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ARTICLE

Preparation and characterization of dialdehyde starch crosslinked feather keratin film for food packaging application

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Feathers, a byproduct of the poultry industry, have long been considered as a solidwaste, posing a series of environmental and economic problems. However, feather keratin (FK) extracted from feathers is a valuable source of biodegradable and biocompatible polymer. The aim of this study was to develop and characterize novel casting films based on feather keratin (FK) crosslinked by dialdehyde starch (DAS) and plasticized with glycerol for applications in biomedicine. The microstructure, crystallization behavior, light transmission, moisture content, solubility, tensile properties, water vapor barrier property, and cytotoxicity of the FK-DAS films were investigated. The fracture surface of the crosslinked film showed a more compact microstructure than that of the control film, and the crosslinked films were completely amorphous and very transparent (transparency value <2). These results indicate that the addition of DAS increased the transparency value and moisture content and decreased the solubility, indicating the crosslinking between the FK and DAS. The films with 2% DAS showed increased tensile elongation and water vapor permeability compared to the control films, whereas the tensile strength of the film decreased, most probably because the crosslinking effect was counterbalanced by the plasticization of DAS. DAS increased the water resistance of the FK films, thus expanding their potential application in the food packaging

1 Introduction

In recent years, increased attention has been focused on ecofriendly biobased materials owing to their applications in packaging, tissue engineering, and drug delivery systems. The main biobased materials could be fabricated from the renewable resources such as proteins, polysaccharides, and lipids [1]. Proteins are usually preferred owing to their biodegradability, biocompatibility, and low toxicity [2]. One of the best protein sources is feather keratin (FK), which can be obtained in large quantities from the poultry industry [3]. It is estimated that 3−4 billion pounds of feathers is generated as a byproduct in the poultry industry in the United States [4] and >1.5 billion pounds is generated in China [5]. Although feathers are inexpensive, renewable, biodegradable, and easily available, they have limited applications in industrial applications. Currently, they are used for animal feed, making duvet and down coat; however, most of the feathers end up in the landfills as solid wastes, posing environmental and economic problems [4, 6]. Feathers contain >90% FK, which has ~7% cysteine residue content more than that in other proteins. The cysteine residues can be oxidized to generate inter- or intramolecular disulfide bonds and form crosslinked network, leading to thermal stability, high mechanical strength, hydrophobicity and good stability in the solid state [7, 8].

So far, several types of biomaterials such as keratin films [2, 9-11], keratin scaffolds [12, 13], and microcapsules [14] prepared from keratin have been reported. The films developed totally from the keratin plasticized with polyhydric alcohol by the casting technique have relatively poor tensile strength and high moisture sensitivity similar to other protein-based films. Some studies have been focused towards improving the keratin film properties by crosslinking agents [2, 15, 16]. Aldehyde crosslinking agents such as formaldehyde, glyoxal and glutaraldehyde are often added to improve the tensile strength, water barrier property, thermal stability, and reduce the solubility of the protein-based films [17-19]. However, there is always concern about the toxicity of the aforementioned aldehyde residues in the material limiting its application in biofield and food packaging [20]. Compared to the low molecular weight aldehydes, dialdehyde starch (DAS) has low toxicity and has been suggested as an alternative to glutaraldehyde. DAS is a polymeric aldehyde obtained by the controlled periodate oxidative cleavage of C2−C3 bond of the anhydroglucose units of the native starch. The dialdehyde groups could form covalent and hydrogen bonds with the polar group in the protein molecule, and the potential industrial applications of DAS are based on its crosslinking ability and low toxicity [21].

Although there are some reports of DAS used as a crosslinking agent in various proteins such as soy protein isolate (SPI) [20, 22], collagen [23], corn zein [24], flour starch–protein [25], and whey protein [26], to the best of our knowledge, studies on the DAS-cross-linked keratin materials are very rare. Therefore, this study is focused on the evaluation of the microstructure, crystallization behavior, light transmission, moisture content, solubility, tensile properties, and water vapor permeability of the FK-DAS film. Moreover, this study is based on our recent reports on the DAS-crosslinked FK/polyvinyl alcohol blend films [27]. The material produced comprised degradable polymers, and thus is expected to be more ecofriendly.

