

Effect of Glycerol on the Physicochemical Properties of Cereal Starch Films

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Abstract

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The physical properties of corn, wheat and rice starch edible films with different level of glycerol were evaluated. Starch films exhibited an apparent endothermic peak in the range of 151–199°C with corn starch film with 1.6% glycerol having a relatively lower T_o and higher T_p . X-ray diffraction spectroscopy indicated that the corn, wheat, rice starch powders had ~ 39–49% crystallinity, whereas Fourier transform infrared spectra showed peaks associated with the tightly bound water present in the rice, corn, wheat starches. Overall, glycerol addition could enhance the water vapour pressure barrier properties of the films, but their tensile strength was reduced. Corn starch films were identified as the most suitable choice for edible packaging as its thermal characteristics indicated suggested a more acceptable sealability. Rice starch films is proposed as the better choice for coating as it showed better flexibility as indicated by lower tensile and higher elongation properties.

Keywords: edible coating; edible film; plasticizers; DSC

Abbreviations: XRD – X-ray diffraction; FTIR – Fourier Transmission Infrared; WVP – water vapor permeability; TS – tensile strength; E – elongation; DSC – differential scanning calorimetry; XRD – X-ray diffraction; FTIR – Fourier transform infrared spectroscopy

Edible films and coatings are both human and environment friendly packaging materials which can preserve food products by preventing or delaying the spoilage process. They act as a partial moisture, oxygen barrier and/or as a carrier of targeted functional ingredients such as preservatives and antioxidants further enhancing their functionality (FABRA *et al.* 2011; ANDRADE *et al.* 2012).

Edible coatings and films made from carbohydrates are excellent moisture and/or oxygen barriers because of their tightly packed and ordered hydrogen-bonded network structure. Starch based

films are important due to their physical and barrier properties that are similar to synthetic polymers i.e. transparent, tasteless, odorless, semi-permeable to CO₂, and impermeable to O₂ (VÁSCONEZ *et al.* 2009; MOREIRA *et al.* 2011). Furthermore, starch films are cost effective due to the availability of starch from a wide range of agricultural sources such as cereals, pulses and tubers (LIU 2005; XU *et al.* 2005; PARETA & EDIRISINGHE 2006).

In the manufacture of films, plasticizers are often required to increase film flexibility and reduce brittleness by reducing the intramolecular hydrogen

bonding along the polymer chains thereby increasing the intermolecular spacing (JUNG & ARISTIPPOS 2005; JANJARASSKUL & KROCHTA 2010). One of the most commonly used plasticizers for starch films is glycerol due to its molecular structure that is similar to the glucose units of starch thus increasing the chance of chemical interaction with starch (MALI *et al.* 2005; GARCÍA *et al.* 2009; MOHAMMADI *et al.* 2013).

Use of XRD and FTIR spectroscopy are important in studying the difference in the hydrogen bond-forming abilities and retrogradation of starch during film formation (MA & YU 2004). FTIR analysis is also a powerful tool to analyze the interaction between plasticizers and starch molecules during film formation. Much work has been reported on the comparison of different types of starches for coating applications but there is a lack of studies on the physicochemical properties of films prepared from different cereal starches and the role of glycerol as a plasticizer for improving the functionality of these starch films. The aim of this study was to fill the gap in this knowledge.

MATERIAL AND METHODS

Film making. Corn, wheat and rice starch were obtained from MP Biomedicals (LLC, France). The amylose content of the starch was as follows: corn 25%, wheat 23%, and rice 15%. Four grams of each starch was dispersed in 100 ml of distilled water to prepare 4% (w/v) of starch solution. The solution was stirred and heated at 80°C for 30 minutes. Then either 1.6 and 1.8% (w/v) glycerol (Sigma-Aldrich, USA) were added to the starch solutions. The solutions were mixed thoroughly before they were cast onto flat plastic plates. The cast films were dried at 60°C for at least 20 h and then the dried films were peeled from the plates. The dried films were stored at 20% RH and 25°C for 24 h prior to testing.

Thickness. Thickness of films was measured with a micrometer (Mitutoyo, Japan). Four measurements from different part of each film were taken. The average film thickness was used to calculate other edible films parameters.

