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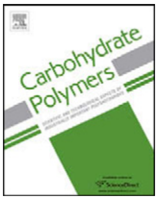

Effects of glyoxal cross-linking on baked starch foam

Mustafa-Kemal Uslu*, Süleyman Polat

Department of Food Engineering, Faculty of Engineering, Akdeniz University, Dumlupınar Bulvarı, 07070 Antalya, Turkey

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ABSTRACT

Starch trays and plates were prepared from native corn starch and corn starch cross-linked with glyoxal at different concentrations (0.126, 0.269, 0.271, 0.468 g/kg) using a foam baking process. The effect of cross-linking on baking parameters, including density, colour, water absorption, and tensile and flexural properties, was determined. Also, the morphologies of the trays were examined using a scanning electron microscope. Cross-linking considerably reduced the baking time, density and water absorption of the trays. Trays made from starch cross-linked with 0.126 and 0.269 g/kg glyoxal presented the best properties, with a homogenous microstructure and smooth surface quality. These trays had the lowest density (0.27 g/cm^3) and had approximately 53% reduction in water absorption. Moreover, both the tensile and flexural strain of these foams was significantly higher than other foams.

1. Introduction

Currently, the use of single-use foam trays, made of expanded polystyrene, has risen. About 1 million ton single-use foam packaging, mostly in the tray form, is annually produced from expanded polystyrene (Anonymous, 2007). Decomposition of these foam products is not possible and recycling of them is very difficult (Franz & Welle, 2003; Vlieger, 2003). The environmental pollution caused by these products has led to an increased interest in developing biodegradable foams produced from renewable resources. Starch is one of the possible alternative materials for making biodegradable foams. Not only is starch renewable and biodegradable, it is also inexpensive and abundant. Several studies have demonstrated the production of starch-based foam containers. Starch foams have been produced by an extrusion process (Cha, Chung, Seib, Flores, & Hanna, 2001; Ganjyal, Weber, & Hanna, 2007; Guan & Hanna, 2004; Manoi & Rizvi, 2010; Silva, Ibezim, Ribeiro, Carvalho, & Andrade, 2006; Willett & Shogren, 2002), a solvent exchange technique (El-Tahlawy, Venditti, & Pawlak, 2007, 2008; Patel, Venditti, Pawlak, Ayoub, & Rizvi, 2009) or by baking in a mould (Cinelli, Chiellini, Lawton, & Imam, 2006; Glenn, Orts, & Nobes, 2001; Lawton, Shogren, & Tiefenbacher, 2004; Salgado, Schmidt, Molina, Mauri, & Laurindo, 2008; Shey, Imam, Glenn, & Orts, 2006; Shogren, Lawton, & Tiefenbacher, 2002). Foams made through the extrusion process and the solvent exchange technique are difficult to mould into shaped products. The baking process has produced foam products with desired shapes. Some of these starch foams had excellent physical and mechanical properties and could function well as a replacement for expanded polystyrene trays. However, the hydrophilic characteristic of starch limits the use of these foam products.

Cross-linking the starch is one potential way to produce water-resistant material because cross-linking considerably reduces the swelling power, solubility, water-binding capacity and hydrophilicity of starch (Kaur, Singh, & Singh, 2006; Zhou, Zhang, Ma, & Tong, 2008).

Dialdehydes are the multifunctional reagents that cross-link starch by reacting with the hydroxyl groups of starch and introduce intermolecular bridges between the polysaccharides chains. Glutaraldehyde ($C_5H_8O_2$) is a dialdehyde that has been used extensively to cross-link starch in previous studies (El-Tahlawy et al., 2007; Natarajan et al., 2005; Sung, Huang, Huang, Tsai, & Chiu, 1998; Wang & Hsieh, 2001). Glyoxal ($C_2H_2O_2$), another dialdehyde, has been used to cross-link starch-based paperboard coatings to improve their water resistance, and it is listed as an accredited chemical substance in the production of paper for food packaging by the Federal Institute for Risk Assessment in Germany and by the Food and Drug Administration in the U.S. (Anonymous, 2011a, b). No studies have been conducted to investigate the foam produced from starch cross-linked with glyoxal.