2 Materials and Methods

2.1 Materials

Urea, sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$), sodium dodecyl sulfate (SDS), soluble starch, sodium periodate and hydrochloric acid were purchased from Guangzhou Chemical Ltd. (China). The chicken feathers were collected from farmer's markets.

2.2 Preparation of DAS

Soluble starch (10g) was added to a sodium periodate solution (100 mL, 0.3 mol L^{-1}) under vigorous mechanical stirring, and the pH value of the solution was adjusted to 1.5 using a hydrochloric acid solution (1 mol L^{-1}). The reaction solution was stored at 35 °C for 4 h under exclusion of light. Next, acetone was added to the reaction solution. The resulting precipitate was filtered and cross-washed with distilled water and acetone until all iodate compounds had been removed. The filter cake was dried at 40 °C for 12 h. Finally, the dried product was milled and sieved through a 100 mesh sifter to obtain the DAS powder.

2.3 FK extraction

After cleaning and disinfection, the chicken feathers were hydrolyzed based on an amendment reported by Andrew *et al.* [28]. The feathers were steeped with a 7 mol L^{-1} urea solution (1:15, w/v) at 50 °C for 24 h. Then, $Na_2S{\cdot}9\ H_2O$ (40 wt% of the feather) and SDS (1 wt% of the feather) were added to the mixture and the extraction was done at 50 °C for 30 min under constant stirring. The extraction solution was then centrifuged at 1,000 × g for 15 min, and the supernatant was adjusted to neutral using a 1 mol L^{-1} hydrochloric acid solution. The neutral solution was desalinated by dialysis using a dialysis bag in distilled water at 5 °C for 72 h (Oso-T8280, 8000-14000, Union Carbide, USA). Then, the dialyzate was stored at 5 °C before usage. The dialyzate FK concentration was 2 wt%, measured by applying the dry weight method.

2.4 Preparation of the blended films

The FK solution was adjusted to pH 9.5 with 0.1 mol L^{-1} NaOH solution and then heated at 40 °C for 10 min under continuous stirring. Glycerol was added as the plasticizer at 30% and 40% (based on dry FK weight). DAS aqueous solution was prepared by adding 2 g DAS powder to 48 g deionized water. The pH of the solution was adjusted to 9.5 with 0.1 mol L^{-1} NaOH solution by continuous stirring at 40 °C for 30 min. Then, a certain volume of FK and DAS solutions was mixed and adjusted to pH 9.5 with 0.1 mol L^{-1} NaOH solution. The resulting solution was heated at 60 °C for 20 min under continuous stirring. After defoaming using an ultrasonic cleaner, the mixed solution was poured onto a polyethylene petri dish and dried in an oven at 60 °C for 6 h. A series of FK/DAS films were coded as GD-m-n, where m and n are the weight percentages of glycerol and DAS to FK, respectively. The thickness of the samples was measured by a micrometer and ranged from 0.07 to 0.12 mm under various conditions studied.

2.5 FTIR spectroscopy of DAS

Fourier transform infrared (FTIR) spectra of the native starch and the DAS were recorded using an IR Spectrum Scanner (Spectrum 100, Perkin-Elmer, USA) at a resolution of 4 cm^{-1} in the wave number range from 450 to 4000 cm^{-1}.

2.6 Scanning electron microscopic (SEM) observation

Micrographs of surface and cross-section of the films were investigated by scanning electron microscopy (SEM) at an acceleration voltage of 20 kV using a Quanta 400 SEM (Oxford, England, UK). Prior to the SEM observations, the samples were coated with a fine gold layer.

2.7 X-ray diffraction (XRD)

An X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (D/max 2200 UPC, RIGAKU, Japan) operated at 30 kV and 30 mA.

