J Food Sci Technol (February 2018) 55(2):532–539
https://doi.org/10.1007/s13197-017-2962-4

ORIGINAL ARTICLE

Edible films developed from carboxylic acid cross-linked sesame protein isolate: barrier, mechanical, thermal, crystalline and morphological properties

Loveleen Sharma[1] · Harish Kumar Sharma[1] · Charanjiv Singh Saini[1]

Revised: 25 October 2017 / Accepted: 26 October 2017 / Published online: 18 November 2017

Abstract Films were developed from sesame protein crosslinked with three different carboxylic acids (malic acid, citric acid and succinic acid) at 1, 3 and 5% (w/w, on protein isolate basis). The effect of crosslinking on physical, mechanical, thermal and morphological properties was studied. Succinic acid crosslinked films exhibited least water vapor permeability the highest tensile strength and overall showed superlative properties among other films. X-ray diffraction showed single main crystalline reflection at 20° indicating amorphous structure of films. DSC curves of films indicated single melting peak in the range of 103–161 °C. All films exhibited weight loss in three stages. FTIR exhibited peak at 1700 cm^{-1} confirming crosslinking reaction between carboxylic acids and protein. Crosslinked films were compact, nonporous and smooth as compared to film from native sesame protein isolate.

Keywords Sesame protein isolate · Cross linking · Carboxylic acid · Tensile strength · Transparency · Films

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s13197-017-2962-4) contains supplementary material, which is available to authorized users.

✉ Charanjiv Singh Saini
charanjiv_cjs@yahoo.co.in

Loveleen Sharma
sharmaloveleen88@gmail.com

Harish Kumar Sharma
profh.sharma27@gmail.com

[1] Department of Food Engineering and Technology, Sant Longowal Institute of Engineering and Technology, Longowal, Punjab 148106, India

Practical applications

Crosslinking is a common approach to improve the performance of films from natural polymers. However, the chemicals used for crosslinking are expensive, toxic and limits the use of films for food applications. Citric acid, succinic acid and malic acid are natural carboxylic acids and can also be produced through fermentation. Edible films were developed from native and carboxylic acid crosslinked sesame protein isolate. Films from crosslinked sesame protein isolate resulted in good mechanical, barrier, thermal and morphological properties and can be used for the packaging or coating applications of fruits and vegetables and also provides partial barrier to moisture and considerate in reducing moisture loss. So crosslinking with poly carboxylic acids effectively improved the overall properties of films and can be used as a substitute for nonedible crosslinking agents. So far, there is no work reported on carboxylic acid crosslinking of sesame protein isolate, as well as preparation of edible films. So the crosslinked films can be used for the packaging applications of food products.

Introduction

Plant proteins are widely used for making films and have continuously increasing interest of researchers due to their utilization in food packaging due to environment concerns and demand of high quality products. Proteins based on plant and animal sources are favoured for films especially for food applications because of their biodegradability, non-toxicity, excellent water vapour permeability (Tao et al. 2015; Ket-on et al. 2016). So far, various types of protein have been used to develop edible films, which include corn zein, wheat gluten, soy protein, mung bean protein, and peanut protein (Bourtoom 2008; Saglam et al. 2013). Sesame (*Sesamum indicum*) is a tropical, oil seed crop. After oil extraction, sesame meal is obtained as a by-product, which is utilized as an animal feed in India. Sesame meal contains about 35–40% protein.

Crosslinking is a common approach to improve the performance of films from natural polymers. However, the chemicals used for crosslinking are expensive, toxic and limits the use of films for food applications. Carboxylic acids such as citric, malic and succinic acids have been used to improve the properties of cellulose, proteins, starch and protein based films (Yang et al. 1997; Reddy and Yang 2010; Reddy et al. 2012). Generally, appearance and resistance to wrinkling are improved by crosslinking of cotton and silk fibers but it also has been observed that the mechanical properties and water stability of regenerated protein fibers can be improved by crosslinking with carboxylic acids (Yang et al. 1996). In dry crosslinking, at least three carboxylic groups are necessary for crosslinking reaction while in wet crosslinking, carboxylic acids with less than three carboxylic groups such as malic acid (with two carboxylic groups) can be used (Reddy et al. 2009). Citric acid, malic acid and succinic acid are cheap and non-toxic organic acids suitable for crosslinking.

The objective of this work was to develop the edible film by crosslinking sesame protein isolate with three organic acids i.e. citric acid, malic acid and succinic acid and to study the effect of cross linking on solubility, transparency, color, barrier, mechanical, thermal, crystalline, structural and morphological properties of edible film.