In the present study, corn starch was cross-linked with glyoxal, and foam trays were produced from native and cross-linked starches using the baking process. The objective of this study was to

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* Corresponding author. Tel.: +90 242 3102458; fax: +90 242 2274564.
E-mail address: mkuslu@akdeniz.edu.tr (M.-K. Uslu).

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evaluate the effect of glyoxal cross-linking on the physico-chemical and mechanical properties of the starch foams.

2. Materials and method

Food-grade corn starch was purchased from Cargill Türk (İstanbul, Turkey). The glyoxal solution (40%) was obtained from BASF Turk Chemical Co. (İstanbul, Turkey). Guar gum was supplied by Incom Co. (Mersin, Turkey), and other reagents were purchased from Sigma–Aldrich Co.

2.1. Glyoxal treatment

Starch (40 g, dry basis) was suspended in distilled water (60 ml). Different amounts of glyoxal were added using a micropipette: 0.13, 0.38, 0.64 and 1.27 g/kg (based on the dry weight of the starch). The mixture was allowed to react for 24 h at 25 °C with continuous stirring. Then, the slurry was filtered through a filter paper, and the starch was washed with distilled water (3 × 300 ml) and dried at 50 °C for one day. The treated starches were grounded with a hammer mill (IKA Labortechnik, Staufen, Germany) and passed through a 250-μm sieve.

2.2. Determination of reacted amount of glyoxal

The amount of glyoxal that remained in the suspension after cross-linking was determined by modification of a method previously described (Barros, Rodrigues, Almeida, & Oliva-Teles, 1999). The filtrate (1 ml) was passed through a solid phase extraction (SPE) column (270 mg, Chromafix C18, Macherey-Nagel GmbH & Co. KG, Düren, Germany) and washed with 10 ml of water. Less-polar interferences were retained on the column, and the more polar glyoxal was collected and reacted with 5 ml of 0.5% o-phenylenediamine (previously passed through another SPE column for 30 minute) to form less-polar quinoxaline. The mixture containing quinoxaline was diluted with acetate buffer (pH = 4.5) to 25 ml and passed through a SPE column, in which the quinoxaline was retained and *o*-phenylenediamine (more polar in acetate buffer) was almost completely eluted with 2 ml acetate buffer. Then, 1 ml of acetonitrile was injected into the column to extract the quinoxaline. All of the elutions through the SPE column were facilitated using a Phenomenex vacuum manifold. The extract containing quinoxaline was filtered through a 0.45-μm membrane filter and injected into the HPLC system. The chromatographic separation was performed on a solvent delivery system (20AD, Shimadzu, Japan) coupled with an auto-sampler (SIL-20A Prominence, Shimadzu) and a Nucleodur C18 (Macherey-Nagel GmbH & Co.) column (5 μm, 250 mm × 4.6 mm) and preceded by a guard column of the same material (5 μm, 8 mm × 4 mm) and a photo diode array detector (SPD-M20A, Shimadzu), which were controlled by LC solution software. Each run was conducted using isocratic elution performed on the column, which was maintained at 30 °C by using a column oven (Varian Mistral, CA) for 20 min. The mobile phase was acetonitrile (HPLC grade) at a 0.8 ml/min flow rate. The samples (20 μl) were analysed in duplicate. Quinoxaline was quantified at 315 nm. The peaks in every sample chromatogram were identified by matching the with the retention times of the authentic standards, and they were also confirmed by the spiking of authentic standards into the samples. The peaks were externally quantified by using the calibration curve of the authentic standards.

2.3. Viscosity measurement

The viscosity measurement was performed by modifying a previously described method (Shi & BeMiller, 2002). The viscosity of modified starches was measured by Brookfield DV-II+Pro (Brookfield Engineering Laboratories, Inc., USA) using a starch viscosity measurement system. Spindle #27 was used and rotated 100 rpm during the viscosity test. 12 ml of the 7% native or cross-linked starch suspension was loaded into a sample cell, and the cell was placed in the sample holder. The sample was equilibrated to 60 °C while stirring. Then, the spindle was inserted into the sample, and the viscosity measurement began. The temperature of the sample was raised to 95 °C (2 °C/min) and held constant for 2 min and then cooled to 30 °C in 3 min.

