

PREPARATION AND CHARACTERIZATION OF STARCH BASED EDIBLE/ BIODEGRADABLE FILMS

Soliman, E. A.¹; Manal S. Tawfik²; H. El-Sayed³ and Y. G. Moharram²

¹ Dept. of Chemical Industries, Moubark City of Scientific Res.

² Dept. of Food Science and Technology, Fac. of Agric. Alex. Univ.

³ Dept. of Chemical Industries, National Res. Centre, Egyptian Academy of Scientific Research and Technology

*Corresponding author. E-mail: mana92t@yahoo.com

ABSTRACT

To prepare good starch-based films the optimum concentration of high amylose starch was 8%. The various factors affecting the formation of these films were studied by measuring the physical (thickness and surface density), chemical (moisture content and water solubility), optical (light transmission and colour), mechanical (tensile strength and elongation at break) and barrier (water vapour and oxygen permeability) properties and examination of the ultrastructure of the prepared films. The suitable type and level of plasticizers used for preparing such films with good mechanical and barrier properties were glycerol at 40% or sorbitol at 50% level of starch weight. The sorbitol-plasticized starch films were more stable throughout the storage. Addition of glutamic acid as a co-plasticizer improved the different properties. The combination of starch with gelatin, agarose, agar, or PEG₁₀₀₀ were examined. Starch-agar blend films gave best physical, mechanical and barrier properties. Moreover, the IR spectra of these films were obtained and the characteristic IR bands for these spectra were assigned. Addition of glutamic acid and combination of starch with different polymers caused changes in the IR spectrum of starch film.

Keywords: Starch films, plasticizers, co-plasticizers, edible films, biodegradable films

INTRODUCTION

Petroleum-based plastic (polymeric) materials have become an integral part of contemporary life because of their many desirable properties such as durability and resistance to degradation. The non-degradable plastics accumulate in the environment at a rate of 25 million tons per year, and nearly represent 20% by volume of municipal solid waste (MSW). Packaging materials and containers represent approximately 30% of MSW by weight but appear more significant because they occupy two-third of trashcan volume due to its bulk. (Hunt *et al.*, 1990; Rowatt, 1993; Williams and peoples, 1996; Lee, 1996).

The authors are also considered the main culprit due to their non-degradability. In addition to the disposal problem of plastic packaging materials and their harmful effects on the environment, there are some problems concerning their use in contact with foodstuffs such as migration of various substances from the plastic material matrix to the food as monomers, byproducts from polymer degradation, solvent residues of polymerization and forming processes, plasticizers, stabilizers, and other additives that may have toxicological risk and/or off-flavour properties (Baner *et al.*, 1994; Tawfik and Huyghebaert, 1998).

Successful recycling requires waste gathering, sophisticated sorting processes and effective technologies. On the other hand, the solid waste landfilling sites throughout the world are limited and many of them on use

became at or near capacity. Further more, landfill leachate contamination of groundwater system is a major reason to close many of these landfills. (White, 1993; Poirier *et al.* , 1995).

Biodegradable polymeric systems fall into two main groups; starch-based polymeric systems which are blends or grafts of non-degradable synthetic polymer with starch and can be regarded as semi-biodegradable because of its breakdown primarily into non-degradable smaller fragments, and nonstarch-based systems which are completely biodegradable because they are fully composed of biodegradable polymers (White, 1993; Poirier *et al.* , 1995).

Although Edible / biodegradable polymer films are not feasible to entirely replace synthetic plastic packaging films, the interest in the study of these films has increased during the last decade. They are environmentally friendly materials and offer numerous advantages over other conventional synthetic packaging materials. Therefore, they have the potential to reduce and replace synthetic plastic materials in some food applications (Anker, 1996).

Polysaccharides are used for formulating edible and biodegradable films including, cellulose, starch, pectin, alginate, carrageenan, chitin and their derivatives. Generally, the films of such biopolymers are strong and highly effective against diffusion of various gases. Due to their hydrophilic nature, they exhibit poor water vapour barrier properties (Banker, 1966; Kester and Fennema, 1986; Gontard and Guilbert, 1994; Krochta and DeMulder-Johnston, 1997).

Generally polysaccharides films may be used in food system to control mass transfer and extend shelf life of food (McHugh *et al.* . 1996). They are used as an edible coating for nuts (Kaya and Maskan, 2003).

Starch is one of polysaccharides. The linear amylose molecules can arrange themselves next to each other to form hydrogen bonds between their hydroxyl groups. Such structure is responsible for the formation of starch films (Ring *et al.* , 1987).

Native starch usually exists in a crystalline beads or grains. To prepare thermoplastic starch films, such structure must be destroyed by application of pressure, heat, mechanical work and plasticizers, such as glycerol and low molecular weight polyhydroxy compounds, polyethers and urea (Shogren *et al.* , 1992).

In this study starch was used for preparing edible/biodegradable films. The influences of starch concentration, type and level of both plasticizers and co-plasticizers, combination with other polymers on the visual appearance, texture, physical and mechanical characteristics, as well as barrier properties of the starch based films were investigated.

MATERIALS AND METHODS

Materials:

This study used the following materials shown in Table 1 for preparing starch based films.