Water vapor permeability (WVP). The WVP of films was determined using the gravimetric cup method according to MCHUGH *et al.* (1993) with some modifications. A dried crucible (diameter between 60–610 mm) was filled with 20 g of silica gel to control the RH of the internal surrounding of

the crucible to 0%. A film was placed on top of the crucible to cover it at a distance of about 2 cm from the silica gel surface. The water vapor transmission rates (WVTR) of each film were determined at 60% RH and 25°C. Before putting the crucible in a desiccator, the weight of each crucible was taken. Weight gains were measured by weighing the crucible to the nearest 0.0001 g daily for a period of 7 days. Weight gained against time was plotted to calculate the WVTR in g/m²-day. Three replicates for each formula of starch were used. The WVP of film was calculated using equations below:

$$\text{WVTR} = \Delta m / (Am \times \Delta t) \quad (1)$$

$$\text{WVP} = \text{WVTR} (L / \Delta p) \quad (2)$$

$$\Delta p = P_s (RH_o - RH_i) \quad (3)$$

where: WVTR – calculated at 25°C and 60% RH; Δm – weight gain by silica gel (g); A – exposed area of film (m²); Δt – time period; L – average of film thickness for each specimens expressed in millimeter; Δp – the partial water vapor pressure difference between the two surfaces of the film specimens expressed in Pascal; P_s – partial water vapor pressure at 25°C; RH_o – relative humidity of outside; RH_i – relative humidity of inside the crucible

Textural properties. The texture of each film in terms of tensile strength (TS) and elongation (E) were measured using a Universal Texture Analyser (TA-HD plus model; Stable MicroSystems, UK) according to JIMÉNEZ *et al.* (2012), with some modification. TS and E were calculated from the stress versus strain curves, estimated from force-distance data obtained for the different films (2.5 cm wide and 8 cm length and different thicknesses) at 25°C (six replicates). The primary grip separation was set at 40 mm and samples were mounted on the film-extension grips of the machine and stretched at 1 mm/min until breaking. TS (MPa) was calculated by dividing the maximum load (N) with the initial cross sectional area (m²) of the specimen and E (%) by dividing the ratio of the final length at the point of break to the initial length of a specimen (40 mm), Young's modulus (MPa) is experimentally determined from the slope of a stress-strain curve (XU *et al.* 2005).

Thermal properties. A differential scanning calorimetry (DSC) (DSC823e; Mettler Toledo, Sweden) was used to determine the thermal characteristic of starch films. Measurements were made in triplicate at a heating range of 27–220°C and a scanning rate of 10°C/min in a closed aluminum pan (40 μ l) with-

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out pins containing about 3 to 6 mg of sample. An empty pan was used as the reference. The samples were conditioned in 20% RH for 24 h before DSC measurements were taken. The onset (T_o), peak (T_p) and outset (T_{ot}) of starch films were determined.

X-ray diffraction (XRD). The crystalline structure of the films and the starch powders from which they were prepared were studied by XRD (PW3040/60 X'Pert PRO; PANalytica, The Netherlands) at 40 kV and 40 mA. Scattered radiation was detected in 2θ of 5–70° at a speed of 2°/minute.

The relative crystallinity (X) was calculated from equation 4 according to the BULTOSA and TAYLOR (2003).

$$X = I_c / (I_c + I_a) \times 100 \quad [\%] \quad (4)$$

where: I_c – the integrated intensity of crystalline phase; I_a – the integrated intensity of the amorphous phase

Fourier transform infrared spectroscopy (FTIR). Infrared spectra, in ATR mode, of native starch powder and starch films were recorded by a FTIR (Model Spectrum100; Perkin Elmer) with capability of covering the spectral range of 4000–280 cm^{-1} at a resolution of 4 cm^{-1} with three replications for each sample.

Statistical analysis. Analysis of variance (ANOVA) was performed for all data at a confidence interval of 95%. Minitab (16.1) software was used to analyse the data.

RESULT AND DISCUSSION

Film thickness. The thickness of edible films is an important parameter since it directly affects the biological properties and the shelf life of the coated food (SKURTYS *et al.* 2010). The variations in thickness is dependent on many factors including composition, processing parameters, amylose percentage, and size of starch granules (ROMERO-BASTIDA *et al.* 2005; GARCÍA *et al.* 2009). In the present research, thickness of the different type of films did not vary significantly (Table 1).

