogradation process of starch.[166]

6.2 Poly(ε-caprolactone)/PS blends

PCL is a commercially available biodegradable plastic that belongs to the group of linear polyesters. PCL is a tough, biodegradable, compactable and non-toxic material with high solvent, water, and oil resistance.[167] It is often blended with other biopolymers such as PLA,[168] PHA,[169] and starch[110] owing to its higher viscoelastic properties. However, the high cost of PCL restricts its broad use in applications, especially in the packaging sector.[170] Thus, the incorporation of inexpensive natural polymers such as starch could reduce the cost and enhance the biodegradability of PCL. However, to overcome the poor interfacial adhesion during blending PCL and starch powder, the PCL is blended with plasticized starch. According to the study conducted by Shin *et al.*,[110] melt blending polyca-

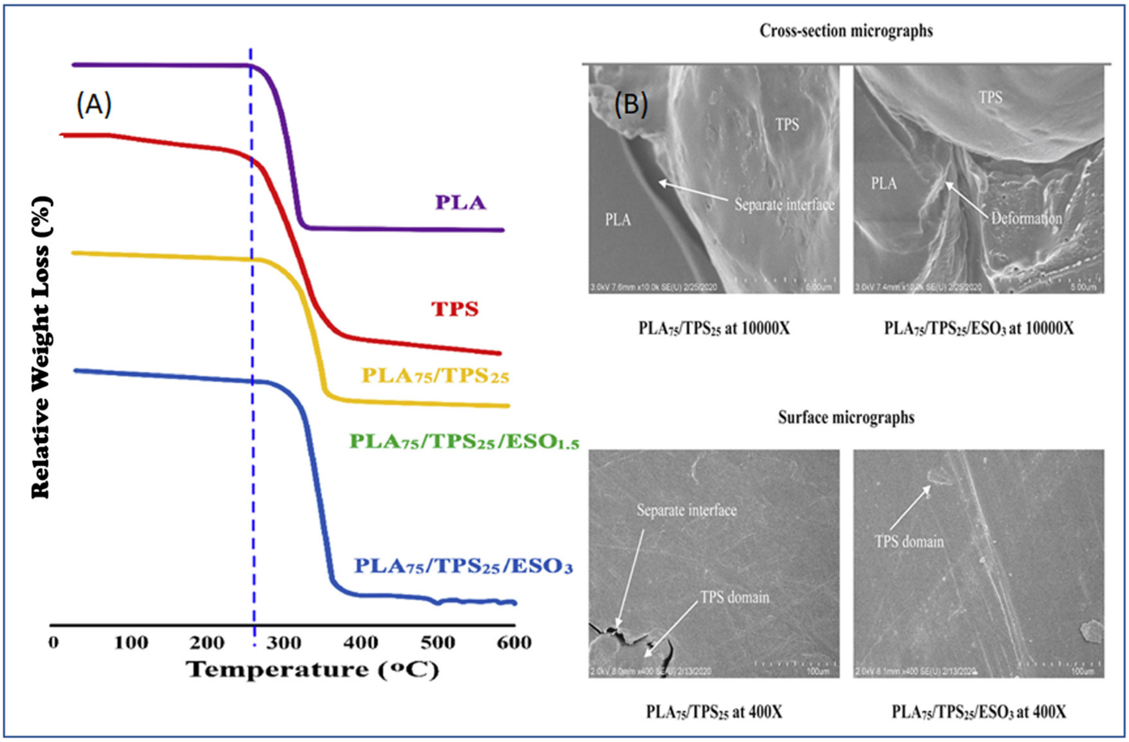


Fig. 12 (A) Thermogravimetric analysis of PLA/starch films with or without epoxidized oil as compatibilizer/plasticizer. (B) Cross-section and surface SEM of PLA/starch film without epoxidized oil and with epoxidized. Reproduced from ref. 165 with permission from Elsevier, copyright 2021.

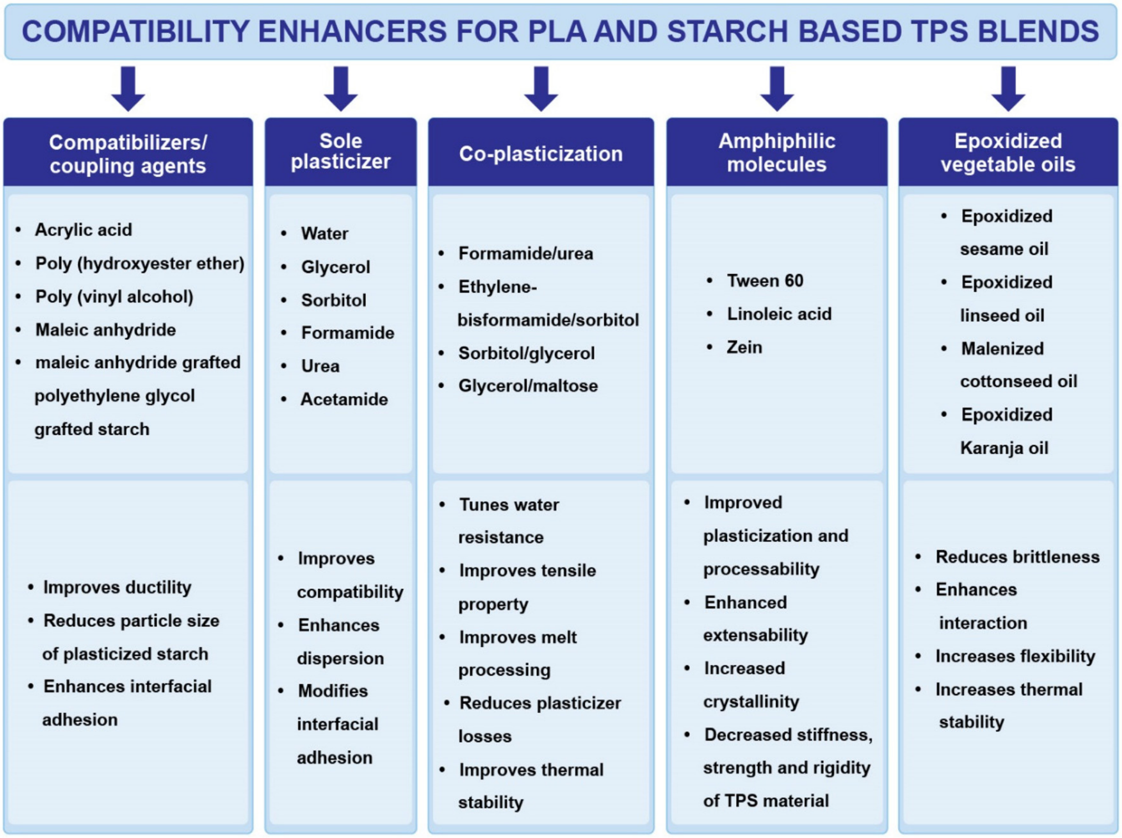


Fig. 13 Shows the compilation of different strategies and resultant properties obtained on use of compatibilizers/coupling agents, individual (sole) plasticizer, co-plasticization, amphiphilic molecules and epoxidized oils in PLA/starch-based blends systems (drawn by author).

prolactone with corn-based PS as the dispersed phase, followed by compression molding to films of thickness 0.5 mm, improved the interfacial adhesion between PS/PCL blend by forming H-bonding between the ester carbonyl group of PCL and hydroxyl group of PS.