Table (1): Materials used in the study

Materials	Specifications	Source
1- Natural & synthetic polymers:		
High amylose starch (HAS).	70% amylose & 30% amylopectin.	American Maize Products Co., (Hammond, IN).
Gelatin type A (G 2500).	300 bloom.	Sigma Chemical Co., (St-Louis, USA).
Agarose type I-B (A0576).	≤7% moisture, ≤0.25% ash, ≤0.12% sulfate, Gel strength (1% gel) ≥1800 g/cm ² , gel point (1.5% gel) 36 ±1.5°C.	Sigma Chemical Co., (St-Louis, USA).
Agar (A5306)	Bacteriological grade.	Sigma Chemical Co., (St-Louis, USA).
Poyethylene glycol 1000 (P3515).	Average molecular weight (AMW) =1000.	Sigma Chemical Co., (St-Louis, USA).
2- Plasticizers:		
Glycerol.	MW = 92.09, density (d) = 1.26	Prolabo (Vaulx- en-Velin, France).
Sorbitol type 70 PC-USP.	70% aq. solution, MW= 182.17, d=1.28.	El-Gomhouria for Pharmaceuticals Co., (Cairo, Egypt).
Polyethylene glycol 400LP.	AMW= 380-420, d=1.12, viscosity at 20°C=85-105 cS, acidity (as acetic acid) ≤0.05%.	S.d. Fine Chem Ltd., (Mumbai, Inc).
Co-plasticizers:		
Glutamic acid.	99%, MW= 147.13, m.p.= 200-202°C.	Aldrich Chemical (Milwaukee, W).

Methods:

Starch based films preparation

Many formulations were suggested and used to prepare starch-based films with good mechanical and barrier properties. The optimum concentration of starch, the proper type and level of plasticizers, and the best level of glutamic acid as a co-plasticizer were determined. Film was prepared by dissolving plasticizers (2.4%, 3.2%, 4.0% glycerol; 3.2%, 4.0%, 4.8% sorbitol; 3.2%, 4.0%, 4.8% polyethylene glycol₄₀₀) with or without co-plasticizers (0.08%, 0.16%, 0.24% glutamic acid) in distilled deionized water, then starch (5%, 6%, 7%, 8%, 9%, 10%) was gradually added with stirring. The mixture was homogenized using an Ultra-TurraxT-25 homogenizer (IKA-Works, Cincinnati, OH), at 13,500 rpm for 1 min. The obtained suspensions were heated at 100-120°C at a rate of 4°C min⁻¹ with stirring using hot plate and stirrer. The resultant aquagels were spread on 20x20 cm² glass plates of depth of 1 mm using hand operated CAMAG thin layer chromatography spreader (Mutlitz, Switzerland). The spread films were left overnight in a cool incubator at 5°C. The plates were kept at ambient conditions for 5 hrs to complete drying. Films were removed from the plates and cut to appropriate size for testing their mechanical and barrier properties.

To improve the mechanical properties of starch-based films, the following blends; starch-agarose blends (8% starch; 0.005%, 0.01%, 0.02%, 0.03% agarose; 2.4% glycerol) ; starch-agar blends (8% starch; 0.005%, 0.01%, 0.02, 0.03% agar, 2.4% glycerol); starch-gelatin blends (8% starch; 0.08%, 0.16%, 0.24% gelatin, 2.4% glycerol); starch-polyethylene glycol₁₀₀₀ (8% starch, 0.4%, 0.8%, 1.2%, 1.6% polyethylene glycol₁₀₀₀ , 2.4% glycerol) were used to prepare starch based film.

Physical and mechanical properties

Film preparation for analysis: Before measurements of thickness, surface density, tensile strength, and elongation at break, the prepared films were conditioned for 48 hrs in a desiccator containing saturated calcium nitrate solution to maintain the relative humidity (RH) at $50 \pm 5\%$ and room temperature $20 \pm 2^\circ\text{C}$.

Thickness: Film thickness was measured using Tri-Circle 25 hand-held micrometer (China).

Surface density: The weight of 16 specimens ($5 \times 5 \text{ cm}^2$) of each film was weight to the nearest 1 mg. Average weight value divided by the area of the sample (25 cm^2) to calculate the surface density (mg/cm^2).

Tensile strength and elongation: Tensile strength (TS) and elongation percentage at break (E%) of 100mm long x 25mm wide film specimens were detrmind according to the American Standard Testing Methods (ASTM, 1991) using an Instron Universal Testing Machine (Instron Engineering C-operation, Canton, MA).

Optical properties

Light transmission: It was using a modified standard procedure for British Standards Institution (BSI, 1968). Samples of films were cut into a rectangle and placed on the internal side of spectrophotometer cell. The light absorbance values between 400- 800 nm at 10nm intervals were recorded for each sample using a UV-Vis Recording Spectrophotometer UV- 160A (Shimadzu Scientific Instument Corp., Columbia, Md).

Colour: It was assessed using a Lovibond Schofield Tintometer. The tintometer readings were further converted into CIE units using the visual density graphs supplied with the apparatus as described by Mackinnery and Little (1962).

Barrier properties

Film preparation for analysis: Before measurement of water vapour and oxygen permeabilities, the prepared films were conditioned for 48 hrs in a desiccator containing saturated lithium chloride solution to maintain the relative humidity (RH) at $11 \pm 5\%$ and room temperature $20 \pm 2^\circ\text{C}$.

Water vapour permeability: ASTM E-96 method (ASTM, 1990) was used to determine water vapour permeability (WVP) using cups described by Brandenburg *et al.* . (1993). All WVTR values were corrected for the air gap between the water surface and film underside according to McHugh *et al.* . (1993).

Oxygen permeability: It was determined as described by Davis and Huntington (1977).

Chemical properties

Moisture content: It was determined according to ASTM D 644-94 method (ASTM, 1994).

Film solubility: Strips of these films (5x5 cm²) were immersed in conical flasks containing 50 ml distilled water, covered with aluminum foil, then held under slow agitation until all of the sample appeared to be dissipated. Film solubility was expressed as a time (min) required completing film solubility (Ayyad, 1996).

