

Effect of ribose-induced Maillard reaction on physical and mechanical properties of bovine gelatin films prepared by oven drying

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Abstract

The effect of ribose-induced Maillard reaction on the physical and mechanical properties of gelatin films was investigated. Bovine gelatin solution (5 g/100 mL) containing glycerol and sorbitol (1:1) was mixed with 20% (R20), 40% ribose (R40), or 40% sucrose (S40) (weight % is based on gelatin dry weight) followed by heating (90°C, 2 h) and oven drying to produce dried gelatin films. R20 and R40 films were brownish in color with lower light transparency, while CF (control film; without sugars) and S40 were colorless and had higher transparency. Tensile strength and Young Modulus values of the films were in the order; CF > R20 > R40 > S40, while elongation at break was in the order; R40 > S40 > R20 > CF. Water solubility and swelling percentages of the films were in the order; CF > S40 > R20 > R40, indicating the occurrence of insoluble “Maillard complexes” within R20 and R40 films. R20 and R40 films showed maximum light absorption at wavelength of 200 – 350 nm, whilst S40 and CF showed maximum absorbance at 200 – 250 nm. The addition of ribose yielded gelatin films with increased protection against UV light, even though the presence of sugars might had disrupted the inter connection of junction zones and decrease in mechanical properties. Occurrence of the Maillard reaction within R20 and R40 films could be the main reason for differences in physical and mechanical properties of films containing ribose that were formed from heated film-forming solutions.

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Keywords

Gelatin film

Ribose-treated

Maillard reaction

Mechanical properties

Physical properties

Ribose

Introduction

Gelatin films, with its many potential benefits, are widely used in the pharmaceutical/medical and cosmetic products, as well as in food industries to improve the shelf life of the content by controlling water absorption, oxygen permeation and aroma loss (Achet and He, 1995; Bigi *et al.*, 2004; Cao *et al.*, 2007b; Irwandi *et al.*, 2009). Despite this unique property, gelatin film does not have ideal mechanical properties and water vapor barrier, which could limit its applications (Cao *et al.*, 2007a; Bourtoom, 2008; Bourtoom, 2009).

To widen the application of gelatin film, gelatin has been modified via various cross-linking techniques and agents. Chemical and physical treatments can be applied to modify the polymer network through cross-linking of the polymer chains to improve protein film functionality. Increase in the carbonyl content of gelatin by reacting with chemical cross-linkers such as glutaraldehyde has led to increase in stiffness and reduced swelling ability (Rhim *et al.*, 2000; Bigi *et al.*, 2001; Chiou *et al.*, 2008; Martucci *et al.*, 2012). Interactions between gelatin and phenolic molecules, such as ferulic acid and tannin acid, have been reported to modify optical transparency (Peña *et al.*, 2010) and

mechanical properties (Cao *et al.*, 2007a) of gelatin films. Enhanced mechanical properties could also be obtained by treating gelatin with glyoxal and genipin, but high cost of material and potential toxicity limits its possible application (Bigi *et al.*, 2001; Bigi *et al.*, 2002; Spanneberg *et al.*, 2010).

Maillard reaction, a non-enzymatic browning reaction could be used to modify physical and mechanical properties of gelatin film. The interaction between the reactive functional groups of amino acids and reducing sugars during Maillard reaction leads to changes in taste, aroma and structure of the reactants (Martins *et al.*, 2001; Zheng and Xu, 2005). The reactions of protein with a reducing sugar could lead to the advanced stage of glycation and formation of brown polymers, known as melanoidins (Sandwick *et al.*, 2005). Perhaps these polymers could be utilized within protein films to enhance their physical and mechanical properties (Goh *et al.*, 2009).

To our knowledge, the use of Maillard reaction to enhance physical and mechanical properties of gelatin films has never been explored. Therefore, we sought to evaluate the effect of ribose-induced Maillard reaction on the physical and mechanical properties of gelatin film, such as tensile strength, swelling and solubility and light absorption properties.

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Materials and Methods

Materials

Gelatin from bovine skin (Type A, Bloom value 75), D-sucrose, D-ribose, D-sorbitol, glycerol and magnesium nitrate were purchased from Sigma Aldrich (St. Louis, USA). All of the chemicals used in this study were of analytical grade.