2.4. Preparation of starch foams

Native or cross-linked starch (35 g) suspensions in water (65 g) were prepared, and guar gum (0.5% by weight of starch) was added to prevent the settling of the starch. The suspensions were homogenised at 21,000 rpm (Ultraturrax T-25, IKA Labortechnik, Staufen, Germany) for 5 min. The suspensions were baked in the form of trays using a tray mould (165 mm long, 75 mm wide, 35 mm deep and 5 mm plate separation) of an electrically heated baking machine (Neumaerker, Hemer, Germany) or in the form of foam plates using a panel mould (220 mm in diameter, 3 mm plate separation) of the same machine. Slight pressure was applied to close the moulds. The baking temperatures were adjusted to 190 °C, and the baking times were the minimum required, varying between 8 and 11 min. Steam generated from water of the suspension acts as the blowing agent to create foam inside the mould. Starch foams were equilibrated in an environmental chamber (ID 400 Nüve, Ankara, Turkey) with 50 ± 2% relative humidity and 25 °C for 7 days before the analyses.

2.5. Scanning electron microscopy

The morphology of the starch granules and starch-based foams was examined using a scanning electron microscope (ZEISS Leo 1430 SEM, Oberkochen, Germany). A small piece was cut from the foams and mounted on aluminium stubs, after which the foam piece was coated with a thin layer of gold/palladium under vacuum.

2.6. Density and moisture content

The density of the foam trays was determined by weight and volume measurements.

The approximately 6-g tray specimens were placed on Petri dishes and dried in an oven at 105 °C for one day. The percent moisture content of the trays was calculated as the percent weight loss based on the original weight.

2.7. Colour

A CR-400 Minolta chroma meter (Minolta, Osaka, Japan) was used to measure the colour of the trays. Three readings on the surface of the trays were taken using the CIE Laboratory L^* (lightness), a^* (redness), b^* (yellowness) system in daylight conditions. From the colour values, the total colour difference (ΔE) was calculated as:

$$\Delta E = [(L - L')^2 + (a - a')^2 + (b - b')^2]^{1/2}$$

where L', a', and b' values were the mean colour values of the native starch foam.

2.8. Water absorption of trays

The percentage of water absorption in the foam trays was calculated as the percentage of weight increase after the tray was

Table 1
Efficiency of glyoxal cross-linking reaction.

Samples[a]	Added amount of glyoxal (g/kg starch)	Reacted amount of glyoxal (g/kg starch)	Efficiency of cross-linking (%)
C	–	–	–
G1	0.127	0.126	99.2
G2	0.381	0.269	70.6
G3	0.641	0.271	42.3
G4	1.270	0.468	36.9

[a] C, native starch; G1, G2, G3 and G4, cross-linked starches with glyoxal.

completely submerged in 1000 ml of distilled water at 25 °C for 1 min.

2.9. Mechanical properties

Tensile and flexural tests were performed to determine the mechanical properties of the foams using a TA.XT plus (SMS, Surrey, UK) machine with a 50 N load cell. To prepare the samples for the mechanical test, the starch foam panels were cut into strips (100 mm × 25 mm) and conditioned in an environmental chamber (ID 400 Nüve, Ankara, Turkey) with 50 ± 2% relative humidity at 25 °C for 7 days. The tensile strength (S_t) and percent elongation at the break (e_t) of the strips were determined by a tensile test according to ASTM D638M-91a (ASTM, 1992). The test was performed with an initial grip separation of 50 mm and cross speed of 1 mm/s. The flexural tests were performed using the three-point bending method according to EN ISO 178:2003 (ISO, 2003) with a span setting of 3 cm; the foam strips were deformed until they broke. The flexural strength (S_f), strain to break (e_b) and modulus of elasticity (E_b) of the strips were calculated.

2.10. Statistical analysis

All statistical analyses were conducted using The SAS System for Windows v7.00 (SAS Institute, Cary, NC, USA). The values are presented as mean ± standard deviation. The data were subjected to analysis of variance, and significant differences were determined by Duncan's multiple range test.

3. Result and discussion

During the production of the starch foams, the starch must gelatinise and dry. A small amount of pre-gelatinised starch can be used to prevent the setting of the starch in the batter, but it is impossible to produce starch foams using pre-gelatinised starch because of its high paste viscosity. Therefore, cross-linking the starch with glyoxal was performed at room temperature to prevent the gelatinisation of starch. The unreacted glyoxal was easily separated from the suspension by washing and filtering.