Microstructure

Scanning Electron Microscope (SEM) type Joel JSM 5300 (Joel Ltd., Tokyo, Japan) was used to investigate the microstructure of the prepared films. Samples of these films were attached to the aluminum stubs with double sided tape, and then coated with 60:40 gold-palladium alloy by a Joel JFC-1100E sputter coater to a thickness of 100 Å. Samples were examined using an accelerating voltage of 15 Kv (Sawyer and Grubb, 1987).

Infrared spectrum

Genesis II Fourier Transform Spectrophotometer (FTIR) (Mattson Instruments, Madison, WI) equipped with a deuterated triglycine sulfate detector was used for spectral scanning of bio-based films in 4000 - 400 cm⁻¹ range at a resolution of 2 cm⁻¹ using 200 scan. The spectrometer controlled by an IBM-compatible Pentium 200 MHz PC running under Windows based Winfirst Software (Microsoft Corporation). Background spectra were collected every 30 min, and each sample spectrum was ratioed against the most recently collected background spectrum (Jaenfilis and Galloy, 1990)..

RESULTS AND DISCUSSION

Starch concentration

Because of the most of starches consists of 25% amylose and 75% amylopectin (deMan, 1990), high amylose starch, 75% amylose was suggested in this study for film preparation. Starch consists primarily of branched and linear chains of glucose molecules, named as amylopectin and amylose, respectively. Amylose is essentially a linear molecule with a few branches, whereas amylopectin is a highly branched molecule. Preponderance of amylose in starches gives stronger films. Branched structure of amylopectin generally leads to films with different mechanical properties, such as decreased tensile stress (Tharanathan, 2003). As shown from the results in Table (2), the concentrations of starch used in film preparation ranged from 5 to 10%. According to the results in Table 2 the proper concentration of starch to prepare films with good visual appearance, texture, physical, mechanical and barrier properties was 8%. Increasing starch level up to 10% in preparing such films may lead to the absence of homogeneous structure, increase of hydrophilic nature as a result to the differences in structure of the formed films. As illustrated from Fig. (1), the surface of starch film containing 8% starch was more even, nearly free from pinholes or pores with a relatively tight structure. Such characteristics were mainly due to relatively homogeneous orientation of the polymer chains, especially amylose ones. Rise or reduce starch level than 8% in starch films

affected the distribution, orientation and packing of the starch polymer chains into swollen granules.

Fig. 1: SEM Photomicrographs of starch film prepared using 8% starch concentration.



Types and levels of plasticizers

As shown in Table (3) different levels of three types of plasticizers, glycerol (Gly), sorbitol (S), and polyethylene glycol₄₀₀ (PEG₄₀₀) were used. These plasticizers differ in their polarities, molecular weight (MW) and molecular size (MS). Starch films plasticized with sorbitol were more clear (more light transmission) with higher tensile strength, lower thickness, solubility period, moisture content, elongation at break, water vapour and oxygen permeability than those plasticized with glycerol. Such variations can be attributed to the differences in polarity, molecular weight and molecular size between glycerol and sorbitol. The addition of plasticizers overcomes starch film brittleness and improves flexibility and extensibility. Plasticizers must be compatible with the film-forming polymer. They reduce intermolecular forces and increase the mobility of the polymer chains. Hydrophilic compounds such as polyols (glycerol, sorbitol and polyethylene glycol) are commonly used as plasticizers in hydrophilic film formulations (Gontard et al.,1993). The surface of the films plasticized with both glycerol and sorbitol was nearly regular, free from cracks or pinholes, with a relatively crystalline structure (Fig 2). Increasing level of both two types of plasticizers to 50% of starch weight associated with the rise of packing density and compactness of starch polymer chains. Such changes led to orientation of starch polymers chains, particularly with the glycerol plasticized films which also had the high moisture content.

Table 2: Influences of starch concentration on properties of starch-based films.

HAS (%)	Visual appearance & texture	Thickness (µm)	Surface density (mg/cm ²)	Light transmission (%)	Solubility period (min.)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%)	Water vapour permeability (g. mm. m ⁻² h ⁻¹ 'KPa ⁻¹)	Oxygen permeability (cm ³ .µm.m ⁻² .d ⁻¹ .KPa ⁻¹)
5	Translucent & smooth	47±3	5.5±1.0	63.79±1.00	6.92±0.41	8.71±0.25	1.4±0.2	1.2±0.3	19.8±1.7	27.4±2.5
6	Translucent & smooth	54±2	6.5±0.7	62.01±1.04	7.42±0.16	8.31±0.43	1.9±0.4	1.7±0.2	16.2±0.9	25.8±1.9
7	Translucent & smooth	80±6	9.6±0.8	61.53±0.36	7.20±0.09	9.34±0.35	2.6±0.3	1.8±0.4	14.1±0.6	26.1±1.4
8	Translucent & smooth	86±4	11.0±0.8	60.52±1.23	7.64±0.26	10.49±0.40	3.7±0.4	1.8±0.5	13.2±0.7	25.5±1.8
9	Translucent & smooth	85±9	11.2±1.0	60.14±2.00	7.85±0.30	10.74±0.28	3.6±0.7	1.4±0.2	13.7±1.1	24.6±2.0
10	Slightly opaque & rough	84±6	11.5±0.9	55.21±0.96	7.65±0.25	10.98±0.35	3.7±0.2	1.1±0.2	13.4±1.2	27.1±1.8

HAS, high amylose starch

Reported values for each property are means of three replications ± standard deviation but for tensile strength and elongation at break are means of five replications ± standard deviation.