2.8 Light transmittance and transparency

The light transmittance of the films was measured in the visible range (400–800 nm) using a spectrophotometer (UV-1800, Shimadzu Corporation, CHN) following the method described by Limpan [29]. The films were cut and placed in a spectrophotometer cell perpendicular to the beam direction. The transparency of the films was calculated using the following equation:

$\text{Transparency} = -(\log T_{600}) / \chi \text{ or } A_{600} / \chi$

where A_{600} is the absorbance at 600 nm, T_{600} is the transmittance at 600 nm, and χ is the film thickness (mm). A higher transparency value indicates that the film is less transparent.

2.9 Moisture content (MC) and solubility test

Three rectangle specimens (40 mm × 10 mm) of each film were weighted (W_0) and then dried in an oven at 70 °C for 24 h. Then, the specimens were cooled in a desiccator for a few minutes and immediately weighed (W_1). With Oscillation, the dried specimens were immersed in distilled water at 25 ± 2 °C for 24 h with shaking. The resulting wet specimens were dried again in an oven at 70 °C for 24 h, cooled in a desiccator, and immediately weighed (W_2). The MC of the films was calculated by the following equation: MC = $[(W_0 - W_1)/W_1] \times 100$. The solubility of the films (S) was calculated by the following equation: S = $[(W_1 - W_2)/W_1] \times 100$. Each film was tested thrice.

2.10 Tensile Properties

The tensile strength (σ_b) and elongation at fracture (ε_b) of the blend films were measured using a universal testing machine (CMT6503, Shenzhen MTS Test Machine Company Ltd., China) according to the ASTM standard D638 at a speed of 10 mm min^{-1}. The FK/DAS films were conditioned at 25 °C and 55% relative humidity for 48 hours before tensile testing. The films were cut to a size of 75 mm × 10 mm. The thickness of the samples was measured using a micrometer and was in the range from 0.07 to 0.13 mm for the different conditions applied for this study. The results were averaged from three samples.

2.11 Water vapor permeability measurement

Water vapor permeability coefficient in (g m)/(m^2 s Pa) of the films was measured using a water vapor transmittance tester (Perme W3/030, Labthink Ltd, CHN) at 38 ± 1 °C with a gradient of 90 ± 1% RH to 0% RH (dry air) across the film. The results of the three samples were averaged.

3 Results and Discussion

3.1 Fourier transform infrared (FTIR) analysis of DAS

The DAS used in this study, was obtained by applying Yu's method [30] and characterized by FTIR (Fig. 1). The oxidation of the starch by the periodate is characterized by the specific cleavage of the C2−C3 bond of the glucose residues. This cleavage results in the formation of two aldehyde groups per glucose unit, forming 2, 3-dialdehyde polysaccharides. The band at 1735 cm^{-1} is the most characteristic peak for C=O vibrations in the aldehyde groups, while the weaker peak at 1160 cm^{-1} is attributed to the C−O bond stretching of the C–OH group in the glucose residues. The broad bands in the range from 1360 to 1440 cm^{-1} are characteristic for the C=O symmetric stretching vibrations of carboxyl groups. These results indicate that both the aldehyde group and carboxyl groups were introduced into the structure by the selective periodate oxidation of the starch.

The aldehyde groups in DAS can react with amino groups, hydroxyl groups, sulfhydryl groups, the phenolic ring of tyrosine, and the imidazole ring of histidine, which could result in the formation of inter- and intra-molecular cross-links in proteins. Furthermore, the aldehyde groups on the starch molecule could also react with hydroxyl (–OH) groups of the other starch molecules to form hemiacetal cross-linking [20]. In addition, there is the possibility of the formation of hydrogen bonds between the polar groups of FK and DAS. The intra- and inter- molecular interactions and the cross-linking should improve the properties of the casting FK films.

