Tannic acid modifies the material properties of Sorghum Kafirin film

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ABSTRACT

Kafirin, the prolamin protein of sorghum, was made into films and tannic acid (TA) was added to potentially change the film properties. TA increased the maximum tensile stress and Young's modulus of kafirin films, but decreased the strain at break. The oxygen permeability of the films decreased on addition of TA. The glass transition temperature (T_g) of the films increased when TA was added. These findings indicate that TA can modify the properties of kafirin films possibly by cross-linking of kafirin molecules by TA.

INTRODUCTION

Sorghum is an indigenous cereal to Africa. The main protein of sorghum is a prolamin, known as kafirin. Kafirin can be made into films[1]. Protein-based films can be edible and biodegradable. They are also an environment-friendly alternative to synthetic plastics. Chemical modification of protein-based films changes the properties to meet different requirements used for food packaging systems. Tannins, which are naturally occurring chemicals for example tannins have been shown to interact with kafirin[2], indicating that they may potentially cross-link kafirin. This study describes the modification of kafirin films with TA and presents its effects on rheological and barrier properties.

MATERIALS AND METHODS

Materials

Kafirin was extracted from condensed tannin-free white sorghum cultivars[2]. Commercial TA (Merck, Darmstadt, Germany) was used as the modifying agents.

Methods

Kafirin films were produced essentially as described similar to Buffo et al.[1] using the casting method. Kafirin powder was added to ethanol solution; then a combination of plasticizers (1 glycerol: 1 polyethylene glycol: 1 lactic acid), 40% (w/w) with respect to protein; and TA up to 20% (w/w) with respect to protein was added during film casting. Films without tannic acid TA (control) addition were also produced. The films were conditioned for at least 48 h. at 25 °C and 50 % RH before analyses.

Analyses

The tensile properties were determined essentially according to ASTM D882-97[3] using a Stable Microsystems TA-TX2 Texture Analyser (Godalming, UK) fitted with a tensile rig grip. Strips of film (60 mm long and 6 mm wide) were mounted between the tensile grips (40 mm apart). The films were subjected to tension with a crosshead speed of 0.4 mm sec^{-1}. The force (stress) and the elongation (strain) were recorded. The results were expressed as stress at maximum force (σ_y), stress at break (σ_b), strain at break (ε_b) and Young's modulus (E) for the linear region of the stress-strain graph.

Oxygen transmission was measured by ASTM D 1307-90 method[4] using a Mocon Oxtran 2/90 (Modern Controls, Minneapolis, USA). A square portion of film (25 cm^2) was masked between two aluminium sheets with an opening of 5 cm^2 and placed in the instrument. Oxygen permeability was read from the instrument and expressed as $cm^3\ \mu m\ m^{-2}\ d^{-1}\ kPa^{-1}$.

Dynamic mechanical analysis (DMA) of the films was performed under tension at different temperatures using a Rheometrics RSA-II (Rheometric Scientific, Piscataway, USA) basically as described by Stading et al.[5]. The temperature scans were performed from -10°C to 60°C at 5°C min^{-1}. The potential loss of volatile plasticizers and water was controlled by coating the film with a layer of hydrophobic grease. The temperature at which the glassy modulus changed to transition modulus was used as the glass transition temperature (T_g) of the film. Linear regression was applied to fit a line to the storage modulus (E′) in the glassy and transition regions.

RESULTS AND DISCUSSION

The tensile properties of kafirin films, as affected by TA are shown in Table 1. According to ASTM[3] stress at maximum tensile force (σ_y) expresses the maximum force (the internal resistance to an external load) developed in a film during tensile test; strain at break (ε_b) is a representation of the film ability to stretch; and Young's modulus (E) is the ratio of stress to strain in the linear range of the stress-strain graph and measures the intrinsic stiffness of the film.

Mean σ_y, ε_b and E of unmodified kafirin films were 2.4 MPa, 109% and 40 MPa, respectively (Table 1). σ_y and ε_b of the films were similar to those previously reported[1] for kafirin films[1]. Modification of the kafirin films resulted in a significant linear increase in σ_y and E with increasing concentration of added TA from 0 to 20% (Table 1). At 20% level of addition, σ_y of kafirin films increased from about 2.4 MPa to 5 MPa for TA, a 2-fold increase. ε_b of the kafirin films showed a significant decrease when the films were modified with increasing levels of TA. At a 20% level of TA addition, ε_b of kafirin films decreased by about 4-fold. E of the film when modified at 20% with TA and increased more than 4-fold. Thus, kafirin films become stiffer but less plastic when modified with TA.

An increase in σ_y and a decrease in ε_b was also observed when sunflower protein films[6] were modified with gallic acid, chestnut tannins and tara tannins; and collagen strips[7] modified with TA. TA modification of collagen has been referred to as cross-linking because it resulted in an increase in the hydrothermal shrinkage temperature[7]. Pentagalloyl glucose (a hydrolysable tannin) can interact with proline rich protein (PRP) by H-bonds between the hydroxyl groups of tannins and carbonyl groups of protein[8]. PRP can also

Table 1. Functional properties of kafirin films as affected by tannic acid (TA)

	Level of TA addition (% w/w protein)				
	0	5	10	15	20
Tensile properties:					
Stress at maximum force (σ_y) (MPa)	2.4	3.1	2.9	4.1	5.0
Strain at break (ε_b) (%)	109	114	65	34	24
Young's modulus (E) (MPa)	40	86	90	150	184
Oxygen permeability (135 $cm^3\ \mu m\ m^{-2}\ d^{-1}\ kPa^{-1}$)	135	82	68	54	48
Glass transition Temperature, T_g (°C)	35	40	45	46	44
Moisture content (%)	15	14	13	13	12

interact with pentagalloyl glucose by hydrophobic interactions with the pyrrolidine ring of proline[9]. These interactions could lead to cross-linking of protein molecules by tannins[10].

The mean oxygen permeability of unmodified kafirin films was 135 cm³ µm m^{-2} d^{-1} kPa^{-1} (Table 1). Modification of the kafirin films with TA resulted in a significant quadratic decrease in the oxygen permeability. At 20 % level of modification, the mean oxygen permeability of kafirin films modified with TA was 48 cm³ µm m^{-2} d^{-1} kPa^{-1}. Barrier properties of biodegradable and edible films depend on molecular mobility and T_g of the material[11]. The gas permeability of a polymeric material is high above its T_g and low below its T_g.

T_g of kafirin films as measured by DMA is shown in Table 1. T_g of the plasticised kafirin film was 35°C. Modification with TA resulted in a quadratic increase in T_g. T_g of films can be influenced by plasticiser level[12], moisture content[13] and degree of modification[14]. In the present study, the plasticiser level was kept constant. The moisture content of kafirin films modified with TA did not show any significant difference to the control (Table 1), except at high level (20%) of modification with TA where there was a decrease. Therefore, it can be inferred that the increase in T_g of kafirin films was a result of modification with TA. As T_g is a measure of molecular mobility, it can also be proposed that the increase in T_g of the kafirin films indicates a decrease in molecular mobility of polypeptide chains. This is supported by the increase in stress and decrease in strain of the kafirin films when modified with TA.

CONCLUSIONS

TA may be hypothesized to interact through cross-linking of kafirin protein polypeptide chains. Thus, TA modification could decrease protein chain mobility by cross-linking of the kafirin polypeptide chains shown by the increase in T_g. The decrease of kafirin polypeptide chain mobility caused by chemical cross-linking with TA is probably responsible for the increase in tensile stress, Young's modulus; and decrease in tensile strain and oxygen permeability of the films.

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