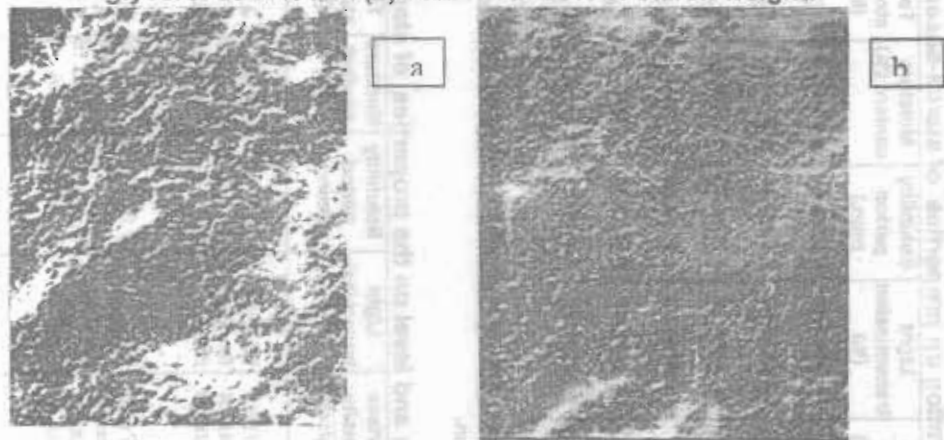
Table 3: Influences of plasticizer type and level on the properties of starch-based films.

Plasticizer type & level	Visual appearance & texture	Thickness (µm)	Surface density (mg/cm ²)	Light transmission (%)	Solubility period (min.)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%)	Water vapour permeability (g. mm. m ⁻² h ⁻¹ 'KPa ⁻¹)	Oxygen permeability (cm ³ .µm.m ⁻² .d ⁻¹ .KPa ⁻¹)
Glycerol										
30%	Almost clear & smooth	79±6	10.7±0.6	62.96±2.04	7.98±0.38	8.86±0.40	3.2±0.3	1.7±0.5	15.3±0.7	22.4±1.6
40%	Almost clear & smooth	58±3	11.4±0.4	61.45±2.20	7.09±0.33	9.72±0.26	3.8±0.2	1.6±0.3	14.1±1.2	25.1±2.4
50%	Almost clear & smooth	87±5	11.2±1.0	60.33±1.86	6.75±0.24	10.58±0.23	2.6±0.3	0.9±0.2	16.4±1.0	23.8±2.7
Sorbitol										
40%	clear & smooth	78±7	10.7±0.8	65.06±2.00	7.63±0.28	5.59±0.18	3.4±0.1	1.4±0.3	5.7±1.1	16.7±1.1
50%	clear & smooth	74±6	9.8±0.7	64.75±0.80	7.55±0.20	5.78±0.24	3.7±0.2	1.1±0.3	6.0±0.8	20.6±1.8
60%	clear & smooth	73±4	9.4±1.1	64.12±0.78	7.00±0.08	5.81±0.16	3.5±0.4	1.0±0.1	6.3±0.4	20.9±2.1
PEG ₄₀₀										
40-60%		NA	NA	NA	NA	NA	NA	NA	NA	NA

Reported values for each property are means of three replications ± standard deviation but for tensile strength and elongation at break are means of five replications ± standard deviation.

Recently, many works dealt with the addition of plasticizers to pure starch-based materials to overcome film brittleness caused by high intermolecular forces. Plasticizers increase film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular volume. The most commonly plasticizers used in starch-based films are polyols, such as sorbitol and glycerol, they avoid cracking of the film during handling and storage (Gontard et al., 1993), affect gas, water vapor and solute permeabilities (Banker, 1996). Jongjareonrak et al. (2006) reported that films without glycerol were mostly brittle, and became flexible in the presence of glycerol, tensile strength generally decreased with increasing glycerol concentration from 25 to 75%. Generally, increasing the plasticizer level over 50% constrained from the regular gradation of starch polymer chains and subsequently reduced the regular structure, light transmission and other physical, mechanical and barrier properties of the resultant films.

Fig. 2: SEM Photomicrographs of starch films plasticized with (a) glycerol at 40% and (b) sorbitol at 50% of starch weight.

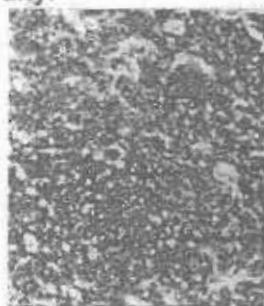


To complete the comparison between performance of glycerol and sorbitol as plasticizers in preparing starch films, storage stability of the films plasticized with 50% sorbitol or 40% glycerol of starch weight was determined throughout the storage at room temperature ($20\pm 2^\circ\text{C}$) and 50% relative humidity for 160 days (Table 4).

During storage of sorbitol-plasticized films the following changes occurred in the film structure; an increase in the homogenous orientation of starch polymer chains especially amylose and subsequently, gradual decrease in their local mobility freedom. The gradual increase in the interaction forces between starch polymer chains which mainly are hydrogen bonds. The changes led to exclude the sorbitol to the film surface after 120 days of storage. These variations were associated with crystalline structure, grainy texture and opaque appearance of such film. Mali et al. (2005) concluded that crystallinity of starch films increased with storage time and films without glycerol were more affected; plasticizer seemed to limit crystal

growth and recrystallization due to the interaction with the polymeric chains. The increases in crystallinity was reflected by the changes in mechanical properties with time, mainly in unplasticized films, with increase in Young's modulus and tensile stresses, decreases in strains at break and water vapor permeabilities. According to this data, it can be concluded that starch films plasticized with sorbitol were more stable than those plasticized with glycerol during storage for 120 days at room temperature and 50% RH (Fig.3). Notwithstanding, the high cost of sorbitol is the main problem of its utilization in preparing starch film.