Materials and methods

Sesame variety RT-127 was purchased from Chandigarh, India. Organic acids (citric acid, malic acid and succinic acid) and all other chemicals and solvents were of analytical grade and obtained from Merck.

Isolation of sesame protein isolate (SPI)

Sesame protein isolate (SPI) was prepared by alkali method developed by Onsaard et al. (2010).

Crosslinking of sesame protein isolate

For the modification of sesame protein isolate, method of alkali catalysed wet crosslinking described by Reddy et al. (2009) with minor modifications was followed. Sesame protein isolate was crosslinked using citric acid, malic acid and succinic acid at 1, 3 and 5% (w/w, on protein isolate basis) levels. Protein isolates were added in solution of citric acid, malic acid and succinic acid. pH 9 was maintained for all solutions by 1 N NaOH. Solutions were stirred for 1 h at 90 °C at 500 rpm. Isolates were dried at 50 °C in vacuum oven for 6 h and then annealed (dry heated) at 100 °C for 1 h in hot air oven.

Film preparation

Films were prepared by dissolving crosslinked protein isolates and 10% of glycerol (v/w, on protein basis) in 100 ml of total film forming solutions. Citric acid crosslinked protein (CACP), malic acid crosslinked protein (MACP) and succinic acid crosslinked protein (SACP) were dissolved in distilled water. pH of solutions were adjusted to 12 and heated with stirring at 90 °C for 20 min in water bath, glycerol was added and solutions were constantly stirred for 30 min. The solution was filtered through muslin cloth and casted on Teflon coated trays at 50 °C for 16 h and peeled off for testing.

Film thickness and conditioning

Thickness of all the films i.e. malic acid crosslinked film (MACF), succinic acid crosslinked film (SACF), citric acid crosslinked film (CACF) and native sesame protein isolate film (SPF) was maintained at constant value of 0.15 mm by pressing films, providing heat and pressure under thermostat control presser. All film specimens were conditioned for 48 h in a humidity test chamber at 50% relative humidity (RH) and 25 °C before testing.

Water vapor permeability (WVP)

The gravimetric modified cup method based on ASTM-E96/E96M (2014) was used to determine the WVP of edible films.

Mechanical properties

Tensile strength, Elongation at break (E, %) and Young's modulus of films were measured according to ASTM 828-97 (ASTM, 2002).

Moisture content

Moisture content of film was analysed as described by Rhim et al. (1998). The determination of moisture content was done in triplicate and the average value was recorded.

Solubility

Solubility of films were determined according to method described by Wu et al. (2013).

Transparency

Film transparency was measured according to method described by Han and Floros (1997) by using a UV–visible recording spectrophotometer (Model UV160U; Shimadzu, Kyoto, Japan).

Color characteristics

Color value of samples were measured in terms of L*, a*, b*, hue, chroma and ΔE values were carried out using a Hunter colorimeter Model D 25 optical Sensor (Hunter Associates Laboratory Inc., Reston, VA, USA).

Fourier transform infrared spectroscopy (FTIR)

FT-IR was recorded on a Perkin Elmer Spectrum 400 (US). FT-IR spectrum of film samples were recorded in transmittance mode at the 4000–400 cm^{-1} region at room temperature.

Thermal properties

The thermal properties of the films were measured using a Differential Scanning Calorimeter (DSC-028 Mettler–Toledo Inc., Columbus OH). Samples were scanned at a heating rate of 10 °C/min from 0 to 300 °C. Thermal Gravimetric Analysis (TGA) was determined with a Mettler Toledo TGA/SDTA System (Greifensee, Switzerland) and the thermogram was obtained in the range of 30–600 °C at a rate of 10 °C/min.

X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of films were measured using Panalytical- X'pert PRO MRD X-ray diffractometer with CoKa < 1 radiation. Diffractograms were taken between 5° and 55° (2 h) at a rate of 1.20°/min (2 h) and with a step size of 0.05° (2 h).

Morphological properties

The microstructure of the surface of dried films was examined by Scanning Electron Microscope (JEOL, JSM 6300 SEM, Tokyo, Japan). The films were fractured, mounted on aluminium stubs using double sided adhesive tape, sputtered with a thin layer of gold. All samples were tested at an accelerating voltage of 7 kV.

Statistical analysis

Each experiment was carried out in triplicates runs. StatSoft (Statistica 12.0) was used to evaluate data by analysis of variance (ANOVA) and Duncan's multiple range test was used to evaluate significant ($P \leq 0.05$) differences.