In an initial study, Averous *et al.*[167] tried to develop a cost-effective and biodegradable plasticized wheat starch/PCL blend with PS as major phase without compatibilizers. The study confirmed that the concentration of glycerol in starch and PCL have great impact on the mechanical properties of the blend, where the addition of flexible PCL into rigid PS enormously enhanced the impact strength and reduced the TS, EB and Young's modulus of the blend. This study confirmed the fact that the addition of toughened polymer could rectify the weaknesses of PS such as low resilience, high shrinkage and high moisture absorption, and the resultant blend would be an environmentally friendly material for packaging with better biodegradability than neat PCL.

For a polymer blend, control of the morphology is an essential factor in attaining effective material properties. Phase morphology of a blend depends on the viscoelastic properties of the respective components, blend composition, interfacial adhesion, and processing conditions. Different phase morphologies of polymer blends can be seen in different forms such as droplets, fibers, laminar or as co-continuous morphology. Furthermore, phase coalescence is an important process that affects the final morphology of the polymer blends and is classified as dynamic and static processes. In the dynamic process, it is a flow-dependent process, where the final morphology of the blend system depends on the balance between particle breakups and coalescence of the dispersed phase during the polymer blending,[171] whereas in the static process, referred to as a quiescent process, the dispersed phase or matrix phase, or both, coarsen through coalescence over time at elevated temperature during blending. Li *et al.*[172] analyzed the coalescence and static and dynamic mechanical properties of the PS/PCL blend, using dynamic mechanical analysis (DMA) and FTIR spectroscopy. It was confirmed that the presence of a higher concentration of plasticizers without external modifiers is more effective in achieving a dual-phase continuity region and strong hydrogen bonding between the starch and PCL in TPS blend systems. This may be because the increase in plasticizer concentration improved the chain mobility and interaction between these polymers, which resulted in enormously higher EB even in higher concentrations of PS.

Another factor to consider in PCL/PS blends is the effect of retrogradation. Recently, Hernandez *et al.*[173] have investigated the effect of PCL in retrogradation of PS/PCL blends. It was found that irrespective of PCL concentration, the process of retrogradation of PS occurred continuously in the binary blend and changed the structural properties of the blend. XRD and FTIR analysis confirmed that the interaction between PCL and PS was negligible compared with the structural changes that were maintained within the PS phase. As a result, the mechanical properties of the blends have shown a similar trend as pure PS, where properties declined initially by plasticization through moisture absorption and then increased by retrogradation over time.

Another approach to reduce the inadequacies of individual polymers during blending is the use of a ternary blend. Bulatović *et al.*[170] experimented with the preparation of a PLA/PCL/PS ternary blend, and showed that the addition of PS as a dispersed phase to PLA/PCL blend resulted in poor adhesion and phase separation that impaired the mechanical properties of these TPS blends, resulting in the formation of an immiscible ternary blend. However, these blend systems could be improved by adequate use of compatibilizers that could enhance the miscibility and functional properties of the blend specifically for biodegradable packaging applications.

6.3 Poly(propylene carbonate)/PS blends

PPC is an aliphatic poly(carbonic acid ester) synthesized by copolymerisation of carbon dioxide and propylene oxide in the presence of a catalyst.[174–176] It is a biodegradable, biocompatible and biobased material with good transparency, gas barrier and high EB properties that could compete with and replace petroleum-based polymers in different applications like packaging, films, and solid electrolytes.[177] PPC could not only minimize the consumption of petroleum resources, but also mitigate carbon dioxide emission that leads to climatic changes and global warming.[178] However, the amorphous structure of PPC has low stiffness, lower T_g and poor thermal stability, limiting its industrial applications to a great extent.[179] PPC is blended with several polymers, specifically with biodegradable polymers such as starch, PLA, PHB (polyhydroxyl butyrate), and chitosan to enhance the biodegradability, processability and material performance compared with individual polymers.[177] Several studies have been done on preparing native corn starch/PPC blends, and the results revealed that the thermal and mechanical properties were improved due to the hydrogen bonding between the hydroxyl group of starch and the carbonyl group of PPC.[180–182] However, it was found that on increasing the starch content, the mechanical properties of the blends were decreased as this weakened the interfacial bonding and compatibility of starch and PPC.[180,182] Thus, plasticization of starch and blending with PPC is a great method to enhance the compatibility of the starch/PPC blend, where it disintegrates granules and overcomes the intermolecular interaction of starch.

The use of reactive compatibilizers was also an effective method to improve the compatibility between starch and PPC. Ma *et al.*[183] prepared blend compositions of PS/PPC and succinic anhydride-compatibilized PS/PPC. It was found that the incorporation of succinic anhydride as compatibilizer in the blend improved the adhesion between PPC and PS and the mechanical properties of the blends, which was attributed to the chemical interaction between the hydroxyl group of PS and the anhydride group of succinic anhydride. In addition, modification of starch through oxidation or grafting or esterification reactions was also found effective in attaining good interfacial interaction and compatibility during blending with PCL.[179,184,185]