Fig. 3: SEM Photomicrograph of starch film plasticized with sorbitol at 50% of starch weight after storage for 120 days at 20 ± 2 °C and 50% relative humidity.



Co-plasticizers level

To reduce the addition level of plasticizer and improve its plasticizing action, the efficiency of glutamic acid as a co-plasticizer was determined. The results of such experiment were presented in Table (5) who indicated that increasing glutamic acid to 2% was associated with slight changes in surface density, moisture content, thickness and oxygen permeability, no changes in the visual appearance and texture, marked decreases in light transmission, solubility period and tensile strength, and noticeable increases in elongation and water vapour permeability. Increasing glutamic acid concentration more than 2% caused an increase in thickness, opacity, and water vapour permeability of the resulted films. Meanwhile, this increase did not highly affect other quality parameters. Fig 4 showed starch film plasticized with glycerol at 30% and glutamic acid as a co-plasticizers at 2% of starch weight.

Combination of starch with other polymers

Gelatin; Different concentrations of gelatins 1-3% of starch weight, were blended with starch to prepare starch-gelatin blend films. As shown from Table (6), increasing gelatin level to 2% increased the opacity, thickness, surface density, elongation and water vapour permeability, reduced light transmission, solubility period and tensile strength, and caused slight changes in moisture content and oxygen permeability of the resulted films.

Table 4: Influences of aging at 20 ± 2°C and 50% RH on properties of HAS/G=2.5 and HAS/S=2.5-based films.

Time (days)	Visual appearance & texture		Thickness (µm)		Surface density (mg/cm ²)		Light transmission (%)		Solubility period (min.)		Moisture content (%)		Tensile strength (MPa)		Elongation at break (%)		Water vapour permeability (g. mm. m ⁻² h ⁻¹ KPa ⁻¹)		Oxygen permeability (cm ³ .µm.m ⁻² .d ⁻¹ .KPa ⁻¹)	
	HAS/G	HAS/S	HA/S/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S	HAS/G	HAS/S
2	Translucent & smooth	Translucent & smooth	86 ±4	72 ±2	11.4 ±0.5	9.4 ±0.3	62.35 ±1.26	66.10 ±1.08	7.33 ±0.26	7.72 ±0.14	12.32 ±0.22	5.71 ±0.16	3.6 ±0.2	3.7 ±0.4	2.0 ±0.6	1.3 ±0.4	12.8 ±0.8	5.8 ±0.6	24.5 ±1.3	20.1 ±1.2
10	Translucent & smooth	Translucent & smooth	75 ±5	70 ±3	10.1 ±0.2	9.3 ±0.2	64.74 ±0.36	65.27 ±0.76	8.03 ±0.38	7.57 ±0.08	6.88 ±0.31	5.60 ±0.14	5.5 ±0.6	3.9 ±0.6	1.6 ±0.3	1.2 ±0.1	12.6 ±0.3	6.0 ±0.7	25.3 ±1.6	19.2 ±1.0
20	Translucent & smooth	Translucent & smooth	76 ±4	68 ±3	10.4 ±0.4	9.1 ±0.2	64.67 ±1.04	65.82 ±0.35	8.10 ±0.06	7.65 ±0.16	6.46 ±0.14	5.53 ±0.26	6.8 ±0.4	4.1 ±0.5	1.4 ±0.2	1.2 ±0.2	11.6 ±1.3	6.2 ±0.4	28.5 ±1.0	18.7 ±1.4
40	Translucent & smooth	Translucent & smooth	75 ±3	67 ±2	10.5 ±0.5	9.0 ±0.1	64.83 ±0.22	65.75 ±0.28	8.15 ±0.32	7.43 ±0.37	6.57 ±0.25	5.62 ±0.13	7.2 ±0.3	3.7 ±0.2	1.2 ±0.2	0.9 ±0.1	11.1 ±0.6	5.6 ±0.1	28.1 ±0.8	19.6 ±1.5
80	Translucent & smooth	Translucent & smooth	73 ±3	65 ±3	10.3 ±0.3	8.8 ±0.2	65.01 ±0.62	64.38 ±0.46	8.13 ±0.12	7.67 ±0.17	6.49 ±0.32	5.63 ±0.09	7.5 ±0.5	3.9 ±0.4	1.1 ±0.3	0.8 ±0.1	10.7 ±0.9	5.7 ±0.4	25.7 ±1.5	19.2 ±1.2
120	Translucent & smooth	Slight opaque & smooth	72 ±2	64 ±2	10.1 ±0.6	8.6 ±0.2	64.85 ±0.77	62.43 ±0.96	7.96 ±0.28	7.56 ±0.30	6.48 ±0.15	5.68 ±0.12	7.2 ±0.6	3.7 ±0.1	1.1 ±0.1	0.6 ±0.1	10.0 ±0.7	8.2 ±0.5	25.2 ±0.9	19.3 ±1.6
160	Translucent & smooth	Opaque & grainy	72 ±3	NA	10.1 ±0.1	NA	64.21 ±0.44	NA	7.83 ±0.15	NA	6.42 ±0.10	NA	7.4 ±0.2	NA	0.8 ±0.0	NA	9.9 ±0.4	NA	25.4 ±1.4	NA

HAS, high amylose starch; G, glycerol; S, sorbitol.

Reported values for each property are means of three replications ± standard deviation but for tensile strength and elongation at break are means of five replications ± standard deviation.

NA, not applicable.

Table 5: Influences of glutamic acid as a co-plasticizer on properties of starch-based films.