Water vapor permeability. The main role of many edible films is to decrease the amount of water transfer from the food to the external environment and vice versa; therefore a lower WVP is considered desirable. There were a significant ($P > 0.05$) differences between the WVP of the starch films developed in this study (Table 1). Wheat, corn and rice starch films with higher amount of glycerol (1.8%) had the highest WVP while, those with 1.6% glycerol had the

Table 1. Some characteristics of different starch films

Films (% glycerol)	Thickness (mm)	WVP ($\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}\cdot\text{kPa}$)	Crystallinity (%)
w + 1.6	0.19 ± 0.01^a	10.40 ± 0.60^b	5.11
w + 1.8	0.19 ± 0.01^a	13.34 ± 0.61^a	5.42
c + 1.6	0.19 ± 0.01^a	10.89 ± 0.49^b	5.56
c + 1.8	0.21 ± 0.02^a	13.27 ± 0.66^a	5.63
r + 1.6	0.19 ± 0.01^a	10.69 ± 0.44^b	5.29
r + 1.8	0.19 ± 0.01^a	13.03 ± 0.52^a	5.71

w – wheat; c – corn; r – rice; WVP – water vapour pressure; each value is mean \pm SD; different letter within the same column indicates significant differences ($P \leq 0.05$)

lower values. Previously, the addition of plasticizers in high amount have been shown to increase the water permeability of the film (SOUZA *et al.* 2012). One of the major problems found in the applications of edible films from starch is their high water vapour permeability in compare with plastic film due to the hydrophilic character of the starch molecule (ROMERO-BASTIDA *et al.* 2005).

Textural properties. Figure 1 shows the textural properties of the films. The rice starch film with 1.8% glycerol had the significantly lowest ($P < 0.05$) TS and that of the wheat starch film with 1.6% glycerol showed the highest ($P < 0.05$). Increasing the glycerol gave a decrease in TS within each starch type. The rice starch film with 1.8% glycerol showed the significantly ($P < 0.05$) highest E , while wheat starch films with 1.6 and 1.8% glycerol showed the lowest E . Addition of glycerol did not show any effect on E of corn and wheat starch films, while rice starch films showed an increase in E value with increased amount of glycerol. Corn starch film with 1.6% glycerol showed the highest Y , whereas rice starch films with 1.6% and 1.8% glycerol showed the lowest Y values. Increasing the amount of glycerol showed reduction of Y in wheat and corn starch films but did not influence the Y value of rice starch film.

The lower TS, Y and higher E observed in rice starch films could be due to the lower amount of amylose content i.e. 15% compared to the two other starches, which contained about 25%. This is supported by GARCÍA *et al.* (2009b) who stated that the mechanical properties of films are influenced by differences in the amylose to the amylopectin ratio with high amylose films being stiffer and stronger than those of from high amylopectin starches (MALI *et al.* 2006; LÓPEZ *et al.* 2008).

Thermal properties. DSC is a technique used to determine the quantity of heat either absorbed or

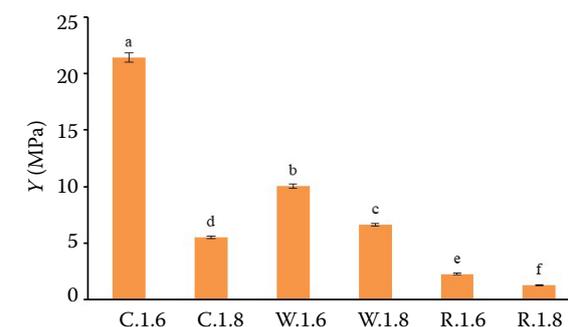
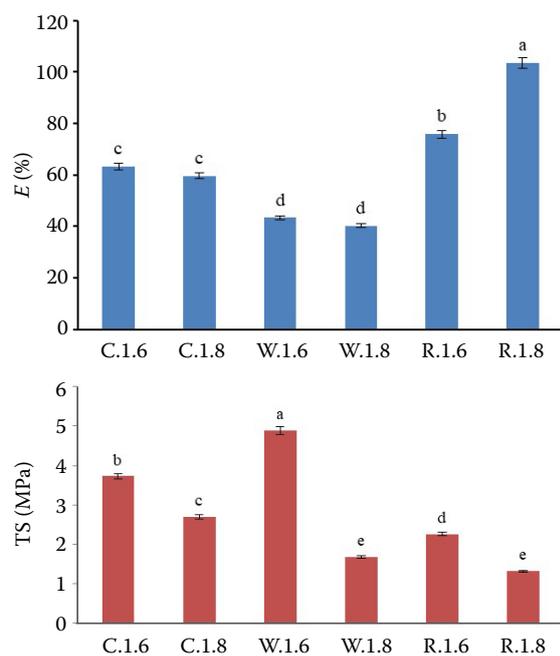