Results and discussion

Water vapor permeability (WVP)

WVP is assumed to be independent of the water vapor pressure gradient applied across the films but in case of edible film, containing hydrophilic materials such as protein depends on this ideal behaviour due to interaction of permeating water molecules with polar groups in the film structure (Hagenmaier and Shaw 1990). It should be low as possible as the main function of an edible film or coating is to hinder the moisture transfer between surrounding atmosphere and food material. WVP (Table 1) was significantly improved with the increased concentration of crosslinker. Among the three organic acids, crosslinked films prepared from 5% succinic acid showed the least permeability of water. WVP lowers with the increased concentration of all three crosslinkers. Crosslinked films prepared from 5% malic acid and 5% citric acid also showed lower permeability of water as compared to films prepared from 1% crosslinked proteins. Highest WVP was observed for film prepared from native (uncrosslinked) protein. Crosslinked proteins make the network of film compact leading to reduced diffusion of water vapors. Crosslinked sesame protein films showed lowest WVP as compared to films from other sources as reported by Saremnezhad et al. (2011) for faba bean protein films and Reddy et al. (2012) for crosslinked peanut protein films.

Mechanical properties

Table 1 summarizes the Tensile Strength, % Elongation and Young's Modulus of native and crosslinked sesame protein films. Intermolecular interactions and intermolecular crosslinking strongly influence the mechanical properties of films (Sinz 2006; Chambi and Grosso 2006). The highest tensile strength was observed in film crosslinked with succinic acid and lowest was observed for a film prepared from native sesame protein. Tensile strength of native sesame protein films was 3.03 MPa and tensile strength varied from 3.68 to 7.03 MPa. Among malic acid, citric acid and succinic acid crosslinked films, highest tensile strength was observed for films crosslinked at 5% and lowest for 1% concentration. Tensile strength and Young's modulus of films were improved by increasing the concentration of cross linker with all three organic acids.

Table 1 Mechanical properties, WVP, solubility, transparency and moisture content of native and crosslinked edible films

Parameters	Native film	MACF			CACF			SACF		
		1%	3%	5%	1%	3%	5%	1%	3%	5%
Tensile strength (MPa)	$3.56^{j} \pm 0.08$	3.68 ± 0.37^{i}	4.40 ± 0.20^{f}	5.79 ± 0.45^{d}	4.16 ± 0.20^{h}	5.56 ± 0.15^{e}	6.56 ± 0.30^{b}	4.2 ± 0.1^{g}	6.33 ± 0.15^{c}	7.03 ± 0.15^{a}
Percent elongation (%)	$5.00^{c} \pm 0.25$	6.30 ± 0.20^{a}	4.40 ± 0.30^{e}	4.76 ± 0.25^{d}	6.15 ± 0.04^{b}	3.43 ± 0.40^{f}	2.56 ± 0.05^{h}	6.17 ± 0.12^{b}	2.85 ± 0.05^{g}	1.39 ± 0.34^{i}
Young's modulus (N/m^2)	$0.147^{h} \pm 0.001$	0.16 ± 0.03^{g}	0.21 ± 0.04^{e}	0.34 ± 0.03^{c}	0.16 ± 0.04^{g}	0.31 ± 0.04^{d}	0.42 ± 0.01^{b}	0.16 ± 0.02^{g}	0.2 ± 0.01^{f}	0.86 ± 0.003^{a}
WVP ($g.m/Pa.s.m^2 \times 10^{-11}$)	$1.160^{a} \pm 0.03$	0.25 ± 0.036^{b}	0.14 ± 0.035^{e}	0.09 ± 0.003^{f}	0.17 ± 0.005^{e}	0.09 ± 0.003^{f}	0.05 ± 0.002^{f}	0.15 ± 0.03^{d}	0.08 ± 0.002^{f}	0.04 ± 0.002^{f}
Solubility (%)	$51.80^{h} \pm 0.15$	71.83 ± 0.76^{a}	66.66 ± 1.5^{b}	61.00 ± 1.00^{c}	60.73 ± 0.64^{d}	58.73 ± 0.64^{e}	54.03 ± 1.00^{g}	58.00 ± 0.73^{e}	55.80 ± 0.7^{f}	51.13 ± 1.02^{i}
Transparency (%)	12.33 ± 0.26^{a}	9.46 ± 0.03^{g}	10.36 ± 0.01^{d}	9.15 ± 0.02^{h}	9.90 ± 0.02^{f}	9.89 ± 0.03^{f}	10.65 ± 0.02^{a}	10.37 ± 0.04^{d}	10.09 ± 0.02^{c}	10.12 ± 0.03^{e}
Moisture content (%)	21.42 ± 0.01^{a}	20.25 ± 0.21^{b}	20.04 ± 0.50^{d}	19.72 ± 0.31^{e}	20.15 ± 0.41^{c}	19.00 ± 0.13^{f}	18.45 ± 0.20^{g}	20.01 ± 0.53^{d}	$18.00^{h} \pm 0.45$	$16.10^{i} \pm 0.12$