Glutamic acid proportions w/w of starch	Visual appearance	Thickness (µm)	Surface density (mg/cm ²)	Light transmission (%)	Solubility period (min.)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%)	Water vapour permeability (g. mm. m ⁻² h ⁻¹ KPa ⁻¹)	Oxygen permeability (cm ³ .µm.m ⁻² .d ⁻¹ .KPa ⁻¹)
Control	Translucent & smooth	79±6	10.7±0.6	62.96±2.04	7.98±0.38	8.86±0.40	3.2±0.3	1.7±0.5	15.3±0.7	22.4±1.6
1	Translucent & smooth	81±8	10.7±0.2	52.12±0.34	6.55±0.25	8.02±0.32	3.7±0.2	2.4±0.2	17.2±1.2	23.6±1.4
2	Translucent & smooth	80±6	10.4±0.2	49.95±1.50	6.17±0.36	9.33±0.25	2.8±0.1	5.0±0.2	19.6±0.9	22.9±1.9
3	Translucent & smooth	84±5	10.8±0.4	43.28±1.76	6.25±0.18	9.78±0.22	2.2±0.3	7.6±0.4	20.5±0.5	23.8±1.2
4	Translucent & smooth	85±6	10.7±0.3	46.94±1.09	6.67±0.28	9.97±0.37	2.3±0.4	7.6±0.3	22.6±1.3	24.1±0.8

Reported values for each property are means of three replications ± standard deviation but for tensile strength and elongation at break are means of five replications ± standard deviation.

Meanwhile, at 3% gelatin level no film formed as a result to ungelatinization of a large amount of starch granules. Generally, these results were much closed with those obtained when glutamic acid was added as a co-plasticizers with glycerol to form starch films. Protein-based film are generally superior to polysaccharide-based film in their mechanical and barrier properties (Cuq et al. 1998). This is because proteins have a specific structure (based on 20 different monomers), which provides a wider range of potential via covalent bonds was found in protein-based films, not in the film from homopolymer polysaccharides (Cuq et al. 1995). The changes were clear from the examination of scanning electron microscope photomicrographs of such films.

Fig. 4: SEM Photomicrograph of starch film plasticized with glycerol at 30% and glutamic acid as a co-plasticizer at 2% of starch weight.



The films appeared hazy and containing many bypasses of gelatin through the starch film matrix. Moreover, these films showed starch in form of planer crystal into the starch matrix, confirmed the mentioned structural changes in starch film as a result to incorporation of gelatin, especially the incompatibility between starch and gelatin. Jongiareonrak et al. (2006) showed that films with greater protein content had higher thickness and mechanical properties but lower water vapor permeability than those with lower protein content. Gelatin has been attracted the attention for the development of edible films due to its abundance and biodegradability (Bigi et al. 2002).

Agarose; Data in Table (6) showed that increasing the level of agarose was associated with a reduction in thickness, surface density, light transmission, solubility period, tensile strength, elongation, water vapour permeability and oxygen permeability and slight changes in moisture content of the prepared films. The visual appearance and texture of such films did not change, since it was translucent and smooth respectively. Increasing agarose level caused a noticeable increase in regularity of the film structure. Such changes led to arrangement of the polymer chains of the formed films in semi-crystalline form. Such structure was responsible for the changes in the determined film quality parameters.

Table (6): Influences of combination of starch with gelatin, agarose, agar and polyethylene glycol₁₀₀₀ on properties of starch-based film.

Properties of polymer w/w of starch	Visual appearance & texture	Thickness (μm)	Surface density (mg/cm ²)	Light transmission (%)	Solubility period (min.)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%)	Water vapour permeability (g. mm. m ⁻² h ⁻¹ KPa ⁻¹)	Oxygen permeability (cm ³ . μm. m ⁻² . d ⁻¹ . Kpa ⁻¹)
Control										
Gelatin										
1	Translucent & smooth	85±3	11.4±0.4	61.45±2.20	7.9±0.33	9.72±0.33	3.8±0.2	1.6±0.2	14.1±1.2	25.1±2.4
2	Translucent & smooth	79±4	10.5±0.2	47.32±1.62	6.65±0.15	9.54±0.26	3.0±0.4	2.1±0.4	15.1±0.4	20.9±1.6
3	Translucent & smooth	84±3	11.2±0.4	45.97±0.76	6.75±0.25	9.81±0.24	2.1±0.2	8.3±0.6	16.4±0.8	23.0±0.9
Agarose		NA	NA	NA	NA	NA	NA	NA	NA	NA
6.25 x10 ⁻²	Translucent & smooth	83±7	10.8±0.5	53.16±0.87	6.02±0.10	10.18±0.45	3.6±0.3	2.2±0.3	12.7±1.3	25.5±2.0
12.50 x10 ⁻²	Translucent & smooth	83±5	10.7±0.7	52.36±1.32	6.23±0.38	10.08±0.18	3.2±0.7	1.8±0.5	12.3±1.6	22.4±2.2
25.00 x10 ⁻²	Translucent & smooth	82±6	10.3±0.4	49.85±0.97	6.18±0.22	9.79 ±0.32	2.3±0.5	1.1±0.1	11.6±1.8	21.2±1.1
37.00 x10 ⁻²	Translucent & smooth	80±8	10.0±0.1	47.36±2.00	6.10±0.03	9.84±0.46	2.2±0.8	1.3±0.2	11.0±1.4	20.0±2.1
Agar										
6.25 x10 ⁻²	Translucent & smooth Yellow	82±4	11.2±0.4	64.71±1.61	7.85±0.28	10.16±0.21	4.7±0.5	1.5±0.4	8.6±1.4	19.7±2.1
12.50 x10 ⁻²	Translucent & smooth Yellow	73±2	10.0±0.1	65.80±0.26	8.33±0.09	10.07±0.40	6.1±0.8	1.2±0.2	7.5±1.1	21.8±1.8
25.00 x10 ⁻²	Translucent & smooth Lighter yellow	70±3	9.7±0.3	65.20±0.95	8.50±0.17	9.97±0.34	6.8±0.4	0.7±0.1	7.8±1.2	18.9±1.4
37.00 x10 ⁻²	Translucent & slight roughness	72±5	9.8±0.3	60.81±1.34	7.60±0.07	10.06±0.25	4.3±0.6	1.1±0.2	10.4±1.0	24.6±1.9
PEG₁₀₀₀										
5	Translucent & slight roughness									
10	Some opacity & roughness	78±4	10.6±0.2	46.31±1.84	6.00±0.25	8.88±0.16	4.4±0.3	1.9±0.6	7.1±0.9	20.4±2.3
15	Some opacity & roughness	80±6	10.9±0.4	44.60±2.40	6.10±0.17	9.24±0.21	4.6±0.5	1.1±0.2	7.9±1.0	18.2±1.6
20	Some opacity & roughness	79±6	10.8±0.2	40.97±1.65	6.43±0.38	8.1±0.19	4.3±0.6	0.9±0.1	7.6±1.2	15.1±1.8
	Some opacity & roughness	81±3	11.4±0.1	36.26±0.94	6.67±0.50	7.86±0.22	5.1±0.4	0.5±0.1	6.9±0.4	14.9±1.3