Recently, much research has focused on the development of oxidised starch, where hydrophilic OH– groups of starch are converted into hydrophobic CO– groups that enhance the compatibility during blending with other degradable polymers. Fig. 14 shows the oxidation process of starch and hydrogen bonding interaction in PPC and thermoplastic oxidized starch (TPOS).[179] The initial structure shows the hydrogen bonds present in native starch (in the figure shown as TPS) and is represented as hydrogen bonding 1. Blending native starch with MA-grafted PPC would usually result in intermolecular and intramolecular hydrogen bondings, represented as hydrogen bonding 1(H-bonding 1) and hydrogen bonding 2 in the figure. The presence of hydrogen bonding 1 in MA-grafted PPC/native starch blend leads to agglomeration and results in poor compatibility between the polymers in the blend. The conversion of native starch to TPOS replaces the hydroxyl group of starch with carbonyl groups and aldehyde groups; further blending TPOS with MA-grafted PPC reduces the formation of hydrogen bonding 1 and results in the formation of hydrogen bonding 2 and hydrogen bonding 3, as shown in the figure. Thus, the oxidation of starch weakens the formation of hydrogen bonding 1 and decreases agglomeration, thereby improving the interfacial interaction between PPC and starch. In the study conducted by Jiang *et al.*,[179] TPOS and aluminic ester-grafted thermoplastic oxidized starch were melt blended with MA-grafted PPC. Aluminic ester was introduced as the coupling agent for oxidised starch to improve the interfacial adhesion between PPC and starch. The aluminic ester-grafted thermoplastic oxidized starch exhibited good dispersion of TPOS in MA-grafted PPC and showed an increase in thermal and TS of the blend.

6.4 Polyhydroxyalkanoate/PS blends

PHAs are a group of thermoplastic polyesters derived from bacteria by the microbial fermentation process. They are crystalline, biodegradable, non-toxic, UV-resistant materials with good physical and chemical properties that are promising materials for single-use packaging applications.[186] However, lower mechanical properties and poor thermal processability constrain their applications. PHB and PHBV (poly(hydroxyl butyrate-*co*-valerate)) are the commonly used PHA-based polymers. PHB is a homopolymer with higher degree of crystallinity (up to 70%) and efficient biodegradability in aerobic and anaerobic conditions. With higher crystallinity PHB exhibits good mechanical properties that are similar to polyethylene, and it is used for food packaging applications. In order to improve the low thermal stability, brittleness, and inadequate barrier properties, PHB is usually blended with low-melting

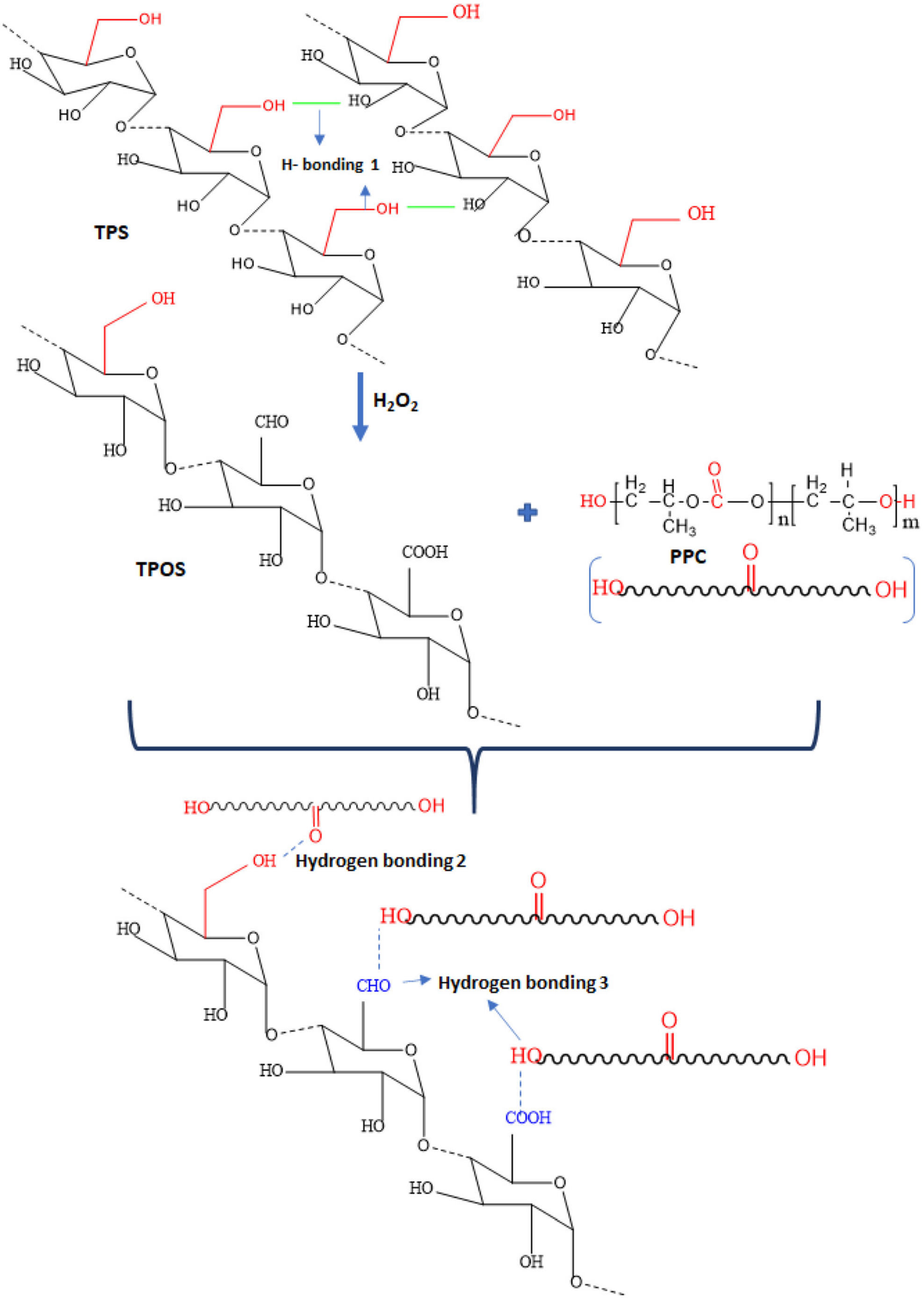


Fig. 14 Hydrogen bonding interaction between PPC and TPOS (molecular structures have been redrawn by author using ChemDraw, from ref. 179 with permission from Taylor & Francis, copyright 2017).

biodegradable polymers. Thus, blending with plasticized starch is a method to improve the properties of both polymers and the resultant material would be completely biodegradable. Although several studies have been conducted on blending starch with PHA, most of them resulted in brittle materials with low elongation.[187,188]

Lai *et al.*[189] initially studied the possibility of PS/PHA blend and the effect of the degree of gelatinisation of starch on the mechanical properties of the blend. Different gelatinisation degrees of 25% and 33% were analysed with glycerol as plasticizer. The study revealed that lower gelatinisation degree and an increase in the concentration of PHA have a significant effect on mechanical properties such as TS and tear strength due to the dissipation of energy during the crystalline deformation of PHA and improved interaction during blending with PS.