Mean ± SD values in row followed by different letters are significantly ($P \leq 0.05$) different (DMRT). Results are means of triplicate determinations

MACF malic acid crosslinked films, *CACF* citric acid crosslinked films, *SACF* succinic acid crosslinked films

However, percentage elongation decreased with increased level of crosslinking. Intermolecular crosslinks in the protein were improved and strong linkages were formed due to which strength and Young's modulus increased. However due to crosslinking, mobility of protein molecules reduced leading to low flexibility and resulted in decreased percentage elongation. Reddy et al. (2012) reported increased tensile strength, Young's modulus and decreased percentage elongation of citric acid crosslinked pea nut protein films. Singh et al. (2010) reported tensile strength of 12.00–16.00 MPa in zein films containing salicylic acid and acetyl salicylic acid.

Moisture content and solubility

Higher water defiance of films is one of the most essential properties for higher water activity foods from a packaging point of view. The amount of water available in films was measured by moisture content (Table 1). Crosslinking of proteins with all three organic acids affected the moisture content of films. Moisture content for crosslinked films varied from 16.10 to 20.25%. Moisture content of films reduced with increased concentration of crosslinker. Films prepared from succinic acid crosslinked sesame protein showed lowest moisture content as compared to other films. Films prepared from malic acid, citric acid and succinic acid crosslinked proteins at 1% concentration did not show significant effect on moisture content. Crosslinking effect prevents the adsorption of water molecules which results in low moisture content.

Solubility of edible films in water represents the applicability of film to pack food rich in moisture and act as an important factor that determines biodegradability. Similar trend was observed for solubility of films as in case of moisture content. Compact films with strong network from 5% succinic acid crosslinked sesame protein films showed least solubility. Films from native sesame protein exhibited highest solubility.

Transparency

Transparency of films, applied for food packaging or coatings directly affects the consumer acceptability (Chen et al. 2010). Transparency of film from uncross-linked sesame protein was observed to be higher as compared to films prepared from succinic acid, malic acid and citric acid crosslinked sesame proteins (Table 1). Films prepared from crosslinked proteins showed transparency in the range of 9.15–10.65%. Sesame protein un-crosslinked and crosslinked films exhibited higher transparency than synthetic films, e.g. polyethylene (1.67%) and oriented polypropylene (1.51%) and films made from whey protein isolate (Ramos et al. 2013).

Color

Crosslinked films exhibited higher L* and lower a* values which represents lighter color of films as compare to native film which was darker in color. Among all the crosslinked films, 5% citric acid crosslinked films showed the higher L* value. (45.33 to 55.00), a* value ranged from 7.19 to 10.06 and b* value from 1.30 to 17.54, ΔE value from 0.13 to 1.68, Hue value from 8.11 to 60.11 and chroma from 9.09 to 20.22 (Table 2). a* value and b* value decreased with crosslinking of films at different levels which showed decrease in redness and decrease in yellowness of films. Darker color of native film might be due to color of protein isolate, alkaline pH conditions and oxidation reactions during film formation. Depletion in darkness with crosslinking might be due to the fact that organic acids reduce the oxidation reactions occurred during film formation.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of edible films from native sesame protein isolate and citric acid, malic acid and succinic acid crosslinked sesame protein isolate films at 5% (highest) level are shown in Fig. 1. The main absorption peaks were located in spectral range (1) 800–1150 cm^{-1} thus being attributed to bands of glycerol. (2) 1200–1250 cm^{-1} attributed to amide III band due to combination of N–H in plane bending with C-H vibrations. (3) 1400–1550 cm^{-1} associated with amide II band due to N–H bending. (4) 1600–1650 cm^{-1} represents amide I band governed by stretching vibrations of C=O and C–N groups. (5) 1700–1750 cm^{-1} attributed to carbonyl groups with disulphide bridges formed due to crosslinking. (6) 3842–3550 cm^{-1} (Amide A) and 3000–2100 cm^{-1} (Amide B), attributed to NH stretching vibrations. It is exclusively localized on the NH group and thus insensitive to the conformation of the polypeptide backbone. Its frequency depends on the strength of the hydrogen bond (Barth and Zscherp 2002). (7) Peaks at 3350–3450 cm^{-1}. The band at 1734 cm^{-1} (indicated by an arrow) is due to the carboxyl, amide and carbonyl bands. Presence of carbonyl peaks certifies the chemical linkages among the three organic acids and sesame protein isolates. Amide I and amide II bands are two major bands of the protein infrared spectrum and are conformationally sensitive. The extent to which the several internal coordinates contribute to the amide I normal mode depends on the backbone structure (Krimm and Bandekar 1986). Proteins are frequently referred to as having certain fractions of structural components (α- helix, β sheets etc.). Peaks in range of 1600 cm^{-1} in Amide I represent β sheets. Singh et al. (2009) found three major bands in Amide I region at 1685, 1650 and 1615 cm^{-1} in zein films. Aggregated proteins in which thermal denaturation was extensive, high content of β sheets structures are commonly found and moreover aggregation is followed by frequent formation of intermolecular antiparallel β sheets (Fabian et al. 1999; Lefevre et al. 2005).