Reported values for each property are means of three replications ± standard deviation but for tensile strength and elongation at break are means of five replications ± standard deviation.

NA, not applicable.

Agar; Results in Table (6) indicated that in general, incorporation of agar into the starch film reduced thickness, surface density, elongation, water vapour permeability and oxygen permeability, increased tensile strength and light transmission, and caused slight changes in solubility period and moisture content of the formed films. Increasing the level of agar more than 25×10^{-2} % of starch weight increased the opacity, tensile strength, water vapour permeability and oxygen permeability, lowered smoothness, light transmission, solubility period, and tensile strength of the film. Addition of agar at 12.5×10^{-2} % of starch weight gave the most homogeneous structure. Generally, it caused the same structural changes mentioned in case of agarose addition. Increasing concentration of agar up to the level of 25.0×10^{-2} % of starch weight decreased the compaction of the polymer chains and formation of tight structure for the resulted films and lowered its elasticity. It may also cause disruption of the starch-starch and starch-agar interaction forces which led to increase film permeability.

Polyethylene glycol₁₀₀₀; In general, incorporation of PEG₁₀₀₀ into starch film caused a slight increase in the opacity and roughness, a marked rise in tensile strength and noticeable decrease in other determined parameters, especially elongation at break, water vapour permeability, and oxygen permeability (Table 6). The above changes depended on the addition level of PEG₁₀₀₀.

Increasing the PEG₁₀₀₀ addition up to 10% of starch weight caused a noticeable reduction in light transmission, moisture content, tensile strength, elongation, water vapour permeability and oxygen permeability of the resulted films (Table 6). Addition of PEG₁₀₀₀ caused an increase in tightness, packing density and compactness of starch polymer chains. Such changes led to an absence of homogeneous orientation of the starch chains of the films. This may be due to the role of PEG₁₀₀₀ as filler.

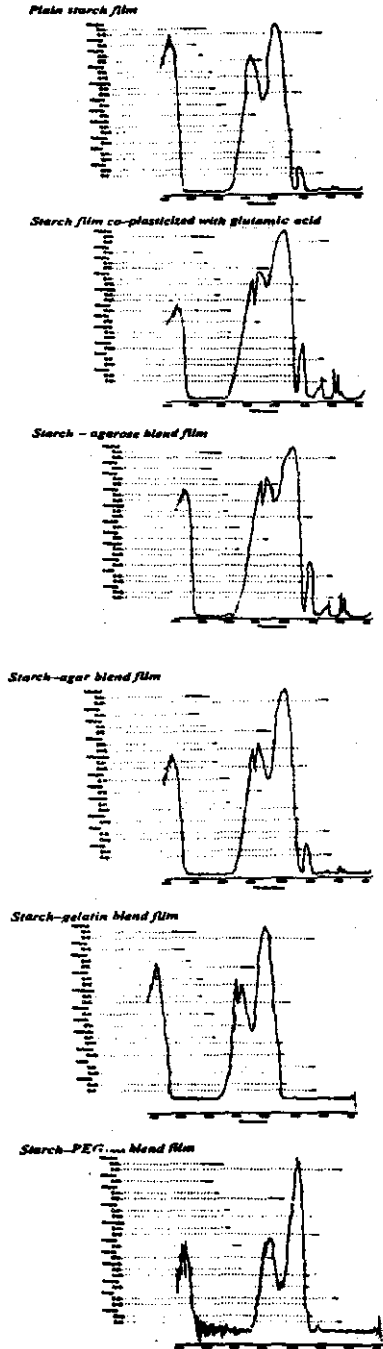
According to the previous results, the proper concentrations of gelatin, agarose, agar, and PEG₁₀₀₀ to prepare starch blend films with each of such polymers with good appearance, texture, physical, mechanical and barrier properties were 1, 37.5×10^{-2} , 12.5×10^{-2} , and 10% of starch weight, respectively (Fig 5).

Among these films, starch-agar blend films had the lowest thickness, water vapour permeability, the highest light transmission, solubility period and tensile strength. This film was translucent, with smooth texture and faintly yellow colour. Starch films are usually modified by the addition of plasticizers. Polyols (glycerol, sorbitol and polyethylene glycol) are commonly used as plasticizers (Gontard et al., 1993). These additives decrease the intermolecular attraction between adjacent polymeric chains, resulting in film flexibility and decrease in film strength (Donhowe & Fennema, 1993; 1994; Laohakunjit & Noomhorm, 2004).