3.1. Efficiency of glyoxal cross-linking

The amount of glyoxal added to the suspension, the amount of glyoxal that reacted with starch and the efficiency of the cross-linking reaction are shown in Table 1. The starch that was treated with higher concentrations of the cross-linker reacted with higher amounts of the cross-linker. However, the efficiency of the cross-linking reaction decreased from 99.2% to 36.9% when the added amount of glyoxal increased from 0.127 to 1.27 g/kg.

3.2. Effects of cross-linking on starch

The appearance of starch granules after the cross-linkage was observed using SEM (not shown). The native and cross-linked samples had very similar morphology. The only difference was that some small holes were observed on the surface of the native starch granules, whereas these holes disappeared when starch was cross-linked with glyoxal. Similar to our results, the cross-linking of starch with adipic–acetic mixed anhydride, phosphorus oxychloride and epichlorohydrin was shown to not significantly change the microstructure of starch (Kaur et al., 2006; Luo, Huang, Fu, Zhang, & Yu, 2009).

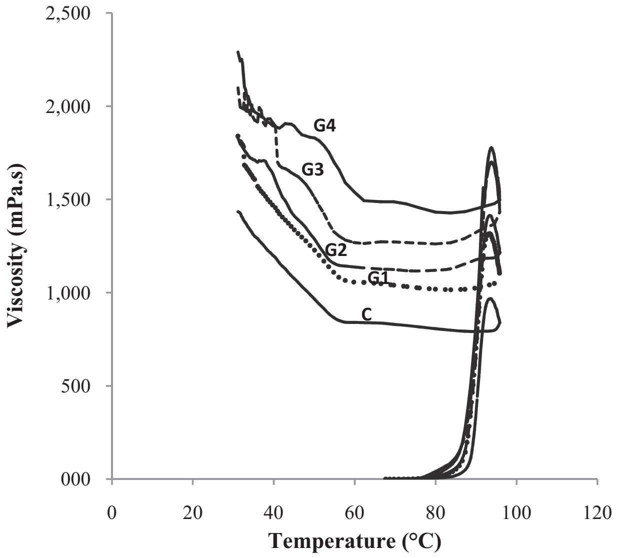

Fig. 1. Pasting profiles of native and cross-linked starches.

The pasting profiles of the starches are presented in Fig. 1. A decrease in the pasting temperatures and an increase in the peak, hot and cold paste viscosities were observed in the cross-linked starch vs. the native starch. The change in the pasting profile was caused by granule strengthening. The peak viscosity of the cross-linked starch may decrease or increase depending on the cross-linker type and concentration. However, the cold paste viscosity of the cross-linked starch generally increases (Kaur et al., 2006).

3.3. Morphology of the trays

The native starch tray had an irregular shape and a surface with many small holes and occasionally cracks. The foam trays made from cross-linked starches had regular shapes and smooth surfaces without any cracks or holes. However, there were frequently white zones on the surface of foam trays made from highly cross-linked starches (G3 and G4) due to the accumulation of non-gelatinised starch granules. The cracks on the surface of the native starch foam and the non-gelatinised starch zones on the surface of G3 and G4 foams were also seen from the surface micrographs of the starch foams (Fig. 2). As seen in the cross-section micrographs of the foams, the cross-linked starch foams had a more expanded structure (Fig. 2). The cell size of the starch foams increased when the cross-linkage in the starch increased. The cell walls of the cross-linked starch foams were thinner than those of the native foams. The more expanded structure of the modified starch foams was likely caused by a quicker (at a lower temperature) gelatinisation of the cross-linked starches and faster water evaporation that were observed during the baking process.