Thermal properties

The properties of films were analysed in terms of thermal performance via DSC (Differential Scanning Calorimetry) and TGA (Thermo gravimetric analysis). DSC curves of melting all films showed single melting peak in the range of 103–161 °C and enthalpy values from 1120 to 500 MJ (Table 3). Films crosslinked with succinic acid at 5% showed highest temperature of melting peak at 161 °C. All films from succinic acid crosslinked sesame protein showed significantly higher temperature of melting peaks than films from citric acid and malic acid crosslinked sesame protein films. Increased concentration of crosslinker showed increase in melting temperature for all three organic acid crosslinked sesame protein films. Crosslinking stabilizes the proteins and increases the melting temperature. Also formation of strong cross-linkages and increased molecular weight due to crosslinking might be responsible for the increased melting point of crosslinked films. High melting point of succinic acid crosslinked films showed that succinic acid act as a strong crosslinker with sesame protein and formed the strongest film network among the all crosslinked sesame protein crosslinked protein films.

TGA scans for all films (Table 3) showed thermal stability of native and crosslinked sesame protein films. All films exhibit weight loss in three stages (temperature ranged between 129 and 450 °C). The first weight loss was observed at 130–170 °C which was due to removal of moisture from films. Second stage of mass reduction was observed at 278–320 °C which was due to evaporation of

Table 2 Color parameters for native and crosslinked edible films

Films	L*	a*	b*	ΔE	Hue	Chroma
Native	45.33	10.06	17.54	–	60.11	20.22
1% MACF	47.00	10.00	5.47	1.68	11.40	28.72
3% MACF	47.34	9.12	5.12	1.74	10.46	29.33
5% MACF	47.42	9.10	5.23	0.13	10.50	29.89
1% CACF	52.17	9.08	3.81	4.74	9.88	22.68
3% CACF	53.10	8.69	3.50	1.05	10.13	19.79
5% CACF	55.00	8.30	3.41	1.94	9.73	20.30
1% SACF	49.31	8.15	3.34	5.90	9.57	11.53
3% SACF	49.45	8.00	3.06	0.16	9.33	11.19
5% SACF	50.51	7.19	1.30	1.40	8.11	9.09

MACF malic acid crosslinked films, *CACF* citric acid crosslinked films, *SACF* succinic acid crosslinked films

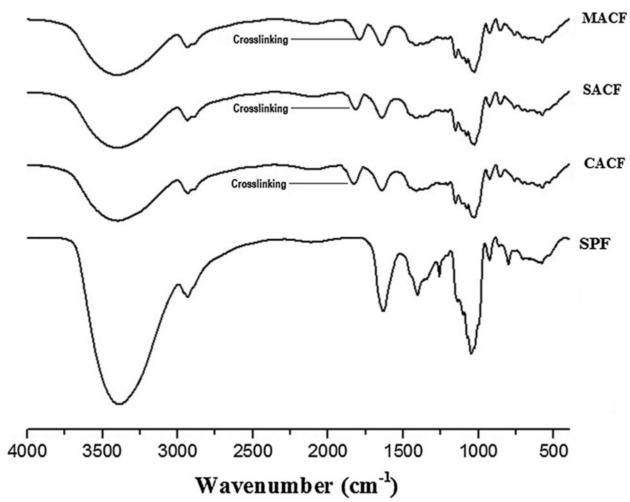

Fig. 1 FTIR absorbance spectra for malic acid crosslinked (MACF), succinic acid crosslinked (SACF), citric acid crosslinked (CACF) and native sesame protein isolate (SPF) films at 5% level