The concentration of amylose and amylopectin content varies with starch source and determines the crystallinity of starch. High-amylose starch is more efficient for film preparation as it has a linear structure with more amorphous regions that ease gelatinisation. The study conducted by Parulekar *et al.*[112] analysed the effect of plasticization of high-amylose starch with glycerol blended with PHA in the presence of compatibilizer. It was found that blending high-amylose PS with PHA was effective in reducing the moisture uptake and retrogradation of starch, and enhanced elongation. However, the major barrier for the PS/PHA blend is the formation of heterogeneous blends due to the higher crystallinity of PS and PHA. Thus, recently Florez *et al.*[190] found that the active use of plasma treatment on PHB material and blending with PS matrix improved the mechanical properties of the blend, as this increases the interaction and changes the crystallinity of the blends compared with untreated PS/PHA blend.

6.5 Poly(vinyl alcohol)/PS blends

PVA is a biodegradable semicrystalline polymer consisting of 1,2-diol units or 1,3 diol units according to the degree of hydrolysis of poly(vinyl-acetate).[63] The existence of a substantial number of hydroxyl groups on the surface of PVA can ease the preparation of blends and composites of PVA, which could be an ideal material for packaging applications.[191] Blending of PVA with economically viable PS can reduce the cost and increase the biodegradability of the polymer. Integration of PVA into starch modifies the structure of the polymer at molecular and morphological levels to augment the mechanical and thermal properties of the starch material.[63] Conventional plasticizers like glycerol and water,[192] sorbitol,[193] citric acid,[193,194] urea[195] and complex plasticizer[196] are effectively employed in the preparation of PS/PVA blends.

An earlier study conducted by Liu *et al.*[192] on melt-blending starch with PVA using glycerine and water as plasticizer found that good processability, rheological and mechanical properties were attained for an optimum plasticizer composition of glycerine and water in a ratio of 50/50. Mao *et al.*[197] studied the effect of PVA concentration on PS/PVA blend where the starch plasticized with glycerol was blended with PVA and samples were tested at 50% relative humidity. It was found that the incorporation of PVA increased the TS and EB of PS. The improvement in the mechanical properties of these blends was ascribed to the effect of intermolecular and intramolecular hydrogen bonding between PS and PVA that resulted in a more efficient compatibility among components.

Park *et al.*[193] analysed the effect of different plasticizers, namely glycerol, sorbitol, and citric acid for PS/PVA blend for film casting. The characteristic results of these blends illustrated that the integration of citric acid provides superior properties than glycerol and sorbitol due to the formation of intermolecular and intramolecular hydrogen bonding between starch, PVA and citric acid, specifically at low-temperature drying of the film (at 5 °C). Later, in another analysis, Shi *et al.*[194] investigated the effect of varying the concentration (5 to 30 wt%) of citric acid on the structural and physical properties of solvent-casted PS/PVA film at 140 °C. They reported that the increase in citric acid concentrations from 5 to 30 wt% decreased the water absorption from 33% to 20%. In addition, the mechanical and thermal properties were improved, where EB increased gradually from 102% to 208%. This may be due to the presence of multiple carboxylic groups in citric acid and esterification resulting in the formation of a chemically crosslinked blend with strong hydrogen bonds, which improved the thermal stability and mechanical properties of the PS/PVA blend film. Recently Kahvand and Fasihi[63] investigated the effect of change in concentration and plasticizing effect of citric acid in a CAPS/PVA blend plasticized with water/glycerol/citric acid by the extrusion technique. The FTIR analysis of PVA and the CAPS/PVA blend showed a characteristic reduction in the PVA hydroxyl functional group frequency peak from 3600 cm^{-1} to 3400 cm^{-1}, and formation of dual characteristic peaks at 1031 cm^{-1} and 995 cm^{-1}, and the broadening of the peak in CAPS/PVA blends is attributed to the confirmation of the development of stronger hydrogen bonds between starch and PVA in the blend systems than in CAPS. Moreover, the XRD analysis of CAPS/PVA blends demonstrated the elimination of PVA crystal structural peaks in the blend with less than 50% PVA, representing the higher compatibility between PVA and starch in CAPS/PVA blend systems. The above study also states that PVA acted as a polymer-based plasticizer for starch; at a concentration above 10% and below 50% it reduced the T_g and storage modulus of the blends, whereas at below 10% PVA, it caused an anti-plasticization effect on the blend by forming a miscible structure and thereby increasing the T_g and storage modulus.

In most of the research on starch/PVA blends, the use of a complex plasticizer system has shown continuous phase morphology that resulted in good rheological and mechanical properties. Zhou *et al.*[196] used the mixture of glycerol and urea as a complex plasticizer for a PS/PVA blend. The results revealed that the complex plasticizer can form more stable and strong hydrogen bonding with starch, PVA and water molecules than glycerol as a single plasticizer.

Another aspect to consider in blending starch with PVA is the hydrophilic nature of PS/PVA blend, which has shown susceptibility to relative humidity; on increasing the relative humidity, TS of the blend was inversely affected. To improve the mechanical and water barrier properties of the PS/PVA blend, different chemical and physical modifications during or after blending are used. Ramaraj *et al.* and Yoon *et al.*[198,199] evaluated the effect of glutaraldehyde as a crosslinking agent in PS/PVA blend. Their results showed that, along with strong adhesion between PS and PVA, crosslinking at the interface of PVA and PS due to the presence of glutaraldehyde improved the mechanical properties such as TS and Young's modulus and solubility resistance.

6.6 Poly(butylene succinate)/PS blends

PBS is an aliphatic polyester derived from the polycondensation polymerisation of succinic anhydride and 1,4-butanediol.[200] Lately, succinic anhydride has been derived from renewable resources that could essentially reduce the carbon footprint of PBS without loss of its overall performance.[201] As a biodegradable polyester, PBS has great applications in the field of packaging films, textiles, and injection-moulded products. Besides biodegradability, these thermoplastic polymers have good melt processibility, chemical and water resistance, thermal and dimensional stability, and excellent mechanical properties.[202] There is plenty of research on blending PBS with TPS to enhance the properties and processability of the polymers.