3.4. Physico-chemical properties of the trays

The batter volume, baking time, density and water content of the trays are shown in Table 2. The batter volume that was required to produce the trays from G1 and G2 was less than that

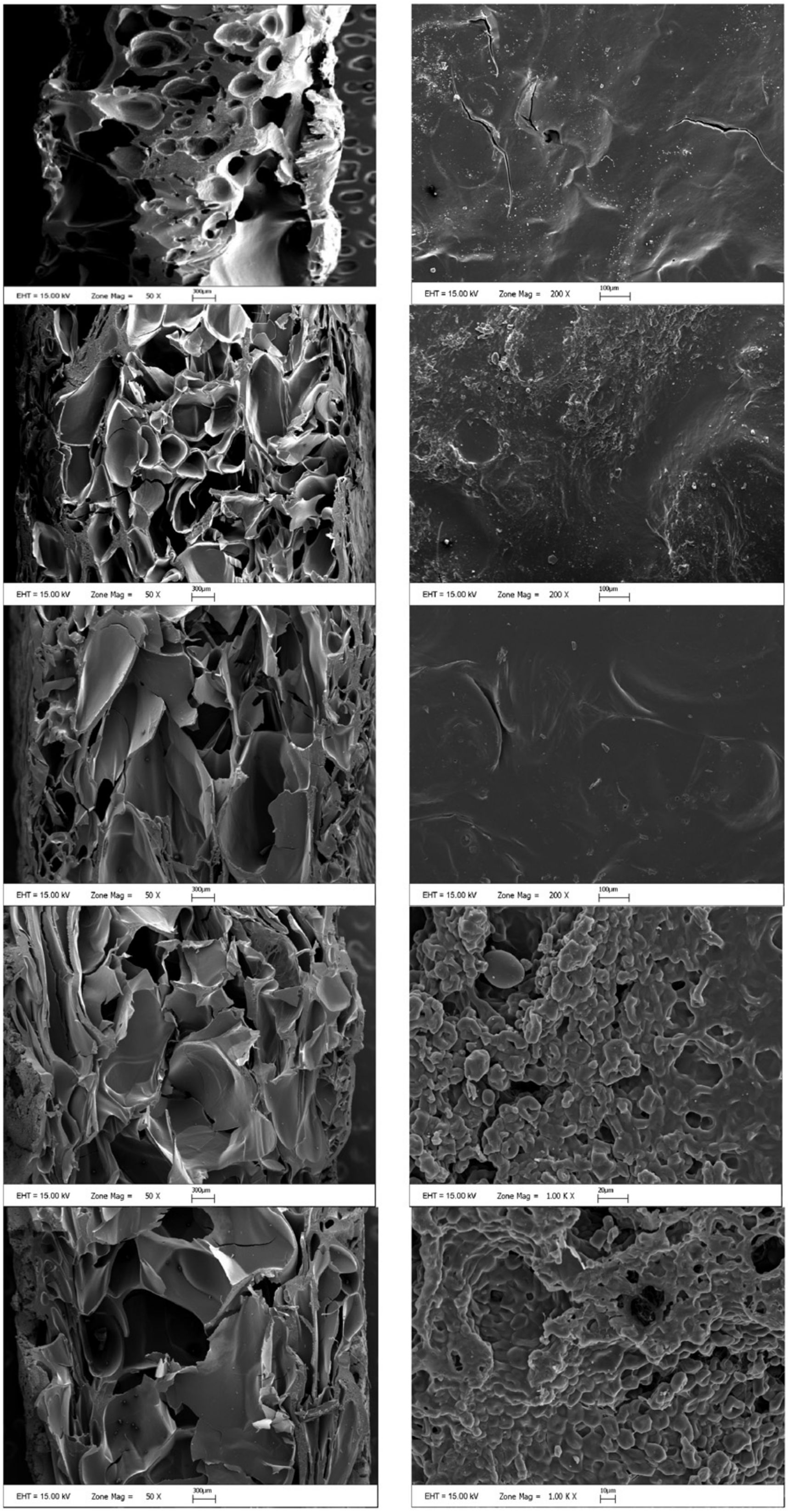

Fig. 2. Micrographs of native and cross-linked starch trays: (a) cross-section and (b) surface.

required for the unmodified cornstarch. However, the highly cross-linked starch (G4) and the native starch foams required the same volume of batter. The baking time of the foams that were made from highly cross-linked starches was lower than that of the lesser cross-linked starches and the unmodified starch. The moisture content of the native and cross-linked starch trays conditioned 50% RH varied between 10.16% and 10.50%, which values were not significantly different.