Preparation of gelatin films

Gelatin solutions (5%, w/v) were prepared by mechanical stirring (Heidolph, MR Hei-Tec, Germany) at $55 \pm 5^\circ\text{C}$ for 15 min to completely dissolve the gelatin. The gelatin film-forming solutions were prepared according to the formulation shown in Table 1. Sorbitol and glycerol were added as plasticisers (Gómez-Estaca *et al.*, 2009). To initiate Maillard reaction, the film-forming solutions were heated at 90°C for 2 h in a water bath (Mettler, WB22, Germany). The hot solutions were poured onto the plastic plates ($24 \times 24 \text{ cm}^2$) and spread evenly. The plates were placed in a convection oven (Esco, OFA-54-8, Singapore) at 50°C for 15 h.

Dried films were carefully removed from the plastic plates and were conditioned in a constant humidity ($50 \pm 3\%$ relative humidity) using saturated magnesium nitrate solution at 25°C for 2 days prior of testing (Cao *et al.*, 2007a; Evageliou *et al.*, 2010). Physical and mechanical analyses were performed immediately after a sample was taken out from the desiccators.

Physical and mechanical analyses

Film thickness

Gelatin film thickness was measured using a micrometer (Mitutoyo, dial thickness gauge 7301, Japan), with sensitivity to the nearest 0.01 mm accuracy. Thickness measurement was calculated from the average of five random positions of the gelatin film.

Swelling properties

The swelling percentage of the gelatin films was determined according to the method as described by Cao *et al.* (1997b) with slight modifications. Films were cut into $2 \times 2 \text{ cm}^2$ and weighted. The cut films were then immersed in deionized water at 25°C for 2 min. Wet samples were wiped with filter paper to remove excess liquid and weighted. Measurements were repeated thrice for each type of gelatin films and the average value of swelling (S) was calculated using the following equation:

$$S (\%) = [(W_2 - W_1)/W_1] \times 100$$

Table 1. Formulations of gelatin film-forming solutions

Samples	5% (w/v) gelatin solution (mL)	Sorbitol (g)	Glycerol (g)	Ribose (g)	Sucrose (g)
CF	100	0.75	0.75	-	-
S40	100	0.75	0.75	-	2
R20	100	0.75	0.75	1	-
R40	100	0.75	0.75	2	-

Where, W_1 is the weight of the dried film (g) and W_2 is the weight of the wet film (g).

Water solubility

Water solubility of the gelatin films was determined according to the method as described by Maizura *et al.* (2007) with slight modifications. Films were cut into $2 \times 2 \text{ cm}^2$ before being stored in a desiccator with silica gel (0% relative humidity) for 7 days. Cut films were weighted to the nearest 0.0001 g and then dispersed in beakers containing 80 mL of deionized water. The samples were maintained under constant gentle agitation for 1 h at 25°C . Then, remainder of the un-dissolved films were recovered through filtering with a filter paper (Whatman No. 1, UK) before subjected to a drying treatment at 105°C for 24 h. Water solubility (%) of film was defined as ratio of the water soluble solids to the initial solids content (Lee *et al.*, 2004). Measurements were repeated thrice for each type of gelatin films and the average value of water solubility (WS) was calculated using the following equation:

$$WS (\%) = [(W_1 - W_2)/W_1] \times 100$$

where, W_1 is the initial weight of the film expressed as dry matter (g) and W_2 is the weight of the un-dissolved rest of the film (g).

Surface color

The colors of the gelatin films were determined with a colorimeter (Minolta, Spectrophotometer CM-3500d, Japan) as described by Cao *et al.* (2007a) and Jongjareonrak *et al.* (2008). The instrument was calibrated with a black background (zero calibration) followed by air (clear calibration) prior to analysis. Measurements were repeated thrice for each type of gelatin films. The color measurement resulted in CIE (Commission Internationale de l'Eclairage) $L^*a^*b^*$ values for lightness (L^* , black-white axis), redness (a^* , red-green spectrum) and yellowness (b^* , yellow-blue spectrum).

Light absorption

The light barrier properties of films were measured by exposing the films to light absorption at wavelengths ranging from 1,100 – 190 nm (Peña *et al.*, 2010), using an UV-Vis spectrophotometer (Shimadzu, CPS-240, Japan). Plot data were recorded every 1 nm. Measurements were repeated thrice for each type of gelatin films.