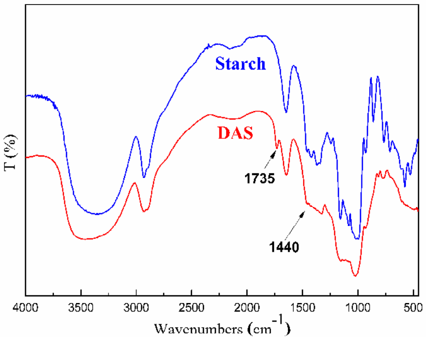

Fig. 1 FTIR spectra of starch and DAS

3.2 Film appearance and microstructure

The glycerol plasticized FK films were homogeneous, transparent, and flexible. Their surfaces appeared smooth without visible cracks or holes. These films did not show any change in the appearance when different amounts of DAS were used; however, the surfaces of GD40 series films were slightly oily compared to the GD30 series films, which may be caused by the effusion of glycerol. The FK–DAS films were easily peeled from the casting plates, except for those containing DAS >10 wt%, and the surface of the films was rather sticky, probably because of the hygroscopic nature of DAS.

The SEM images of the surface and the cross-section for the control film (Fig. 2A) and DAS-modified film (Fig. 2B) are shown in Fig. 2. The surface of GD40-0 and GD40-5 films exhibited smooth structure except the presence of few particles, which may be caused by the crystallization of salts during the drying. Furthermore, the cross-section of the crosslinked film (Fig.2D) shows more homogeneous and compact microstructure than that of the control film (Fig. 2C), probably because of the inter- and intramolecular crosslinking in the proteins promoted by DAS. Moreover, there was no presence of the aggregates or particles, different from that observed in the hot-pressed gelatin films crosslinked by DAS [21].

3.3 X-ray diffraction (XRD) analysis

XRD is widely used in the study of the degree of sample crystallinity. The XRD pattern of the pristine FK shows broad diffraction peaks at 2θ values of ~9 and 20°, which are typical fingerprints of the partially crystalline materials (Fig. 3a). In the diffraction pattern of GD30-0, the peak intensity at 2θ value of 9° was much lower than that of the pure FK powder, and the peak width at 2θ value of 20° was larger, indicating an amorphous behavior, because of the external plasticization effect from more glycerol and less ordered protein per unit volume. The XRD patterns of the FK film crosslinked by 2%,5%, 10% DAS showed the highest peak intensities of ~215, 224, and 265 counts at ~20°, respectively, and the peak width at 2θ value of 9° was larger than that of film GD30-0 (Fig. 3b).

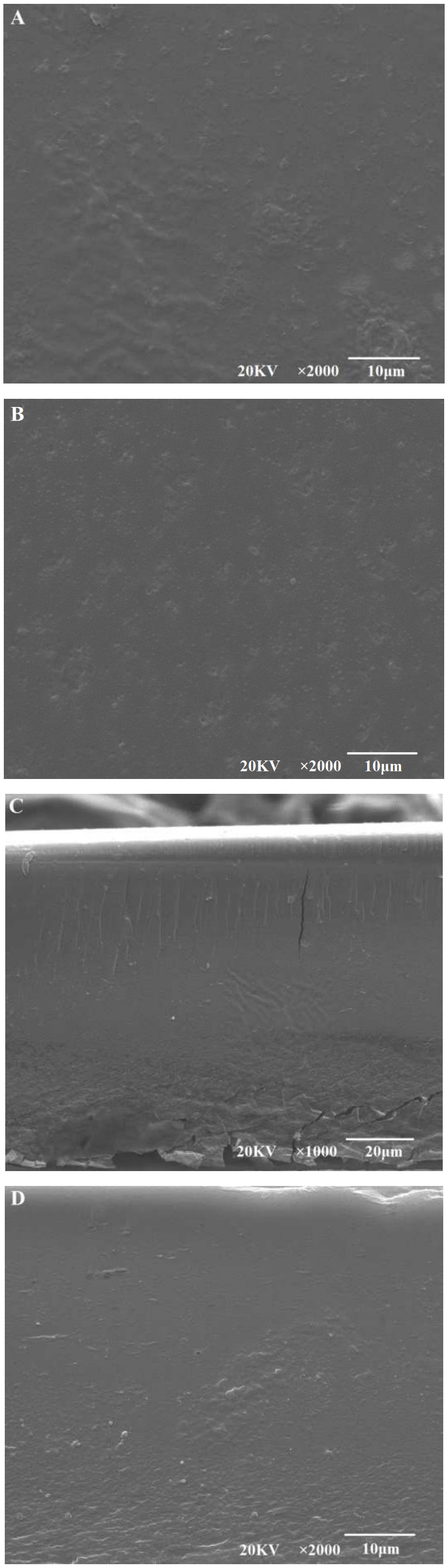

Fig. 2 SEM images of surface morphology of GD40-0 (A) and GD40-5 (B), and cross-section morphology of GD40-0 (C) and GD40-5 (D).