plasticizer glycerol and also covalent bonds formed between protein, succinic acid, citric acid and malic acid during crosslinking were cleaved at this temperature resulting in mass reduction. Last weight loss was observed at temperature in the range of 375.2–420.2 °C. Maximum weight loss was observed in case of all un- crosslinked and crosslinked sesame protein films. Weight loss at this temperature might be due to breaking of S–S, O–N and O–O linkages of proteins and degradation of succinic, citric and malic acids. With increased concentration of crosslinker, temperature of thermal degradation of crosslinked films increased from 510 to 545 °C. 5% succinic acid crosslinked films showed highest degradation temperature which indicates that thermal stability of crosslinked films increased with increase in concentration of crosslinking agent. Increase in degradation temperature rises due to formation of strong cross-links between sesame protein and succinic acid, citric acid and malic acid. All TGA scans showed single decomposition curve for all the films which indicates the good compatibility between proteins and all organic acids. Decomposition temperature in the range of 230-250 °C was reported by Su et al. (2010) for soy protein isolate and CMC blends.

X-ray diffraction (XRD)

Crystal structure of films and effect of crosslinking on sesame protein isolate films was investigated by XRD (Fig S1). The XRD of sesame protein film and crosslinked film shows only one main crystalline reflection at 20° which indicates the major structure of films was amorphous. However, intensity of diffraction was more for crosslinked films as compared to sesame protein film, which indicates the slight increase in crystallinity with the crosslinking of sesame protein isolate with all three organic acids. No new diffraction peaks were observed in case of crosslinked films.

Morphological properties

High degree of porosity was observed throughout the film, while porosity reduced and increase in compactness was observed in case of citric acid, malic acid and succinic acid crosslinked sesame protein films (Fig. 2). All crosslinked films had rough, coarser and slightly irregular surface as covalent and non-covalent bonding was induced in case of crosslinked protein films. Compactness in films was responsible for the decrease in WVP and increase in tensile strength. Porosity in 1% malic acid modified film was observed to be decreased as compare to native film whereas, all other crosslinked films were observed to be non-porous. High compactness and rough surface was observed in case of succinic acid modified film at 5% level

Table 3 DSC and TGA analysis of native and crosslinked edible films

Films	DSC			TGA			
	Tm (°C)	ΔH (MJ)	Tdi (°C)	Weight loss (%)	DTG max (°C)	Weight loss (%)	Residual mass (%)
Native	108	1087	278.0	17.90	375.2	45.61	4.1
MACF (1%)	103	1120	281.0	24.10	381.4	46.20	3.8
MACF (3%)	121	987	283.0	24.31	383.1	49.10	3.5
MACF (5%)	125	863	289.2	26.00	385.0	51.30	3.5
CACF (1%)	110	1051	285.0	45.00	382.1	55.00	3.2
CACF (3%)	123	974	287.1	46.40	393.0	58.14	3.1
CACF (5%)	138	743	292.6	46.70	395.0	59.10	3.0
SACF (1%)	142	712	291.3	45.30	412.0	64.00	2.8
SACF (3%)	158	529	297.0	47.00	417.1	64.60	2.5
SACF (5%)	161	500	320.0	47.60	420.2	65.10	2.1

MACF malic acid crosslinked films; *CACF* citric acid crosslinked films, *SACF* succinic acid crosslinked films