Transparency of the gelatin films was determined according to the method described by Gómez-Cuillén *et al.* (2007) and Hoque *et al.* (2010). The transparency (*T* value) of the films was calculated by the following equation:

$$T \text{ value} = (\text{Abs}_{600})/x$$

Where, Abs_{600} is the value of absorbance at 600 nm and x is the film thickness (mm). The greater *T* value represents the lower transparency of film.

Mechanical properties

Tensile strength, elongation at break and Young Modulus of the gelatin films were measured with a texture analyser (Stable Micro Systems, TA-TX2, UK) attached with a 5 kg load cell according to ASTM standard method D882-01 (ASTM, 2001). Films strip of 60 mm in length and 20 mm in width were attached to the texture analyser with proper alignment and calibration. The initial hold separation was set at 60 mm, and crosshead speed was set at 10 mm/min.

Tensile properties were calculated from the plot of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length) (Perez-Gago and Krochta, 2001). Tensile strength was calculated by dividing the maximum load with the initial cross sectional area of the specimen (ASTM, 2001). Elongation at break was calculated by dividing the extension at rupture of the specimen with the initial gage length of the specimen (100 mm) and then multiplied by 100 (ASTM, 2001). Young Modulus, a measure of intrinsic film stiffness, is the slope of the linear range of the stress–strain plot (Mauer *et al.*, 2000). Tensile strength, elongation at break and Young Modulus measurements for each type of film were repeated at least eight times, from which an average was obtained (Cao *et al.*, 2007a).

Statistical analysis

Collected data were expressed as mean \pm standard deviation. Comparison of means was performed by one-way analysis of variance (ANOVA). The significance of the difference between means was determined by Duncan's test ($P < 0.05$). Statistical analyses were performed using Statistical Package for Social Science for Windows, version 14.0 (SPSS, Chicago, USA).

Results and Discussion

Physical properties

All prepared films were transparent with smooth surfaces and thickness between 0.14 to 0.20

Table 2. Physical properties¹ of gelatin films

Samples ²	Thickness (mm)	<i>T</i> Value ³	CIE Color Parameter		
			CIE <i>L</i> *	CIE <i>a</i> *	CIE <i>b</i> *
CF	0.14 \pm 0.01 ^a	0.31 \pm 0.01 ^c	95.97 \pm 0.014 ^a	-0.52 \pm 0.014 ^a	3.8 \pm 0.005 ^b
S40	0.17 \pm 0.01 ^b	0.36 \pm 0.02 ^c	95.31 \pm 0.069 ^a	-0.34 \pm 0.027 ^a	4.90 \pm 0.037 ^b
R20	0.20 \pm 0.02 ^c	0.76 \pm 0.06 ^b	69.32 \pm 0.151 ^b	23.79 \pm 0.017 ^b	97.21 \pm 1.128 ^a
R40	0.17 \pm 0.02 ^b	1.16 \pm 0.06 ^a	66.63 \pm 0.135 ^c	27.57 \pm 0.080 ^a	100.00 \pm 0.50 ^a

¹Comparison within the columns was shown in the table with the data written as mean \pm standard deviation ($n = 3$). Means followed by the different superscript letter (a – c) are statistically significant at the 5% level.

²CF, gelatin film without sugar (control); R20, gelatin film with 20% (w/w) of ribose; R40, gelatin film with 40% (w/w) of ribose; S40, gelatin film with 40% (w/w) of sucrose.

³*T* value is used to measure the transparency of the film.

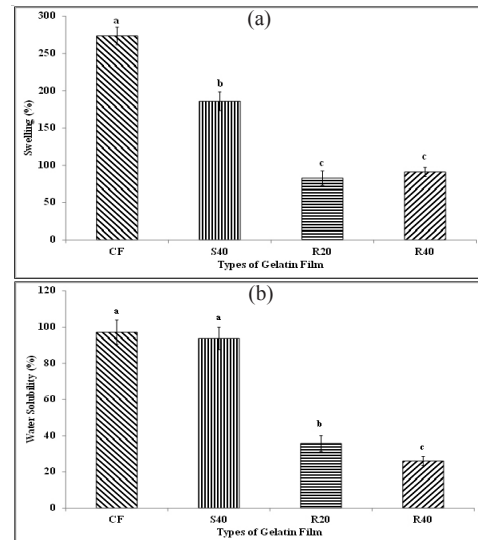


Figure 1. (a) Swelling and (b) solubility of control film (CF), ribose-gelatin films (R20 and R40) and sucrose-gelatin film (S40). The error bars represent the standard deviation of the means. Different superscripts (a – c) on top of error bars indicate significant differences between at $P < 0.05$.