From these patterns, it is obvious that the intensity of the peak at ~20° of GD30-10 film is higher than the other two films, probably because of the diffraction peak of DAS at ~2θ value of 20° [31]. In other words, all the FK-DAS films were completely amorphous.

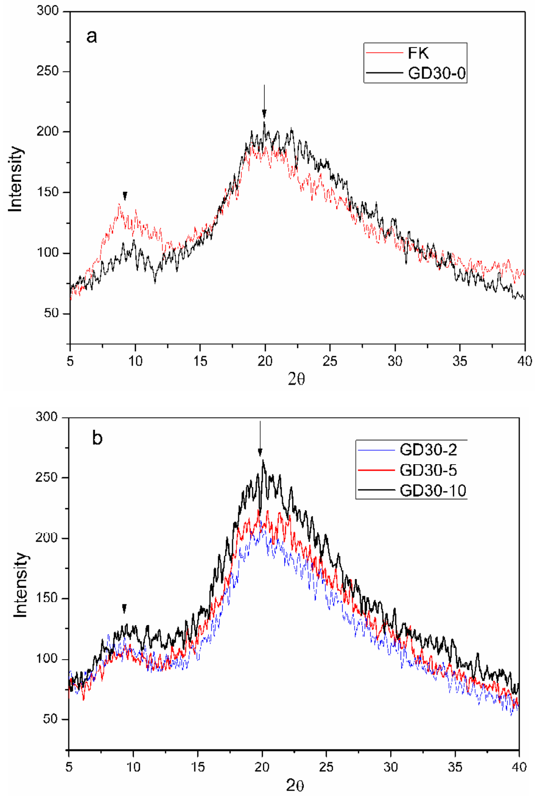

Fig. 3 (a) XRD patterns of (a) pristine FK powder and GD30-0 film. (b) FK films crosslinked with 2, 5, and 10 (wt%) DAS.

3.4 Light transmittance (T) and transparency

T in the visible range as well as transparency values of the GD30 and GD40 series films at different concentrations of DAS are listed in Table 1. In the visible range (400–800 nm), all the prepared FK films showed a low transparency value of <2, corresponding to a relatively good transparency. and the results were consistent with the results of the XRD analysis (all the FK-DAS films were completely amorphous). Furthermore, all the films exhibited good transmittance at 800 nm in the range ~84.04–85.06% and ~79.69–89.17% for the GD30 and GD40 series films, respectively. The transparency values of the GD30 series films considerably increased with increasing DAS contents, probably attributed to a darker color resulted by the Maillard reaction. Notably, the films in the GD40 series were more transparent than those in the CD30 series, particularly at higher DAS contents (5% and 10%). The results indicate that the change in the content of either glycerol or DAS affected the film transparency, and the film transparency was highly dependent on the concentration of glycerol. In contrast, DAS has a minor role in the film transparency [32]. The FK films exhibited a transparency value similar to that obtained for the whey protein concentrate films with 40% glycerol (1.29 A_{600}/mm) [33]; however, they exhibited less transparency than the films prepared from dialdehyde carboxymethyl cellulose crosslinked gelatin with 30% glycerol (0.82 A_{600}/mm) [34]. Compared to the commonly used synthetic films such as low density polyethylene (3.05 A_{600}/mm) and oriented polypropylene (1.67 A_{600}/mm), the FK film was also more transparent [33].

Table 1 T and transparency of the FK films at different glycerol and DAS contents.