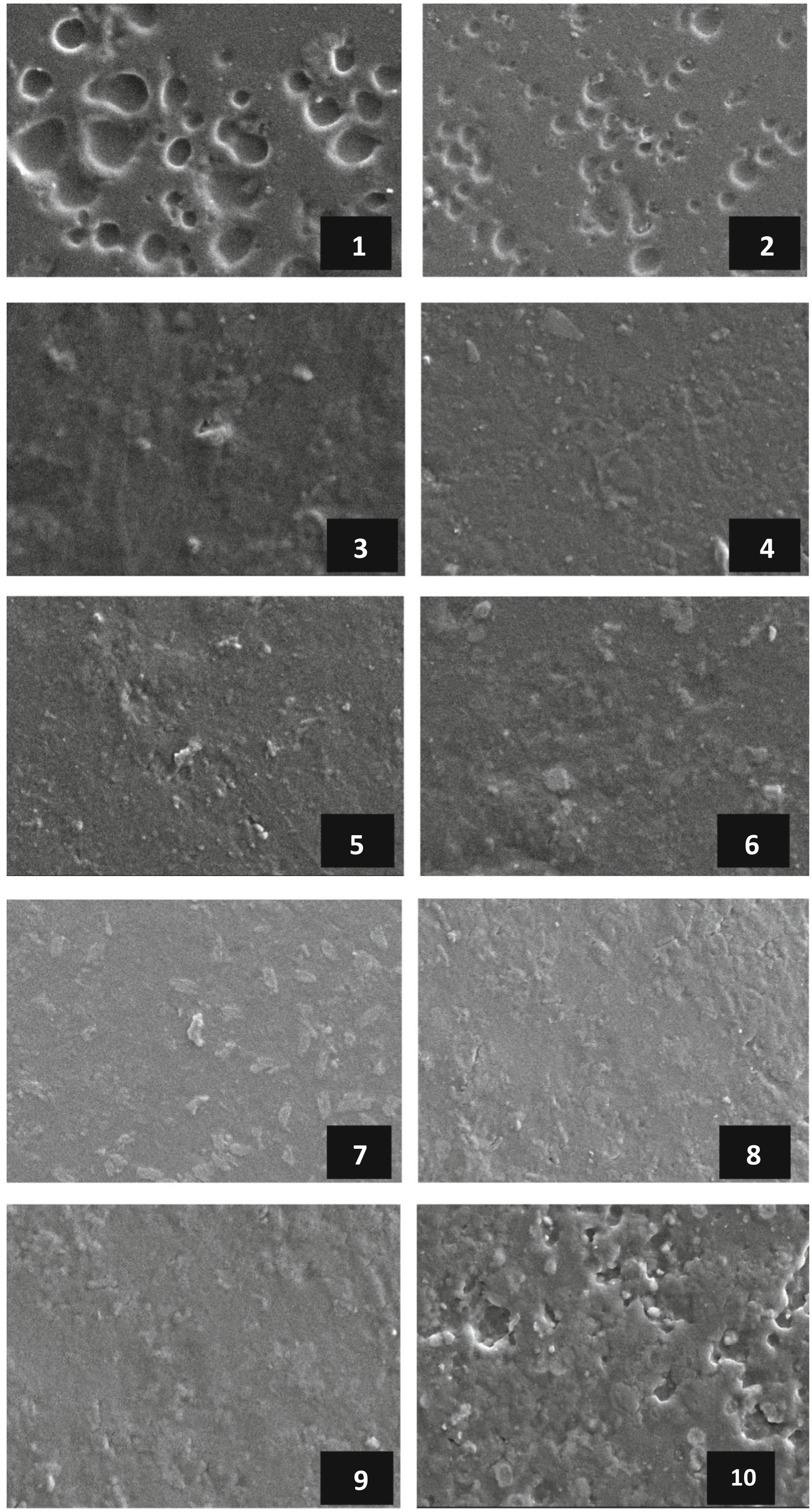

Fig. 2 SEM images at X3000 magnification **1** native; **2** 1% MACF; **3** 3% MACF; **4** 5% MACF; **5** 1% CACF; **6** 3% CACF; **7** 5% CACF; **8** 1% SACF; **9** 3% SACF; **10** 5% SACF

potentially due to higher crosslinking effect and hence showed better permeability and strength properties than other films. Reddy et al. (2009) observed smooth and homogeneous surface of films prepared from citric acid crosslinked peanut protein.

Conclusion

All three carboxylic acids effectively crosslinked sesame protein, improved the strength and considerably decreased the water vapor permeability of films. Among all the crosslinked films, films prepared from 5% succinic acid crosslinked protein resulted in optimum properties as compared to other films. Crosslinked protein films showed higher thermal stability. Crosslinking also improved morphology of films as native sesame protein films exhibited high degree of porosity while crosslinked films were observed to be non-porous. All the three organic acids used in the study can be obtained from fermentation process and are considered as green chemicals. The acids effectively improved the overall properties of films by modifying the protein isolate. Carboxylic acids used in the study can be used as a substitute for non-edible crosslinking agents and the films can be used for the packaging applications of food products. Further research should be focused to improve the optical properties of films.