Figure 1. Mechanical properties of edible films made by different starches and amounts of glycerol

C.1.6 – corn starch film with 1.6% glycerol; C.1.8 – corn starch film with 1.8% glycerol; W.1.6 – wheat starch film with 1.6% glycerol; W.1.8 – wheat starch film with 1.8% glycerol; R.1.6 – rice starch film with 1.6% glycerol; R.1.8 – rice starch film with 1.8% glycerol; TS – tensile strength; Y – Young's modulus; E – elongation at break

released when substances undergo physical or chemical changes (OTHMAN *et al.* 2011). DSC thermograms can analyse the transition temperature i.e. onset (T_o), peak (T_p) and outset, (T_{ot}).

Thermal transition temperatures can be used to determine sealing temperatures of polymers. A significant difference between T_o and T_p is important to achieve good sealing. If the T_o and T_p values are very close, a film would almost completely melt during sealing, as at this temperature, the film loses its structure (TANNER *et al.* 2003).

The starch films exhibited an apparent endothermic peak in the temperature range of 151–199°C. Corn starch film with 1.6% glycerol had the lower T_o (151.44°C) and higher T_p (173.88°C) (Table 2) which showed a better seal ability. In contrast, the wheat starch with 1.6% glycerol showed the lower differ-

Table 2. Thermal characteristic of starch films by differential scanning calorimetry

Film (% glycerol)	T_o (°C)	T_p (°C)	T_{ot} (°C)
w + 1.6	150.55 ^b	151.57 ^c	158.3 ^c
w + 1.8	151.43 ^b	167.11 ^{ab}	167.46 ^{bc}
c + 1.6	151.44 ^b	173.48 ^a	198.4 ^a
c + 1.8	161.41 ^a	166.42 ^{ab}	195.77 ^a
r + 1.6	158.05 ^{ab}	162.96 ^b	167.68 ^{bc}
r + 1.8	154.16 ^b	159.73 ^{bc}	186.97 ^{ab}

w – wheat; c – corn; r – rice; T_o – onset; T_p – peak; T_{ot} – outset; each value is mean \pm sd. A different letter within the same column indicates significant difference ($P \leq 0.05$)

ences between onset and peak temperature (1.02°C) which resulted in lower seal ability.

X-Ray diffraction. XRD is a powerful method that can be used to study the retrogradation of thermoplastic starch and to evaluate the differences in hydrogen bond-formation between starch films (MA & YU 2004). Figure 2 demonstrates the X-ray diffraction patterns of starch films and powders. The peaks observed were mainly at 2θ between 16° and 23°. The X-ray diffraction patterns of cereal starch powders have higher intensity peaks in range of 16–23°, suggesting that starch powders have the higher crystallinity. The corn, wheat, rice starch powders had 40.48, 49.07, and 39.26% crystallinity, respectively. In terms of the starch films, their crystallinity increased when the plasticizer concentration increased from 1.6% to 1.8% (Table 1). ZHANG and HAN (2010) observed similar trends by addition of glycerol in crystallinity of starch films. The results in present study may be due to the fact that by increasing the amount of glycerol the free volume in the starch polymer matrix increases which can increase starch chain mobility which is favourable to the crystallite growth.

Fourier transform infrared spectroscopy. FTIR analysis is a powerful tool to analyse, in a qualitative way, the interactions between plasticizers and starch molecules (HUIHUA *et al.* 2013; THAKUR *et al.* 2016). In Figure 3, the spectrum of starches in powder and film formats is reported. The bands at 3297, 3295, 3292, and 3289 cm^{-1} corresponds to O-H stretching which is the major signal of starch, however the bands

