Fabrication and characterization of the enhanced tensile strength xanthan/curdlan/gelatin blend films for food-packaging applications

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Abstract. Food packaging films are generally used to protect the food from outside harsh environment. Moreover, their main purpose is to prolong the shelf life and to maintain the freshness of food. Generally, plastic materials are widely used for this purpose. However, these plastic materials are causing a serious threat to our environment due to the problem of non-degradability. In this regard, biodegradable biopolymer materials are contemplated as an important alternative due to the environment friendly characteristics. However, the packaging films prepared from single pure polymers have been reported to possess very poor mechanical properties. Therefore, blending of two or three biopolymers is considered to synergistically improve the mechanical properties of biopolymer based films. In this work, we made a novel blended films of xanthan (X), curdlan (C) and gelatin (G) by mixing different ratios of all three polymers. After successfully preparing and optimization of these blended films, mechanical properties and moisture absorbance properties of all these films were determined. Based on the results, it was concluded that the highest tensile strength of 38.22±0.7 MPa was found in the T2 treatment of 20:20:60 ratio of X/C/G blend films. In addition, highest elongation at break of 18.92±0.5% was also found in the same ratio of X/C/G blend films. Moreover, characterization techniques such as FT-IR and SEM analysis were also performed to analyze the structural properties of blend films. Finally, SEM micrographs indicated that all the blend films exhibited a uniform, smooth, homogenous and compact outer surface morphology. In short, this novel xanthan/curdlan/gelatin films resulted in improved mechanical properties of blend films, which confirm its suitability as promising food packaging material.

1. Introduction
Food packages often help people with preserving eatable stuffs, which leads an important role of solving the global food scarcity problem [1]. In order to protect the food from outside harsh environment, appropriate food packages should provide both physical protection as well as microbiological protection to the food [2]. Currently, food industries are utilizing plastic materials to preserve their products. However, these non-degradable materials are prepared by polymerization by using different raw materials. So, the procedure of making plastic materials determines its non-biodegradability and non-renewable nature [3]. Thus, many researches are focused on the development of biodegradable materials with the aim to replace the synthetic plastic materials [4]. Moreover, numerous factors have contributed to increase the use of biopolymer based packaging materials, such as the large environmental impact caused by plastics due to their non-biodegradable nature [5]. Therefore, bio-based raw materials in this regard, at very recent, are getting attention on account of possessing environment friendly characteristics at their disposal.

Nowadays, the materials which are mostly most used for preparing biodegradable films are polysaccharides, lipids and proteins including starch, alginate, cellulose, chitosan, chitin, pectin,
waxes, zein and mineral oils [6]. Biopolymers made films could meet the critical needs as biopolymers are able to provide safety on health factors, preserves high quality foods and alleviate the environmental concerns. Therefore, the utilization of these biopolymers in the preparation of food packaging materials has gained much importance and attention due to their biocompatibility, biodegradability and natural nontoxicity [7]. Xanthan is a heteropolysaccharide, which is produced by fermentation process using Xanthomonas campestris. In addition, it is an anionic polysaccharide which is widely used in food industries [8]. Although xanthan is able to form xanthan hydrogel due to its cross linking process, its industrial value is limited because of pH sensitivity, short term salt and poor thermal stability. Moreover, packaging films made up by pure xanthan exhibits poor mechanical properties. Thus, composting/blending with other polymers for film production is one of the ways to improve the mechanical properties of films. Many researchers have been focused on preparing blend films such as konjac glucomannan with xanthan gum, xanthan with locust bean gum, xanthan with tara gum or k-carrageenan or xanthan [9-13]. Curdlan is a neutral linear microbial polymer consisted of \((1\rightarrow3)-\beta\)-glucan repeating units. Previously, blending curdlan with xanthan alleviated the poor mechanical property issue [1]. However, the elongation at break and tensile strength could be further improve by adding other protein based polymer such as gelatin. Therefore, adding gelatin in xanthan/curdlan blend films is of great significance.

Gelatin, being an important multifunctional ingredient has been widely used in the food, cosmetic and pharmaceutical industries as a thickener, emulsifier, stabilizer or even as a microencapsulating agent [14]. It is considered as one of the best biomaterials for the development of biodegradable films due to its wide abundance, biodegradability and good film formation properties [15]. Gelatin can further help to modify or optimize the properties of xanthan/curdlan blended film due to its unique chemical structure. In a previous study, blend films made of cassava starch and gelatin was found to possess overall good properties with higher gelatin concentrations, which increase water solubility, water vapor permeability and mechanical strength values. Therefore, gelatin is contemplated as a best blending material for improving the mechanical properties of xanthan/curdlan blend films. In this work, we fabricated novel blended films of xanthan, curdlan and gelatin by mixing different ratios of all three polymers as shown in Table I. Moreover, moisture absorbance properties, mechanical properties and characterization properties of all these novel xanthan/curdlan/gelatin blend films were determined.

| Treatments | Xanthan % | Curdlan % | Gelatin % |
|------------|-----------|-----------|-----------|
| T0         | 50        | 50        | 0         |
| T1         | 35        | 35        | 30        |
| T2         | 20        | 20        | 60        |
| T3         | 5         | 5         | 90        |

2. Materials and methods

2.1. Materials
Xanthan, curdlan and gelatin were purchased from the local distributors of industries in China. Glycerol and sodium aside were obtained from Aladdin Industrial Corporation (China).