Usually, the blending of hydrophilic natural polymers and hydrophobic thermoplastic polyesters would result in thermodynamically immiscible blends with poor adhesion and polymer performance. Thus, blending of these polymers was carried in the presence of suitable compatibilizers or by chemical modifications. In earlier studies, Zeng *et al.*[202] synthesized reactive PBS having terminal NCO– group by reacting hydroxyl-terminated PBS with toluene-2,4-diisocyanate (TDI) and used this as reinforcing phase in PS/reactive PBS blend by reactive extrusion technology. This methodology has strengthened the tensile properties of the PS and resulted in low water absorption for the blend. In contrast, Li *et al.*[203] evaluated the effect of different starch types such as waxy starch (0% amylose) and normal starch (26% amylose) on blending with PBS. This study revealed that the utilization of waxy starch eased the plasticization and processability of the blend. The presence of highly branched amylopectin in waxy starch hindered the absorption of water molecules, and further addition and increase in the concentration of PBS improved the tensile strength and water resistance properties of these blends. On comparing plasticization of starch with ionic liquid and commercial plasticizer glycerol, XRD and SEM analysis of 1-butyl-3-methylimidazolium chloride, ionic liquid plasticized starch (ILPS) showed the destruction of more crystalline phase in starch and resulted in a higher plasticization effect than glycerol.[204] Thus, better dispersion of ILPS was achieved in ILPS/PBS blend, which exhibited an effective increase in TS and EB compared with the glycerol-plasticized starch/PBS blend.

7. Starch-based bio composites and bio nanocomposites

The major drawbacks of PS as a matrix material for packaging application are its high water absorption and lower mechanical properties.[74] The hydrophilic nature of PS and other properties like surface tension, higher moisture absorption and thermal properties, especially T_g, further influence the applications.[99] Possible approaches to enhance the properties of PS are blending with biodegradable polymers,[167] incorporation of cross-linking agents[199] or preparing multilayer films.[205] In addition to the above techniques, the use of natural fibres/fillers or organic fillers as reinforcing material could enhance the TS, lower the density, and reduce energy consumption.[206] The utilization of natural fibres over synthetic fibres improves biodegradability and minimizes health and environmental hazards. Besides, the similarity in chemical structure of plant fibres and starch offers good compatibility between matrix and reinforcing fibre. It has been found that the addition of cellulose fibres or micro fibres to PS improved the water resistance and thermal resistance of the biocomposite due to the higher crystallinity and thermal resistance of cellulose fibres compared with starch.[206] The study conducted by Campos *et al.*[207] on the effect of raw and chemically treated oil palm mesocarp fibres as reinforcement for PS proved that even with raw fibres, the composite system could achieve good intermolecular interactions and superior mechanical properties compared with treated fibres. This is because of the van der Waals force of interaction between the silica group of fibre and –OH group of starch. Lately, there have been studies on using different morphologies of PVA, such as microspheres and electrospun fibres, as a reinforcement for PS-based composites.[208–210] The results showed that the addition of a lower concentration of these microspheres and fibres effectively enhanced the mechanical properties of the biocomposites.

Fitch-Vargas *et al.*[211] developed an environmentally friendly biocomposite material from acetylated sugar cane fibre-reinforced acetylated corn starch in the presence of glycerol as plasticizer. The optimum concentrations of 12.0 wt% fibre and 24 wt% glycerol content formed better interactions and shown better mechanical properties and water resistance. The fibre and matrix chemical surface modification and plasticizer content influenced the formation of more bonding between matrix and fibre than matrix–matrix interaction and enhanced the elongational properties of the composition. The researchers proposed this composition as an alternative to fossil fuel-based packaging material. Later Ferreira *et al.*[212] developed biodegradable trays for food packaging applications from cassava starch and different agricultural residues such as sugarcane bagasse, cornhusk, malt bagasse, and orange bagasse. The resultant trays showed higher rigidity and complete biodegradation in a 60-day period compared with expanded polystyrene trays.

Interfacial tension or surface tension is a significant parameter for surface wettability. PS exhibits higher wettability that limits its packaging applications. Thus, the incorporation of fillers such as talc,[213] calcium carbonate,[214] clays[215] and cellulose[216] is widely studied. However, reinforcing micro fillers into the biopolymer matrix could reduce the mechanical properties of the biocomposites, as they act as a stress concentrator in the system. This could be minimized by reducing the particle size of fillers to the nano range. Furthermore, the integration of nano fillers such as chitin nano particles or cellulose nanocrystals could improve the surface wettability and water resistance due to the formation of a difficult tortuous path for the penetrant molecules.[217] Recently, starch-based bio nanocomposite films were developed by incorporating different starch nano particles with a high surface to volume ratio; these films showed a reduction in water vapour transmission rate due to hindrance of the polymer chain moment.[217] Some of the research on the preparation of starch-based bio/nano/hybrid composites developed from organic fillers and fibres with different starch sources and plasticizers is shown in Table 3.

8. Global production and market analysis of TPS as packaging material

Thermoplastic starch-based films have been developed and marketed from the year 1999.[228] The starch-based products were mainly developed by blending with polyesters such as PCL to develop biodegradable and compostable materials. Primarily, starch-based carry bags were introduced in the markets of Scandinavian and Mediterranean countries for collecting organic waste, where the waste management was well organized.[229] These bags showed properties similar to the bags developed from LDPE material. However, the high cost and water permeability of biobased or biodegradable food packaging materials have limited their marketability in the food packaging sector, although the breathability of starch-based films has found applications in fruit, vegetable and bread packaging.

Recently, Mordor Intelligence[230] assessed the impact of COVID-19 in a growth market on the trends and forecast of thermoplastic starch manufactured by injection moulding and extrusion for bags, films, and other applications in the geographical areas of Asia-Pacific, North America, Europe, and the rest of the world in the period 2020–2025. The global production of the TPS market was about 179.58 kilo metric tons in the year 2019 and is anticipated to reach around 255.82 kilo metric tons in 2025 with a compound annual growth rate of 7.01%.[230,231] The expected fastest CAGR hike rate of thermoplastic starch is due to environmental regulations and the ban of single-use plastics in the Asia-Pacific region.[230] There are companies such as Novatec, Plantec, Biome, and Biotec that are focused on developing TPS for packaging applications.