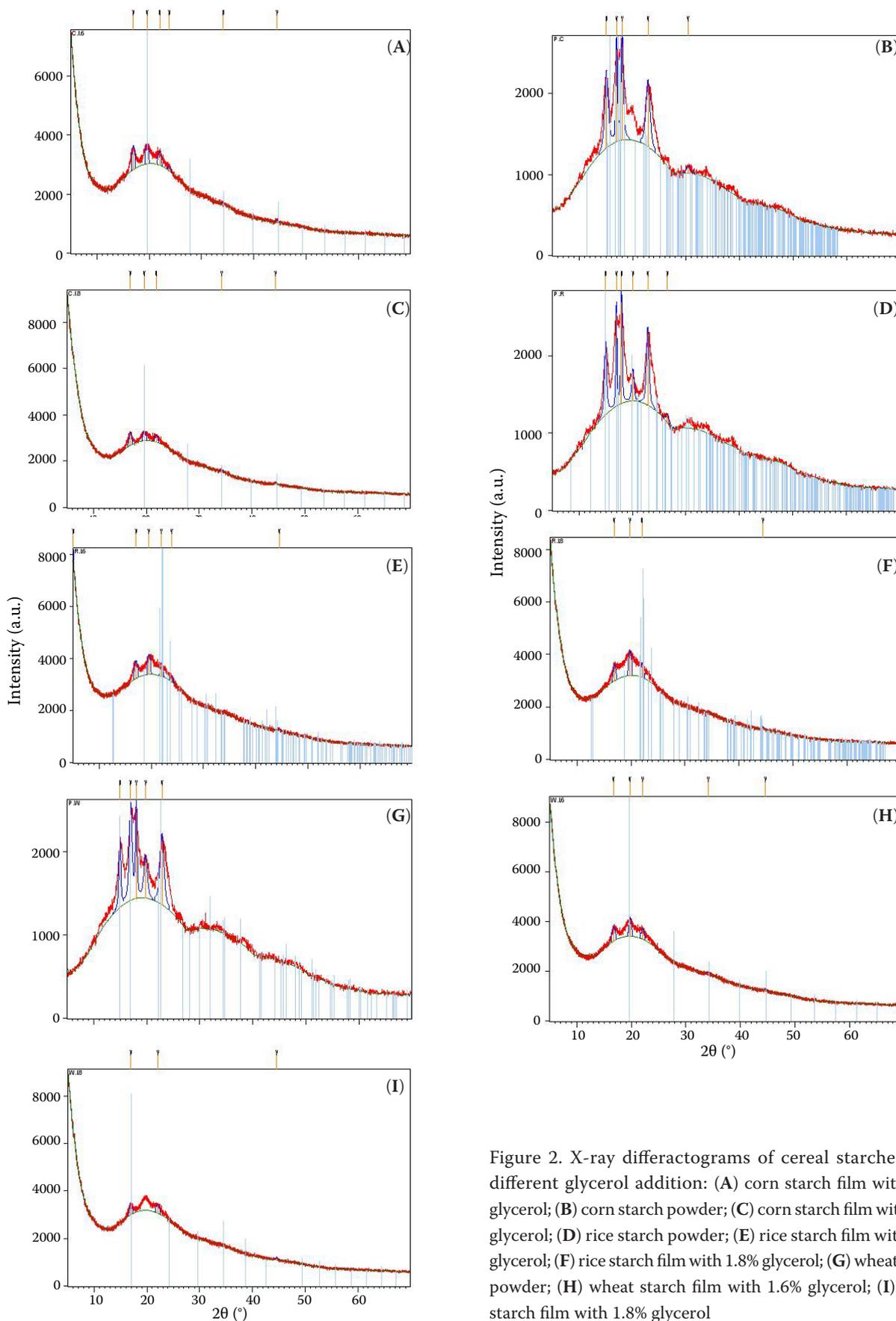


Figure 2. X-ray diffractograms of cereal starches with different glycerol addition: (A) corn starch film with 1.6% glycerol; (B) corn starch powder; (C) corn starch film with 1.8% glycerol; (D) rice starch powder; (E) rice starch film with 1.6% glycerol; (F) rice starch film with 1.8% glycerol; (G) wheat starch powder; (H) wheat starch film with 1.6% glycerol; (I) wheat starch film with 1.8% glycerol