mm (Table 2). Sucrose did not seem to influence the thickness of the films. Nevertheless, R20 and R40 films showed significantly higher thickness ($P < 0.05$) compared to CF and S40. The addition of ribose increased *T* values and hence decreased the transparency of the gelatin films (Table 2). The *T* value of the films was in the order of $R40 > R20 > CF, S40$. When ribose was added into the gelatin solutions, ribose molecules disrupted the homogeneity of protein chains and the occurrence of the Maillard reaction caused a reduction in light penetration of the films. Decreased in gelatin films transparency has also been reported by Gómez-Cuillén *et al.* (2007) and Tongnuanchan *et al.* (2012) with the incorporation of nutra leaves extracts and citrus essential oils, respectively. Films with lower transparency provide better protection against light, hence ribose-induced Maillard gelatin films could be useful barriers to reduce light-induced lipid oxidation and consequently improving certain aspects of food quality.

In general, neat gelatin films were almost colorless. With the addition of ribose which led to the occurrence of Maillard reaction during heating of the film-forming solution, R20 and R40 films were

yellow-brown in color and were significantly lower ($P < 0.05$) in L^* values and significantly higher ($P < 0.05$) in b^* values compared to those of CF and S40, indicating a decrease in lightness and increase in yellowness (Table 2). Sucrose, a non-reducing sugar, was incapable of inducing Maillard reaction, thus was used to act as the second control for the experiments (Tan *et al.*, 2012a; Tan *et al.*, 2012b). The browning in R20 and R40 films could be resulted from the formation of brown polymers (melanoidins) during final stage of Maillard reaction (Manzocco *et al.*, 2000; Rhim *et al.*, 2000). R40 displayed significantly lower ($P < 0.05$) L^* value than R20, perhaps due to the presence of the higher amount of melanoidins. The “Maillard films” prepared may find interesting applications in certain food or nutraceutical areas.

One important property of an edible film is its swelling ability. Swelling percentages decreased significantly ($P < 0.05$) with the use of ribose on the gelatin films (Figure 1a). The swelling percentages for R20 and R40 films were 69% and 66%, respectively, and were significantly lower ($P < 0.05$) than S40 and CF. The rate of swelling can be influenced by hydrogen interactions between amino acid side chains of gelatin and hydroxyl group of sugars, which makes it more hydrophobic (Rhim *et al.*, 2000; Bigi *et al.*, 2001; Cao *et al.*, 2007b). This would explain the higher swelling of S40 films compared to R20 and R40. The Maillard reaction has been shown to exert an effect on protein cross-linking of soy protein isolate films (Goh *et al.*, 2009). Thus, it is probable that certain extend of the Maillard cross-linking had occurred in the R20 and R40 films. Cross-linking in protein network had been shown to reduce its ability to incorporate water and resulted in a decrease in swelling (Lee *et al.*, 2004; Spanneberg *et al.*, 2010). Hence, the decrease in swelling ability in R20 and R40 could well be due to the increased occurrence of Maillard network within these films, which make the film's network denser and weaker in water absorption. Cross-linking agents such as glutaraldehyde (Bigi *et al.*, 2001), genipin (Bigi *et al.*, 2002), ferulic acid and tannin acid (Cao *et al.*, 2007a) have also been shown to exert similar effects. The reduced swelling property of R20 and R40 films could be beneficial in oral drug delivery application.

In recent years, application of cross-linking techniques in pharmaceutical fields is gaining popularity with the aims to achieve controlled drug release delivery rate and drug release delivery at targeted locations in the gastrointestinal tract (Revathi and Raju, 2012). A study by Frutos *et al.* (2010) had demonstrated the ability of hydrogels based on methacrylic acid and poly (ethylene glycol)

macromonomer (cross-linked with tetraethylene glycol dimethacrylate) inside soft gelatin capsules as a pH-dependent drug release system. In addition, gel beads of cross-linked bovine serum albumin (BSA) developed by Gan *et al.* (2009) showed increased stability of the BSA gel beads in artificial saliva and simulated gastric fluid over non-cross-linked gel beads that led to delay action in releasing the content.