Novamont is one of the largest producers of thermoplastic starch-based blends and composites, and has more than 1000 patents related to starch-based composite technology. Corn

Table 3 Starch-based bio/nano/hybrid composites with different starch source and plasticizers and the resultant properties

Starch source (plasticizer)	Polymer/reinforcement (natural fibre dimension)	Fabrication technique	Observation	Ref.
Corn (glycerol and natural rubber latex)	Sisal, hemp (10–15 mm)	Melt blending	Increase in fiber content improved the T_g, Young's modulus, and TS but reduced EB The incorporation of rubber latex as plasticizer enhanced water resistance without affecting mechanical properties	218
Corn starch (glycerol)	Poly(vinyl alcohol) fiber	Compression molding	Multilayer structure Higher mechanical properties than PP and PE Orientation of fiber in same direction reduced stress concentration and improved mechanical properties	208
Maize starch (glycerine)	Flax fiber	Extrusion	Higher impact strength and flexural strength at 20 wt% flax fiber addition Fully biodegradable under aerobic condition and could be used for biogas production	219
Rice (glycerol)	Cotton fiber (2.11 and 5.27 mm)	Compression molding	Improved thermal stability and Young's modulus and reduced water absorption Smaller fibers with higher aspect ratio exhibit better properties	220
Arrowroot starch (glycerol)	Arrowroot fiber	Solution casting	Effective stress transfer between matrix and fiber Improved TS and tear strength Moderate resistance to water absorption on fiber loading	221
Cassava (sorbitol and glycerol)	Cellulose nanocrystal from kenaf fiber (70–190 nm)	Solution casting	Crystallinity and TM of the composite have been improved Good interfacial interaction between matrix and filler	222
Sugar palm starch (sorbitol and glycerol)	Nanocrystalline cellulose from sugar palm	Solution casting	Improved mechanical, thermal and water barrier properties Good dispersion and adhesion of filler with matrix due to H-bonding interaction between components	223
Potato starch (glycerol)	Kaolin clay	Casting method	Increased water barrier, wettability and surface hardness properties on filler addition Reduced mechanical properties	224
Sugar palm starch (sorbitol and glycerol)	PLA/sugar palm nanocellulose	Compression molding	Increase in PS content reduced mechanical properties and water absorption Low interaction between PS and PLA in absence of compatibilizer	225
Pea starch (glycerol and water)	PCL/flax fiber	Compression molding	Poor compatibility and interfacial adhesion between PS and fibers Presence of PCL improved TS and moisture absorption in composite system	226
Cassava starch (glycerol)	PLA/PBAT/jute fiber	Extrusion	Increase in fiber content improved TM and crystallinity of the composite Jute fiber acted as a nucleating agent for PLA and compatibility promoter between PS and PLA/PBAT/jute	227

starch-based Novamont products are sold under the brand name MATER-BI®. The products developed from this material have properties similar to those of traditional polymers. They have good processability, compostability, antistatic property and mechanical properties that vary from soft to tough or rigid according to the composition.[232] Biome Bioplastics (**https://biomebioplastics.com/**) is a branch of United Kingdom-based developer Stanelco, which develops highly functional plant-based bioplastics which are biodegradable and compostable. In collaboration with German company Biotec (**https://en.biotec.de/**), they develop different bioplastic resins and possess a large number of patents on development of TPS.[232] Among a large range of products developed and sold through Biotec and Biome, BiomeEP1 (potato starch based) and BiomeEP2 (corn starch based) are flexible film resins without plasticizers developed by Biome that have improved adhesion and printability with good strength, flexibility, and tear strength. Similarly, Bioplast GF106/2 is a plasticizer-free potato starch-based industrial compostable resin developed by Biotec suitable for blown film extrusion processing for packaging applications. Tecnaro (**https://tecnaro.de/en/**) is another German company developing bioplastics resins containing more than 50% plant-based materials such as starch by grafting technology. ARBOBLEND® is a 100% biobased blend developed by Tecnaro from different biopolymers, organic additives and natural fillers, and is an efficient resin material for developing films and packaging products. Furthermore Cereplast, Inc. (**https://www.cereplast.com**), BIOP Biopolymer Technologies (**https://www.biop.eu**), and Plantic Technologies (**https://www.plantic.com.au**) are a few of the other companies developing starch and thermoplastic-based resins for packaging and other applications. In addition, major TPS-based companies and their products are shown in Table 4.

9. Challenges and real-life applications for starch-based materials

The dreadful effect of fossil fuel-based packaging material on the marine and terrestrial environment from depositing of waste is alarming to human and environmental health. The development of biodegradable and sustainable packaging material, especially for certain single-use plastic, would be a probable solution to reduce the rapid increase in packaging waste and its discarding.[240] Starch-based blends and composites are the preferred material for certain packaging applications over synthetic and natural polymer materials, owing to their aptitude to meet commercial and ecological demands. Natural and mineral filler reinforcement is an excellent technique to improve the mechanical and water permeability of thermoplastic starch composites. Different studies have stated that the incorporation of cellulose fillers in PS not only enhanced the mechanical properties but also improved the moisture barrier properties of the starch-based composites.[241,242] The decrease in moisture permeability of composite is due to the decrease in diffusion coefficient that is imposed by the cellulose crystals by forming hydrogen bonding with starch, and further due to the decrease in sorption of the penetrant.[243]

Antimicrobial property is an integral part of packaging material in improving the shelf life of food products by preventing the growth of microbes on the surface of the food. To obtain efficient antimicrobial property biologically active agents are usually incorporated into the matrix material, such as selenium nanoparticles, essential oils *etc.*[244] Selenium nanoparticles, derived from plant extracts or microorganisms, with properties such as antioxidant, anti-microbial, and anti-fungal characteristics and used for food packaging appli-

Table 4 Companies producing thermoplastic starch-based blends and composites

Company producing TPS	Product name	Source material	Total production per year	Place/country	Applications	Ref.
Novamont	MASTER B	Starches, cellulose, vegetable oils	150 000 tonnes	Novara/Italy	Agriculture, packaging, organic waste collection bags, food service, carrier bag	233
BioLogiQ Inc.	NuPlastiQ (Pellets)	Potato starch	2 million tons	Hong Kong/China	Flexible bags, pouches, jugs, handle bags, trash bags, agricultural & industrial films	234
Biotec	BIOPLAST 300, BIOPLAST 400, BIOPLAST 500, BIOPLAST GF106/02	Potato starch and other biopolymers	25 000 metric tons	Germany	Blown film extrusion	235
Kuraray	Plantic	Corn starch	—	Japan	Multilayer film, gas and aroma barrier film, packaging applications	236
Biome Bioplastics Limited	BiomeEP1 BiomeEP2	Potato starch Corn starch	—	UK	High-speed, full color print applications or lamination film	237
Agrana Beteiligungs	AGENACOMP, AMITROPLAST	Thermoplastic starch and biodegradable polyester	—	Austria	Carrier bags, fruit and vegetable bags, bio-waste bag, mulch film, non-woven fibers	238 and 239