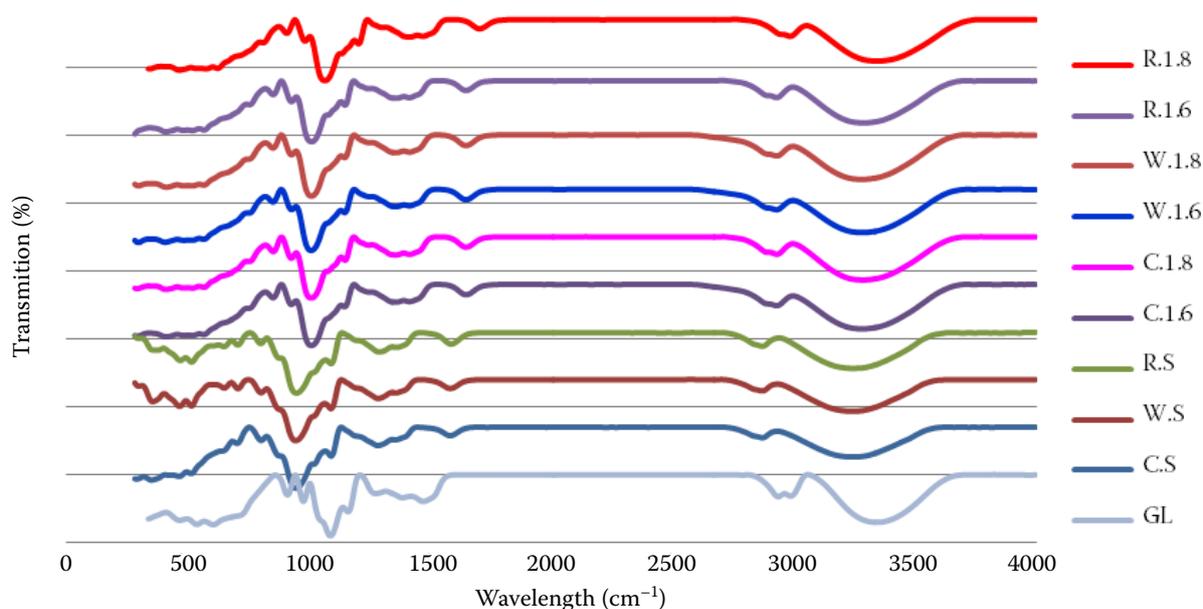


Figure 3. FTIR of cereal starch films, starch powders and glycerol

GL – glycerol; C.S – corn starch powder; W.S – wheat starch powder; R.S – rice starch powder; C.1.6 – corn starch film with 1.6% glycerol, C.1.8 – corn starch film with 1.8% glycerol; W.1.6 – wheat starch film with 1.6% glycerol; W.1.8 – wheat starch film with 1.8% glycerol; R.1.6 – rice starch film with 1.6% glycerol; R.1.8 – rice starch film with 1.8% glycerol

at 2925–2926 and 2931 cm^{-1} correspond to the C-H stretching in rice, corn, wheat starch powders and glycerol, respectively. The bands at 1638–1642 cm^{-1} are associated with the tightly bound water present in the rice, corn, wheat starches due to the hygroscopic nature of starch. Changes in structure and crystallinity are reflected in the focus area between 1200 and 950 cm^{-1} which is the fingerprinting region unique for a molecule (DE GIACOMO *et al.* 2008; YAO *et al.* 2011). In addition, the bands at 1000–1003 cm^{-1} are characteristic of the anhydroglucose ring O-C stretching the rice, corn and wheat starch powders. When two components are mixed, the physical blends versus chemical interactions are affected by changes in the characteristic spectra peaks (YIN *et al.* 1999). By addition of glycerol to the starches, the band of O-H stretching reduced, so the films containing glycerol formed stronger hydrogen bonds with water. The position, but not intensity of this band could be sensitive to hydrogen bonding with water (LIU *et al.* 2011; MUSCAT *et al.* 2012). The rice and corn films with 1.8% glycerol showed the higher band at 3282–3291 cm^{-1} in comparison with the presence of 1.6% glycerol, however, the wheat starch showed vice versa. Also, by addition of 1.8% glycerol to the rice and corn the band at 1007–1008 cm^{-1} is reduced more than the presence of 1.6% glycerol, while the wheat starch showed lower band in presence of 1.6% glycerol.

CONCLUSIONS

In conclusion, addition of glycerol as plasticizer improved the barrier and thermal properties of the starch films. The rice starch due to its cost and functional properties such as more flexibility and higher elongation can be utilized for the preparation of edible starch films and corn starch can be used as packaging materials due to higher tensile strength and better potential sealing ability. However, further research is required focusing on the practical applications of these starch glycerol films on various food products including fruits, vegetables and nuts.

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