IR-Spectra of starch-based films;

According to Fig. 6 and Table (7), the characteristic IR bands of pure starch film include the inter- and intra-molecular H bonds and O-H stretching (st.), C-H st., C=O st., O-H deformation (d.), C-H d., C-O st., C-H d. out-of plane bands.

Fig. 6: IR spectra of starch – based films



Generally, the complexity of a multicomponent film spectrum increases as constituents are added to the film. This increase is reflected by an increase characteristic bands intensity of the first film (before the addition). Such changes can be due to overlap the characteristic IR bands of the added component with the film spectrum and/ or appear other bands as a result to interact the multiple components of the film.

Table (7) : Characteristic IR bands of starch-based films.

Film	Characteristic IR bands
Pure starch	3605-3095 combination bands (O-H st. & Inter- and Intra-molecular H bonds). 2946; 2870 (C-H st.). 1656; 1640 (C=O st. in ester and acid). 1395; 1386; 1300; 1242; 1206 (O-H d. & C-O st.). 929; 850 (C-H d. out-of-plane).
Co-plasticized starch (with glutamic acid)	3546-3085 combination bands (O-H st. & Inter- and Intra-molecular H bonds) & N-H st.). 2968; 2860 (C-H st.). 1642 (C=O st. in ester and acid). 1411; 1355; 1338; 1242; 1207 (O-H d. & C-O st.). 926; 860 (C-H d. out-of-plane).
Starch-agarose blend	3610-3086 combination bands (O-H st. & Inter- and Intra-molecular H bonds). 2951; 2880 (C-H st.). 1644 (C=O st. in ester and acid). 1357; 1349; 1338; 1240; 1204 (O-H d & C-O st.). 927; 855 (C-H d. out-of-plane).
Starch-agar blend	3610-3197 combination bands (O-H st. & Inter- and Intra-molecular H bonds). 2965-2853 combination bands (C-H st.). 1658; 1640; 1629 (C=O st.). 1434; 1422; 1404; 1397; 1238; 1203 (O-H d. & C-O st.). 1072 (S=O st.) 925 (C-H d. out-of-plane).
Starch-gelatin blend	3580-3178 combination bands (O-H st. & Inter- and Intra-molecular H bonds & N-H st.). 2896; 2856; 2783; 2770 (C-H st.). 1690; 1646; 1681; 1652; 1640 (C=O st.). 1606; 1504 (C-C skeletal st.). 1436; 1430; 1411; 1403; 1381; 1219 (O-H d. & C-O st.). 929 (C-H d. out-of plane).
Starch-PEG ₁₀₀₀ blend	3546-3100 combination bands (O-H st. & Inter- and Intra-molecular H bonds). 2940; 2836 (C-H st.). 1656; 1632; 1614 (C=O st.). 1472; 1451; 1440; 1428; 1419; 1408; 1313; 1255 (O-H d. & C-H d. & C-O st. 941; 929 C-H d. out-of-plane).

St. =Stretching, d. =deformation

CONCLUSION

The optimum concentration of high amylose starch to prepare good starch-based films was 8%, the suitable type level of plasticizer used for preparing good starch-based films was sorbitol at 50% level of starch weight, Glutamic acid at 2% level could be as a co-plasticizer with glycerol to improve the different characteristics of the starch-based films and also lowered the cost of the film preparation.

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إعداد و توصيف أفلام النشا الغذائية و القابلة لتتحلل الحيوي

عماد علي سليمان^١، منال سعيد توفيق^٢، حسني السيد^٣، يحيى محرم^٢

^١ قسم الكيمياء الصناعية، مدينة مبارك للأبحاث العلمية

^٢ قسم علوم و تكنولوجيا الأغذية، كلية الزراعة، جامعة الإسكندرية

^٣ قسم الكيمياء الصناعية، المركز القومي للبحوث، الأكاديمية المصرية للبحث العلمي و التكنولوجيا.

تم تحضير أفلام النشا من النشا عالي الاميلوز و كان التركيز الأمثل هو ٨%. تم دراسة العوامل المؤثرة علي شكل الفيلم بقياس الخواص الفيزيائية (السك، الكثافة السطحية)، و الخواص الكيميائية (محتوي الرطوبة، الذاتية في الماء)، و الخواص الضوئية (النفاذية الضوئية، اللون)، و الخواص الميكانيكية (قوة الشد، الاستطالة)، و خواص الحجز (نفاذية الماء، الأوكسجين)، كذلك اختبار التركيب القوي للأفلام المحضرة. كان النوع الأمثل للملدنات المستخدمة لتحضير أفلام النشا ذات الخواص الميكانيكية و خواص الحجز الجيدة باستخدام الجليسرول عند تركيز ٤٠% أو السوربيتول عند تركيز ٥٠%. استخدام السوربيتول كمادة ملدنة مع أفلام النشا كان أكثر ثباتا أثناء التخزين. إضافة حمض الجلوتاميك كمساعد تلدين يحسن من الخواص لمختلفة. تم اختبار دمج النشا مع الجيلاتين، الأجاروز، الأجار، البولي إيثيلين جليكول ١٠٠٠. أنتجت أفلام النشا - الأجار أفلام لها خواص فيزيائية و ميكانيكية و خواص حجز جيدة. بالإضافة إلى ذلك تم استخدام طيف الأشعة تحت الحمراء لهذه الأفلام و تم التعرف علي خواص حزم الامتصاص. إضافة حمض الجلوتاميك و خلط النشا مع بوليمرات أخرى أدى إلى حدوث تغيرات في حزم طيف الأشعة تحت الحمراء لفيلم النشا.