Table 2
Baking parameters, density and water content of the native and cross-linked starch trays.

Sample	Batter volume (ml)	Baking time (min.)	Density (g/cm^3)	Water content (%)
C	146	11	0.44 ± 0.042a	10.20 ± 0.42
G1	120	10	0.27 ± 0.032c	10.31 ± 0.35
G2	120	9	0.27 ± 0.025c	10.50 ± 0.62
G3	140	8	0.33 ± 0.038bc	10.31 ± 1.08
G4	146	8	0.36 ± 0.049b	10.16 ± 1.50

Values followed by different letters are significantly different ($p < 0.05$) (Duncan's multiple range test). Values are mean ± standard deviation.

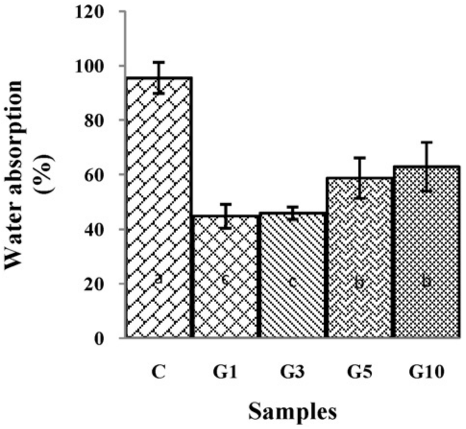

Fig. 3. Percent water absorption of native and cross-linked starch trays.

The density of the starch foam depends on the source (Shey et al., 2006), concentration, amylose content of the starch (Shogren, Lawton, Doane, & Tiefenbacher, 1998) and concentrations of other ingredients (Glenn et al., 2001). Corn starch is the most abundant and cheapest starch. However, an average density of the native corn starch trays (0.44 g/cm^3) was found to be higher than that of starch foams made from different starch source. The densities of pure wheat, potato and cassava starch foams were reported to be 0.09–0.22, 0.11–0.15 and 0.14–0.48 g/cm^3, respectively (Cinelli et al., 2006; Glenn et al., 2001; Preechawong, Peesan, Supaphol, & Rujiravanit, 2004; Salgado et al., 2008; Shey et al., 2006). Cross-linking significantly decreased the densities of the trays (Table 2) and these trays owned the medium density. The trays made from G1 and G2 had the lowest density values (0.27 g/cm^3). A low density is ideal for foams because of the reduced cost and lighter product.

The colour parameters of the starch foams were significantly affected by cross-linking (Table 3). The L^*, a^*, b^* and ΔE values of the cross-linked starch foams were higher than those of the native starch foam. Cross-linking of the starch resulted in a brown colour of the foams. Similarly, aldehyde-based resins used in the paper industry have been shown to cause a severe browning in starch-based paper coatings (Shogren et al., 2002).

To test the water resistance of the foam trays, the unmodified and cross-linked starch trays were submerged in distilled water for one minute. The cross-linking treatment significantly reduced the water absorption of the foams (Fig. 3). In particular, the foams made from G1 and G2 were the most water-resistant foam trays. For example, the starch foam produced from G1 absorbed 53% less water than the native starch foam. The increase in resistance of G1 and G2 foams against water probably resulted from an improvement in the surface quality of the foams and a decrease in the hydrophilicity of the starch due to the reaction between the hydroxyl groups of starch and glyoxal. Non-gelatinised starch accumulation on the surface of the foams produced from G3 and G4 caused a slight increase in the percent water absorption of these foams. According to our knowledge, there has not been any report regarding the water absorption of foams produced from cross-linked starch with glyoxal. However, this cross-linking agent (or insolubilising compound) has been used in the paper industry for the preparation of water-resistant starch-based coatings on paper to increase printability and decrease susceptibility to moisture (Dellinger & Helou, 2005; Kelly & Lowery, 1975).