cations would extend the shelf-life of food products. However, there are no studies on selenium nanoparticles-incorporated starch composites for packaging applications. Essential oils are another widely used material for achieving antifungal and antimicrobial properties. Campos-Requena *et al.*[215] used carvacrol, a natural phenolic compound, in PS/layered silicate bio nanocomposite film for an antimicrobial packaging application. The study analysed the effect of nano clay and plasticizer concentration in obtaining efficient Young's modulus and thermal resistance for packaging applications. The results showed positive change with nano clay and negative effect with plasticizer concentration that indicates the formation of intercalated or exfoliated structure in the composite with a higher concentration of silicate particles. Besides, the addition of nano clay improved the half-life of the essential oil by the optimal release of an antimicrobial agent through the difficult tortuous path. In another study, PS and PCL multilayer films were developed by Ortega-Toro *et al.*[245] with spray coating of potassium sorbate on interlayers to plasticize and augment the adhesion between the films. This technology enhanced the mechanical, oxygen and water barrier and antimicrobial properties of the multilayer film due to the interaction between potassium sorbate with starch and PCL, and the film is an efficient material for packaging applications.

Starch foams are another material extensively used for packaging applications. Starch foams are usually prepared by softening and expanding the starch with water as blowing agent at high temperature and pressure.[232] The optimum concentration of water content for foam preparation is between 16% and 18%, whereas above and below this concentration would change the foam cell structure from open to closed.[246] The starch foam is an excellent replacement for polystyrene foam owing to its higher shock absorption, and antistatic, insulation and biodegradability property. However, the low mechanical strength of starch foam limits its application in food packaging. Thus, different studies have been conducted on improving the mechanical properties of starch foam by incorporating diverse agricultural residues such as malt bagasse,[247] kraft fiber & chitosan,[248] sesame cake,[249] cotton fibre & natural rubber,[250] fish scale,[251] and grape stalks[252] as reinforcing fillers for foam production. The integration of natural reinforcement has shown similar mechanical properties to those of commercial petroleum-based foams, and further enhances the biodegradation of the amorphous form

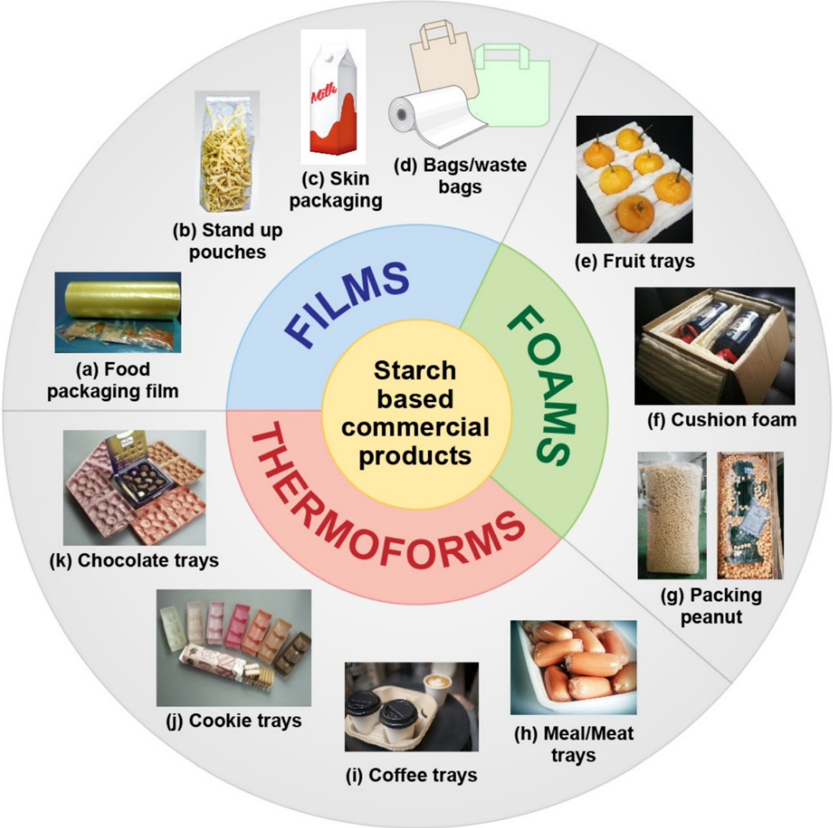


Fig. 15 Real-life applications of starch-based materials classified as: (i) films which includes (a) food packaging films, (b) stand-up pouches, (c) skin packaging and (d) bags/waste bags; (ii) foams which includes (e) fruit trays, (f) cushion foam, (g) packing peanuts; (iii) thermoforms which includes (h) meal/meat trays, (i) coffee trays, (j) cookies trays, (k) chocolate trays. ((a) (Reproduced from ref. 255 with permission from Elsevier, copyright 2019), (b) and (h) pixabay free images, pictures (e), (f), (g), (j), (k) have been taken from open access article under a Creative Commons licence attribution-non-commercial-no derivatives 4.0 international ref. 246, picture (i) from "Icons" of Microsoft office.)

of material. Reinforcement such as sesame cake contains a higher concentration of fibres and proteins (22.7% of fibres and 35% of proteins) that makes it ideal for food processing and in developing starch-based composites.[249,253] In addition, the presence of lipids in the hydrophobic components in sesame cake or palm oil improves the moisture resistance of the starch-based composite materials.[254] The above studies state that the mentioned compositions are ideal for short-term and low moisture content packaging applications such as dry foods.

Companies such as Novamont, Kuraray, Biotec *etc*. are leading manufacturers of thermoplastic starch-based blends and composites. These starch-based composite products have been used to develop materials such as thermoformed trays, films, foams, and for coatings. The materials developed from these manufacturers have been successfully commercialized in packaging products and are shown in Fig. 15. The commercialized products are classified here into 3 categories: films, foams and thermoformed products. The first category of commercialized starch-based film products includes food packaging films, stand-up pouches, skin packaging (a customized thin film on products, such as in dairy products, that allows product visibility, protection from the environment and minimizes tampering of products) and carry bags/garbage bags. The second category, foams, includes fruit trays, cushion foam, and packing peanuts that are used for protective packaging during shipping and transportation. The third category includes thermoform-processed products such as chocolate trays, cookie trays, coffee trays and meal/meat trays *etc*.