Films	T (%)					Transparency
	400 nm	500 nm	600 nm	700 nm	800 nm	
GD30-0	22.68	49.02	71.42	80.68	84.01	1.46
GD30-2	21.18	50.86	73.57	82.11	85.06	1.48
GD30-5	15.53	50.79	74.54	82.30	84.68	1.60
GD30-10	16.58	52.47	75.10	82.48	84.83	1.78
GD40-0	18.87	45.05	68.74	77.44	79.69	1.63
GD40-2	26.42	55.81	77.20	85.47	89.17	1.40
GD40-5	7.69	43.53	70.85	80.74	84.70	1.25
GD40-10	8.13	41.03	67.08	76.41	80.16	1.33

3.5 MC and solubility

The MC of the films is worth studying, because the mechanical and water vapor barrier properties of the natural polymer-based materials were significantly affected by varying humidity of the material, caused by the strong plasticizer effect of water molecules in the natural polymers. The DAS concentration did not show a drastic effect on the MC of the FK films, which had MC values of ~18% (Table 2). Moreover, the values were close to the literature data of the protein-based films such as modified SPI films [22], gelatin/PVA blend films [35],whey films [33]. In general, the crosslink network structure formed in the protein material could hinder the exposure of the hydrophilic groups of protein; therefore, the humidity of the material obviously decreases. In contrast, the crosslinking agent, DAS, is a polymer containing hydroxyl groups in the molecular chain; therefore, DAS has good ability to bind with water. Therefore, under the above two opposite effects, the MC of the FK films first decreased and then increased with increasing DAS content. The DAS concentration exhibited a significant effect on the solubility of the films (Table 2), particularly in the GD40 series films. The solubility of the FK films decreased with increasing DAS content. Concerning the GD40 series films, the film with 10% DAS content (GD40-10) had ~ 20% lower solubility than that of the control film (GD40-0). The soluble fraction in the FK-DAS films could be attributed to the exudation of glycerol out of the film and to the loss of low molecular weight polypeptide chain that could not be crosslinked by DAS. In summary, the GD40 series films had higher solubility than that of the GD30 series films, probably because of much more glycerol migrating to water.

3.6 Tensile properties

Tensile strength (σ_b) and elongation at break (ε_b) of the DAS-crosslinked FK films are listed in Table 2. It was expected that the DAS-induced crosslinking would increase σ_b and decrease ε_b of the film as in the case of low-molecular-weight dialdehydes such as glutaraldehyde and glyoxal [18]. However, the DAS crosslinked films had lower σ_b values than the control film both in the GD30 and GD40 series films. In the GD30 series films, σ_b decreased by 65% by adding 2% DAS. This anomalous behavior could be attributed to the fact that the bulky DAS molecules can't easily reach the reactive groups in the protein matrix. Furthermore, the crosslinking effect is counterbalanced by the plasticization of DAS with a large number of hydrophilic groups, which bind water molecules to the protein system. The plasticizing effect of water increased the mobility of the polymeric chains, thereby increasing extensibility of the film by ~17%. With increasing DAS content to 5% (GD30-5), the σ_b value increased to 4.14 MPa closed to that of film GD30-0, showing that a denser network was formed in the film. Furthermore, the DAS-induced crosslinking resulted in the lower ductility of the protein matrix, and the ε_b value decreased by ~40% compared to that of the control film (GD30-0). A Similar crosslinking effect was presented in the molded gelatin-DAS films [21]. In addition, at any DAS content, the increase in the glycerol content from 30 to 40 wt% caused σ_b to decrease and ε_b to increase. The plasticizing effect of glycerol in the protein film had been reported and explained well [36-38].