The solubility values of the films further support the swelling data. The solubility values of CF and S40 were similar ($P > 0.05$), that were more than 90% (Figure 1b). These were comparable to those of gelatin films prepared by Giménez *et al.* (2009) and Voon *et al.* (2012). High solubility of CF was due to the hydrophilic nature of gelatin and the presence of hydrophilic plasticiser (glycerol), which was part of the ingredients added during the gelatin film making (Voon *et al.*, 2012). On the other hand, R20 and R40 films had significantly lower ($P < 0.05$) solubility as compared to CF and S40. This could be related to the occurrence of Maillard reaction and cross-linking as previously explained. These interactions prevented the free amino acid residues in gelatin to bond with water, thus limiting its solubility (Shimada and Cheftel, 1988). As R40 had lower solubility than R20, it might be possible to suggest that a higher extend of Maillard cross-linking were present in the R40 films as compared to that of R20. This idea needs further investigation.

A reduction in the water solubility on addition of halloysite nanoclay and nano-SiO₂ to bovine gelatin films has been reported by Voon *et al.* (2012). Low water solubility reflects good water resistance and this is a desirable film characteristic in certain applications, especially when resistance to high humidity condition is of high concern (Xiong *et al.*, 2008). In this study, ribose-induced Maillard gelatin films showed some potential to be a good barrier to prevent humidity-related deteriorations when applied in food or pharmaceutical systems.

All gelatin films exhibited a high level of absorption in the UV range of 200 – 400 nm, especially between 200 and 250 nm (Figure 2). High absorption in this range is related to the presence of peptide bond fragments of gelatin (Bao *et al.*, 2009; Hermanto *et al.*, 2013). However, only R20 and R40 showed higher level of absorption in the range between 250 – 600 nm, and this was more evident in R40 films. Higher absorption in this range could be related to the Maillard browning, which is often measured using absorbance reading from wavelength between 420 – 490 nm (Martins *et al.*, 2001; Wu *et al.*, 2008; Tan *et al.*, 2012a; Tan *et al.*, 2012b). Meanwhile,

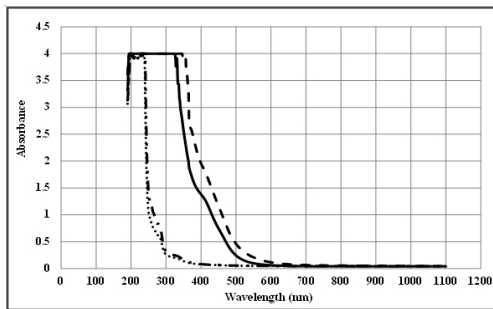


Figure 2. Range in % absorption from wavelength of 190 to 1100 nm for R20 (solid line), R40 (dashed line), S40 (dashed-dotted line) and CF (dotted line) films.

higher absorbance reading at wavelength of 360 nm is related to higher rate of Maillard reaction (Tressl *et al.*, 1995; Davidek *et al.*, 2002; Zheng and Xu, 2005). High level of absorption in the UV and visible range (200 – 400 nm) is a desirable film characteristic in certain applications, especially when resistance to UV exposure condition is of concern (Gómez-Cuillén *et al.*, 2007; Bao *et al.*, 2009). In this study, ribose-induced Maillard gelatin films showed potential to provide some form of barrier to prevent UV-related deteriorations, for example UV light-induced lipid oxidation, when applied in food or pharmaceutical systems. This idea will be further studied.

Mechanical properties of gelatin films

Mechanical properties of protein films provide an indication of expected film integrity under conditions of stress that would occur during processing, handling and storage (Cao *et al.*, 2007a). Tensile strength and elongation at break in mechanical analysis are widely used to characterise the strength and flexibility of films (Park *et al.*, 2001). Tensile strength of gelatin films decreased while elongation at break increased with the addition of ribose (Figure 3a – 3b), suggesting that gelatin films became more stretchable (denoted by higher elongation at break value), but weaker (denoted by lower tensile strength value) with the addition of ribose or sucrose. Tensile strength of sugar-gelatin films decreased by approximately 18%, 33% and 67%, for R20, R40 and S40 films, respectively, compared to CF. Elongation at break of sugar-gelatin films increased significantly ($P < 0.05$) by approximately twice that of CF. The presence of sugars in film-forming solutions could have influenced the network structure of gelatin film (Kasapis *et al.*, 2003; Choi *et al.*, 2004). Sugars could easily fit into protein network by establishing hydrogen bonding with their carboxyl group, which interferes with the inter connection of gelatin molecules causing less number of junction zones during film formation (Veiga-Santos *et al.*, 2007; Evageliou *et al.*, 2010). These hydrogen bonds between the gelatin chains and