References

ASTM (2002) Standard test method for tensile properties of paper and paperboard using constant rate of elongation apparatus, D828-97. In: Annual book of ASTM standards, Philadelphia, PA

ASTM (2014) Standard test method for water vapor transmission of materials, E96/E96M. In: Annual book of ASTM standards, Philadelphia, PA

Barth A, Zscherp C (2002) What vibrations tell us about proteins? Q Rev Biophys 35:369–430

Bourtoom T (2008) Factors affecting the properties of edible film prepared from mung bean proteins. Int Food Res J 15:167–180

Chambi H, Grosso C (2006) Edible films produced with gelatin and casein cross-linked with transglutaminase. Food Res Int 39:458–466

Chen CH, Kuo WS, Lai LS (2010) Water barrier and physical properties of starch/decolorized hsian-tsao leaf gum films: impact of surfactant lamination. Food Hydrocoll 24:200–207

Fabian H, Fälber K, Gast K, Reinstädler D, Rogov VV, Naumann D, Zamyatkin DF, Filimonov VV (1999) Secondary structure and oligomerization behavior of equilibrium unfolding intermediates of the lambda Cro repressor. Biochem 38:5633–5642

Hagenmaier RD, Shaw PE (1990) Moisture permeability of edible films made with fatty acid and hydroxypropyl methylcellulose. J Agric Food Chem 38:1799–1803

Han JH, Floros JD (1997) Casting antimicrobial packaging films and measuring their physical properties and microbial activity. J Plast Film Sheet 13:287–298

Ket-On A, Pongmongkol N, Somwangthanaroj A, Janjarasskul T, Tananuwong K (2016) Properties and storage stability of whey protein edible film with spice powders. J Food Sci Technol 53:2933–2942

Krimm S, Bandekar J (1986) Vibrational spectroscopy and conformation of peptides, polypeptides, and proteins. Adv Protein Chem 38:181–364

Lefevre T, Subirade M, Pézolet M (2005) Molecular description of the formation and structure of plasticized globular protein films. Biomacromolecules 6:3209–3219

Onsaard E, Pomsamud P, Audtum P (2010) Functional properties of sesame protein concentrate from sesame meal. Asian J Food Agro-ind 3:420–431

Ramos OL, Reinas I, Silva SI, Fernandes JC, Cerqueira MA, Pereira RN, Vicente AA, Pocas MF, Pintado ME, Malcata FX (2013) Effect of whey protein purity and glycerol content upon physical properties of edible films manufactured therefrom. Food Hydrocoll 30:110–122

Reddy N, Yang Y (2010) Citric acid cross-linking of starch films. Food Chem 118:702–711

Reddy N, Li Y, Yang Y (2009) Alkali-catalyzed low temperature wet crosslinking of plant proteins using carboxylic acids. Biotechnol Prog 25:139–146

Reddy N, Jiang Q, Yang Y (2012) Preparation and properties of peanut protein films crosslinked with citric acid. Ind Crops Prod 39:26–30

Rhim JW, Gennadios A, Weller CL, Cezeirat C, Hanna MA (1998) Soy protein isolate-dialdehyde starch films. Ind Crops Prod 8:195–203

Saglam D, Venema P, De Vries R, Shi J, Van der Linden E (2013) Concentrated whey protein particle dispersions: heat stability and rheological Properties. Food Hydrocoll 30:100–109

Saremnezhad S, Azizi MH, Barzegar M, Abbasi S, Ahmadi E (2011) Properties of a new edible film made of faba bean protein isolate. J Agric Sci Technol 13:181–192

Singh N, Georget DMR, Belton PS, Barker SA (2009) Zein-iodine complex studied by FTIR spectroscopy and dielectric and dynamic rheometry in films and precipitates. J Agric Food Chem 57:4334–4341

Singh N, Georget DMR, Belton PS, Barker SA (2010) Physical properties of zein films containing salicylic acid and acetyl salicylic acid. J Cereal Sci 52:282–287

Sinz A (2006) Chemical cross-linking and mass spectrometry to map three-dimensional protein structures and protein–protein interactions. Mass Spectrom Rev 25:663–682

Su JF, Huang Z, Yuan XY, Wang XY, Li M (2010) Structure and properties of carboxymethyl cellulose/soy protein isolate blend edible films crosslinked by maillard reactions. Carbohydr Polym 79:145–153

Tao Z, Weng WY, Cao MJ, Liu GM, Su WJ, Osako K, Tanaka M (2015) Effect of blend ratio and pH on the physical properties of edible composite films prepared from silver carp surimi and skin gelatin. J Food Sci Technol 52:1618–1625

Wu J, Zhong F, Li Y, Shoemaker CF, Xia W (2013) Preparation and characterization of pullulan-chitosan and pullulan-carboxymethyl chitosan blended films. Food Hydrocoll 30:82–91

Yang Y, Wang L, Li S (1996) Formaldehyde-free zein fiber-preparation and investigation. J Appl Polym Sci 59:433–441

Yang CQ, Wang X, Kang I (1997) Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid. Text Res J 67:334–342