3.7 Water vapor permeability (WVP)

The effect of DAS and glycerol contents on the WVP of the FK films is listed in Table 3. WVP is affected by the hydrophilicity, flaws of a material, and the internal tortuosity in the structure [19]. The WVP value of the DAS-crosslinked FK films was in the range 3.05×10^{-10} to 5.25×10^{-10} g m/m^2 s Pa, which is greater than that reported for the keratin films plasticized with 9% glycerol prepared by the casting (1.07×10^{-10} g m/m^2 s Pa) and lower than that reported for keratin films plasticized with 30% sorbitol prepared by the casting (8.10×10^{-10} gm/m^{2}sPa) [7]. The results show that the WVP of the FK films first increased and then decreased with increasing DAS content. A similar tendency was observed in the SPI-DAS films plasticized with 50 wt% glycerol, for which a minimum value of 1.59×10^{-9} g m/m^2 s Pa was obtained [20]. This tendency may be caused by the following two factors, because single factor cannot necessarily induce the results. By adding DAS, the crosslinked networks were formed in the FK-DAS films, offering more tortuous path to the water molecules; therefore, the diffusion rate of water molecules decreased in the FK-DAS films. In contrast, compared to the low-molecular-weight aldehydes, DAS is a polymer with bulky molecules, which could expand the interstitial spaces in the protein matrix, increasing the diffusion rate of water molecules in the films. Notably, the WVP value of GD40 series films is greater than that of the GD30 series, indicating that the WVP of films increased with increasing glycerol content, which is common in the protein-based films [7, 39]. The protein network became less dense because of an increase in the free volume of the system, induced by the plasticizing effect, consequently increasing the number of pathways for water molecules transfer in the films. Furthermore, glycerol is fairly hygroscopic and can increase the moisture content of the film, thereby increasing the diffusion rate of water molecules.[1, 39].

Table 2 MC, solubility, tensile properties, and water vapor permeability (WVP) of the FK-DAS films plasticized with 30% and 40% glycerol content.

Samples	MC (%)	Solubility (%)	σ_b (MPa)	ε_b (%)	WVP (10^{-10}gm /m^2sPa)
GD30-0	21.8± 1.1	44.7± 2.1	4.5± 1.2	19.0± 10.0	3.5± 0.2
GD30-2	17.3± 0.9	39.3± 0.8	2.9± 0.8	22.3± 1.8	4.1± 0.1
GD30-5	14.8± 1.5	41.0± 1.1	4.1± 0.4	11.3± 5.7	3.1± 0.4
GD30-10	18.0± 0.4	36.0± 8.3	2.8± 0.4	9.1± 4.2	3.1± 0.2
GD40-0	20.7± 2.5	61.9± 3.1	3.8± 0.7	38.0± 11.4	4.6± 0.8
GD40-2	17.6± 1.2	54. ± 1.8	1.3± 0.1	36.0± 0.9	5.3± 0.6
GD40-5	15.2± 0.9	47.6± 0.7	1.2± 0.1	38.0± 3.5	4.4± 0.8
GD40-10	18.9± 1.3	48.4± 2.3	1.5± 0.3	36.7± 11.8	3.6± 0.3

Conclusions

The glycerol-plasticized FK films crosslinked by DAS were successfully prepared by the casting process. The morphology, crystallization behavior, and light transmission analyses of the films indicate the formation of covalent bonds between FK and DAS. With increasing DAS amount, the solubility and MC of the films decreased, whereas the tensile strength and water vapor barrier property decreased first and then increased. These results were different from the common crosslinking effect induced by the short-chain aldehydes, most probably because of the polyhydric polymeric nature of DAS. In common for plasticizer–polyhydric alcohol in the protein film, the increase in the glycerol content increases water vapor permeability and light transmission. Overall, the DAS-crosslinked FK films were prepared from inexpensive, biodegradable, and ecofriendly material and have potential for applications in packaging.

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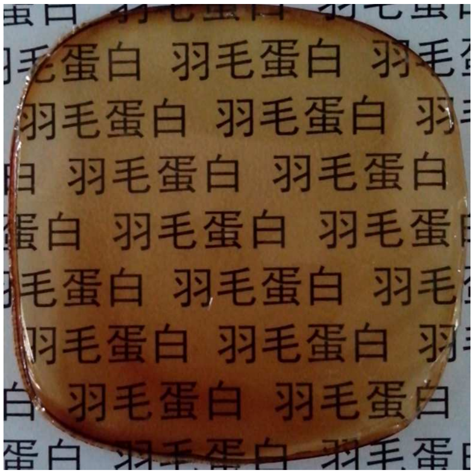

Crosslink effects of dialdehyde starch on mechanical properties, water-resistance, compatability, micromorphology, and water vapor barrier property of feather keratin films.