3.5. *Mechanical properties of the foams*

To test the mechanical properties of the trays, the specimens were prepared from foam palates that had the same formulation as the trays. The results of the tensile and flexural tests are shown in Table 4. The flexural strength (S_b) of the foams was higher than their tensile strength (S_t). This showed that the intact structure of the starch foams was stronger, but some weak points in the structure were present. Both the tensile and flexural properties of the foams were significantly affected by cross-linking. Although the maximum force required to break the cross-linked starch specimens in both the tensile and bending tests was higher than that of the native counterpart, the S_t and S_b of the native starch foam were calculated to be significantly higher because of its lower thickness. The cross-linking did not significantly affect the flexural modulus of elasticity (E_b) of the foams. However, the tensile modulus of elasticity (E_t) of the cross-linked starch specimens was lower than that of the native starch specimens. Moreover, the tensile strain (e_t) and flexural strain (e_b) of the G1 and G2 foams were significantly higher than those of the other foams. In other words, the foams made from cross-linked starches were more flexible. The S_t, e_t, E_t, S_b, e_b and E_b values of the expanded polystyrene (EPS) were reported to be 1.1 MPa, 5.4%, 38 MPa, 1.3 MPa, >5% and 105 MPa, respectively (Glenn et al., 2001). The starch foams had a higher bending resistance compared with the EPS and approximately the same tensile strength as the EPS. However, the results showed that the starch foams were more brittle than the EPS because of the lower E_t and E_b values of the EPS.

Table 3
Colour values of the foam trays.

Samples	L^*	a^*	b^*	ΔE
C	61.78 ± 4.67b	−1.68 ± 0.14c	6.36 ± 0.82d	0.0c
G1	68.59 ± 5.38a	−0.17 ± 0.75b	13.64 ± 1.15cb	10.97 ± 2.88b
G2	70.55 ± 4.15a	0.42 ± 0.49a	14.26 ± 1.31ab	12.53 ± 1.78ab
G3	71.68 ± 3.75a	0.93 ± 0.28a	15.13 ± 0.54a	13.69 ± 2.73a
G4	72.95 ± 4.20a	0.47 ± 0.40a	12.55 ± 1.02c	13.16 ± 3.51ab

Values followed by different letters are significantly different ($p < 0.05$) (Duncan's multiple range test). Values are mean ± standard deviation.

Table 4
Tensile and flexural properties of the native and cross-linked starch foams.

Sample	T[a] (mm)	S_t[b] (MPa)	e_t[c] (%)	E_t[d] (MPa)	S_b[e] (MPa)	e_b[f] (%)	E_b[g] (MPa)
C	1.82 ± 0.39b	1.54 ± 0.37a	0.87 ± 0.28c	378.1 ± 54.1a	7.21 ± 2.09a	3.56 ± 1.32b	147.76 ± 48.82a
G1	3.80 ± 0.45a	1.06 ± 0.44b	1.51 ± 0.57ab	175.1 ± 61.7b	3.20 ± 0.63c	4.79 ± 1.76ab	134.19 ± 46.57a
G2	3.85 ± 0.59a	1.08 ± 0. 42b	1.85 ± 0.79a	153.2 ± 49.3b	3.74 ± 0.66c	5.36 ± 1.91a	102.67 ± 23.46a
G3	3.73 ± 0.40a	0.96 ± 0.27b	1.29 ± 0.44bc	203.1 ± 49.9b	4.04 ± 1.47bc	3.87 ± 1.38b	105.91 ± 21.21a
G4	3.53 ± 0.28a	1.06 ± 0.44b	1.10 ± 0.43bc	211.5 ± 73.1b	4.76 ± 1.29b	4.30 ± 1.27ab	125.56 ± 43.15a

Values are mean ± standard deviation. Values followed by different letters are significantly different ($p < 0.05$) (Duncan's multiple range test).

[a] Thickness.
[b] Tensile strength.
[c] Tensile strain at the breaking point.
[d] Tensile modulus of elasticity.
[e] Flexural strength.
[f] Flexural strain at the breaking point.
[g] Flexural modulus of elasticity.

4. Conclusion

Food packaging trays were prepared from starch that was cross-linked with glyoxal at different concentrations. The cross-linkage of the starch led to a decrease in baking time, density, and water absorption of the trays. The trays made from starch that was cross-linked with 0.126 and 0.269 g/kg glyoxal exhibited the best properties, including not only a notably reduced density and water absorption, but also increased flexibility. The results presented in this study indicated that cross-linked starch trays have good expanded structure and adequate mechanical properties. The properties of the cross-linked trays may be further improved by using some additives such as nano-filler and fibre.

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