10. Conclusions

Biobased blends and composites derived from starch are an efficient replacement for petroleum-based products in single-use plastic packaging applications. The difficulty in using native starch for the development of biodegradable processed plastic products has been rectified by blending with other degradable polymers and/or by reinforcing with natural fibres/fillers or with organic fillers. The inherent hydrophilic and crystalline characteristics of starch have reduced the thermo-mechanical and barrier properties of the resultant starch-based blends and composites due to the inefficiency in achieving intermolecular interaction between blended polymers and reinforcements. Plasticization is an efficient methodology to enhance the thermal resistance and processability of starch by improving the intermolecular adhesion. The plasticization of starch has opened the window towards product development for the packaging industries. However, the performance limitation of starch-based blends and composites compared with the industrial standards that have been developed from petroleum-based products over the past decades is a serious challenge. Different techniques have been used to develop high-performance products from starch that are comparable with petroleum-based products. Functional techniques include the integration of compatibilizers, coupling agents, sole plasticizers, multiple plasticizers, bioactive agents and essential oils. Recently, research has proved that the presence of multiple plasticizers is an effective method to achieve the desired properties for starch-based blends and composites. Glycerol has been a widely used plasticizer for starch; however, the use of a combination of glycerol with an organic acid such as citric acid or tartaric acids could be better for minimizing the retrogradation and aging of the starch system and to reinforce plasticization efficiency. Most of the starch-based biodegradable blends have been prepared with glycerol-plasticized starch. Thus, there must be more research on using multiple plasticizers with starch-based biodegradable blends. Bioactive agents and essential oils are further found to be competent in bringing antimicrobial strength to the TPS blends. Selenium nanoparticles are bioactive agents that have been productively studied with cellulose-based blends and composite systems for packaging applications; however, studies on starch are limited. Similarly, more research must be conducted with essential oils, as these could provide better performance characteristics for starch-based blends and composites for packaging applications, and could be a replacement for harmful compatibilizers and plasticizers.

Research has further proved that the presence of compatibilizers in TPS blended with fillers and fibres is effective. Maleic anhydride-grafted biobased polymers blended with PS and maleic anhydride-grafted starch blended with other biobased polymers were additionally found to be effective in developing biobased blend systems for packaging applications. Another aspect to consider is the advancement of starch-based bio nanocomposite and agro waste-based composites in single-use packaging applications. Since starch is an abundant material obtained from natural resources, deriving starch from agro-waste products and utilizing it in developing starch-based blends and composite would be cost effective and would minimise agri-food waste production.

Multilayer films are a new and innovative technology; multilayer films could be developed with minimum material and better mechanical and barrier properties. TPS blend material coated with hydrophobic polymer layers could minimise the hydrophilic characteristics of the blend and would be useful for packaging film applications such as food packaging, garbage bags, carry bags *etc*. More studies on developing multilayer films from thermoplastic starch formulations with better processability, wettability, and biodegradability that could meet a wide range of packaging applications are needed in the future.

Abbreviations

AFM	Atomic force microscopy
CAGR	Compound annual growth rate
CAPS	Citric acid plasticized starch
DMA	Dynamic mechanical analysis
DP	Degree of polymerization
EB	Elongation at break
EGPS	Ethylene glycol-plasticized starch
AED	Activation energy of decomposition
EVOH	Ethylene-vinyl alcohol

FTIR	Fourier transform infrared spectroscopy
GPS	Glycerol-plasticized starch
HONPS	Hydroxy propylated and oxidised potato starch
ILPS	Ionic liquid-plasticized starch
LDPE	Low density polyethylene
MA	Maleic anhydride
MDI	Methylene-diphenyl diisocyanate
MT	Million tonnes
PBAT	Poly(butylene adipate terephthalate)
PBS	Poly(butylene succinate)
PCL	Polycaprolactone
PHA	Poly(hydroxyalkanoates)
PHB	Polyhydroxy butyrate
PHBV	Poly(hydroxyl butyrate-*co*-valerate)
PHEE	Poly(hydroxyester ether)
PLA	Poly(lactic acid)
PPC	Poly(propylene carbonate)
PS	Plasticized starch
PVA	Poly(vinyl alcohol)
RT	Room temperature
SEM	Scanning electron microscopy
TDI	Toluene-2,4-diisocyanate
TEM	Transmission electron microscope
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
T_m	Melting temperature
TM	Tensile modulus
T_{max}	Temperature at the maximum rate of weight loss
TPOS	Thermoplastic oxidized starch
TPS	Thermoplastic starch
TS	Tensile strength
USD	United States dollar
$\mathrm{V_a}$	V-anhydrous
$\mathrm{V_h}$	V-hydrate
WVTR	Water vapour transmission rate
WXRD	Wide-angle X-ray diffraction
XRS	X-ray scattering
XRD	X-ray diffraction

Author contributions

Project conceptualization, methodology, administration, funding acquisition and supervision, A. K. M. and M. M.; methodology, investigation, data analysis, writing—original draft preparation, A. S.; writing—review and editing, A. K. M., M. M., Q. L. and A. S.; all authors contributed to the discussion, reviews and approval of the manuscript for publication.

Conflicts of interest

The authors declare that they have no known conflict of interest that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the financial support of (i) the Ontario Research Fund, Research Excellence Program; Round 9 (ORF-RE09) Ontario Ministry of Economic Development, Job Creation and Trade, Canada (Project No. 053970 and 054345); (ii) the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), Canada/University of Guelph – HQP program; (iii) OMAFRA – Bioeconomy for Industrial Uses Research Program (Project No. 030251, 030486 and 030578); (iv) OMAFRA – Ontario Agri-Food Research Initiative (Project No. 055217) (v) the Agriculture and Agri-Food Canada (AAFC), Maple Leaf Food, Canada and Bank of Montreal (BMO), Canada through Bioindustrial Innovation Canada (BIC) Bioproducts AgSci Cluster Program (Project No. 054015, 054449 and 800148); and (vi) the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) program Project No. 460788 to carry out this study. This research also benefited from the facility funding to the Bioproducts Discovery and Development Centre (BDDC) lab by FedDev Ontario; Ontario Ministry of Agriculture, Food, and Rural affairs (OMAFRA); Canada Foundation for Innovation (CFI); Federal Post-Secondary Institutions Strategic Investment Fund (SIF); and matching funds from the province of Ontario and numerous University of Guelph Alumni.

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