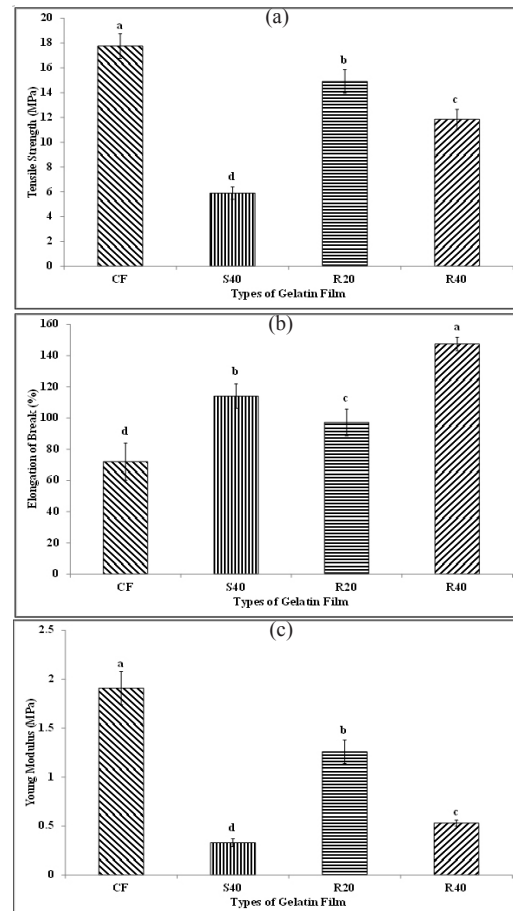


Figure 3. Mechanical properties; (a) Tensile strength, (b) Elongation at break and (c) Young modulus of control film (CF), ribose-gelatin films (R20 and R40) and sucrose-gelatin film (S40). The error bars represent the standard deviation of the means. Different superscripts (a – d) on top of error bars indicate significant differences between films at $P < 0.05$.

sugars might have yielded gelatin films with higher flexibility and lower tensile strength (Jongjareonrak *et al.*, 2006). Of interest is the fact that R20 and R40 films showed significantly higher ($P < 0.05$) tensile strength as compared to that of S40. Perhaps, the carbonyl groups of ribose were able to interact with the free amino groups of gelatin that yielded additional network during film formation (Sandwick *et al.*, 2005). As Maillard reaction has been indicated in these films with possible occurrence of Maillard cross-linking, it is possible that these had enhanced network structure of the gelatin films.

The values of tensile strength of gelatin films prepared in this study were close to those reported for native bovine gelatin films (15.12 ± 0.75 MPa) (de Carvalho and Grosso, 2004). The tensile strength of R20 and R40 films that were significantly lower ($P < 0.05$) than CF, but were still higher than casein films (~ 12.5 MPa) (Chambi and Grosso, 2006) and soy protein films (~ 8.2 MPa) (Rhim *et al.*, 2000). Gelatin films present a high tensile strength and this is related

to its organisational level of the protein network (Chambi and Grosso, 2006). Due to this, gelatin has previously been used as an additive to increase the tensile strength of chitosan films (Arvanitoyannis *et al.*, 1998), casein films (Chambi and Grosso, 2006) and manioc starch films (Fakhoury *et al.*, 2012).

The elongation at break of R20 and R40 films were significantly higher ($P < 0.05$) than S40 and CF, suggesting that R20 and R40 are more elastic and flexible. The higher elongation at break in R40 compared to R20 could again be due to higher extend of the Maillard reaction that yielded more cross-linking within the films. Increase in cross-linking could increase elongation at break properties of the material due to the replacement of weak van der Waals forces to strong covalent bonding sites (Chambi and Grosso, 2006). Depending on the application of the films, high values for elongation at break can be an advantage, especially in long-term packaging application.

The parameter tensile strength is directly related to Young Modulus, so when tensile strength decreases, Young Modulus also decreases. The trend obtained for Young Modulus among the gelatin films was in agreement with the trend obtained for tensile strength (Figure 3a – 3c).

Conclusion

Ribose induced Maillard reaction occurred when ribose was heated with gelatin, resulting in changes in physical and mechanical properties of gelatin films. UV-Vis absorption spectra showed that the Maillard reaction had improved UV and light barrier properties of gelatin films with the increased in absorbance at wavelength between 250 to 550 nm.

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