2.2. Fabrications of films
2% solution of all these polymers were prepared by using standard method [1]. 2% of each solution was prepared by dissolving 2 gram of polymer in 100 mL distilled water. Then, the solutions were completely mixed and left for 12 hours. After that, both these solutions were mixed with the ratio of xanthan/curdlan/gelatin mentioned in Table I. Based on polymer content, 30% glycerol was added in blend solutions. Subsequently, 30 g of these mixtures were poured into the 10×10 cm plastic plates.
After that, these plates were left for drying at 35 °C for 48 hours. Later, all the films were placed for 5-7 days in desiccator.

2.3. Physical properties of films
Moisture content (MC), water solubility and mechanical properties such as Tensile strength and Elongation at break were measured as per the standard methods described in earlier study [16].

2.4. Characterization analysis of films
Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were performed by following the standard method described in earlier studies [6] [17].

2.5. Statistical analysis
For statistical analysis, SPSS 19 software was used. The obtained statistical results were showed as means ± standard deviation (SD). Moreover, Student's test (t) were employed to analyze the mean values. Furthermore, statistical significance of P < 0.05 was used.

3. Results and discussions

3.1. Mechanical properties and moisture absorbance properties of xanthan/curdlan/ gelatin blend films
Mechanical property is considered as one of the most crucial aspect of food packaging films. Overall, the Table 2 reflects the basic trend of xanthan/curdlan/gelatin blended films under different ratios. Tensile strength (TS) is one aspect that researchers examine the most regarding food packaging films. TS refers to the maximum stress force that a film can resist when it is pulled or stretched before breaking. As increasing the concentration of gelatin from 0% to 60%, the tensile strength is improved significantly. On the other hand, in T0 (Control) with 0% gelatin the tensile strength becomes the worst, while adding the gelatin from 0% to 30% then up to 60%, tensile strength keeps rising significantly. When the ratio for xanthan, curdlan and gelatin is 20:20:60 (T2), TS for this treatment of blend film reached its highest value of 38.22±0.7 MPa. Under this ratio, the TS strength achieves its best function, thus when the ratio is 20:20:60, the tensile strength is the most appropriate for the blend film. However, as keep adding gelatin up to 90% within the whole ratio, tensile strength stops its ascending trend instead it drops a little. According to the results shown in Table II, when gelatin concentration achieves its maximum, TS drops from 38.22±0.7 to 35.33±0.9 MPa. This might be due to the chemical bonding and intermolecular forces that affects the tensile strength. Similarly, the Elongation at break (EAB) follows the same pattern as TS does. Compared with T0 50:50 percentage of xanthan and curdlan, increasing the amount of gelatin from ratio 35:35:30 to 20:20:60 enhances the EAB. Gelatin is one of the hydrophilic polymer which possess high quality of elongation at break that eventually helps to improve the rigidity and stiffness of xanthan and curdlan blended films. As the ratio of gelatin increases, EAB also improves in T1 according to the Table II. The elongation at break for this T1 treatment is 15.47±0.4%. For T2 with 20:20:60 ratio, EAB increases up to 18.92±0.5%, which proves that adding gelatin to xanthan/curdlan blended film could help to enhance and strengthen the EAB. For T3 with 5:5:90 ratio, EAB did not increase further as expected, but drops to 14.35±0.4%. In conclusion, T2 with xanthan/curdlan/gelatin ratio of 20:20:60 is considered as the most appropriate ratio for preparing the blend films because under this condition both parameters TS and EAB have reached its maximum values. Thus, blending all these three polymers with 20:20:60 ratio could help to obtain the most optimized xanthan/curdlan/gelatin blended film.

Moisture absorbance properties such as moisture content (MC) and water solubility are also presented in Table II. The lowest value of MC was found in T0 blend film and the highest value of moisture content was found in T3 blend film. However, the MC of blend films started inclining with the increasing concentration of gelatin, which is due to the high hydrophilic property of gelatin towards water. Moreover, the same trend of water solubility was observed in all film samples. Thus, it
can be observed that the water solubility is also increased with the increase concentration of gelatin and highest water solubility (98.43±0.5 %) is found in T3. Based on these results, it is concluded that the incorporation of gelatin resulted in the increase of water solubility of xanthan/curdlan/gelatin blend films. Moreover, all these above-mentioned results are in good agreement with the previous studies worked on blend films [17-20].

Table 2. Mechanical properties and moisture absorbance properties of film samples

| Treatments | X:C:G% | Thickness (mm) | Tensile Strength | EAB % | MC % | Solubility % |
|------------|--------|----------------|-----------------|-------|------|--------------|
| T0         | 50:50:0| 0.06           | 27.76±1.1d      | 12.86±0.6c | 15.94±0.4d | 66.71±0.8d |
| T1         | 35:35:30| 0.06           | 30.33±1.2c      | 15.47±0.4b | 17.34±0.3c | 73.56±1.4c |
| T2         | 20:20:60| 0.06           | 38.22±0.7a      | 18.92±0.5a | 19.12±0.5b | 86.23±0.9b |
| T3         | 5:5:90  | 0.06           | 35.33±0.9b      | 14.35±0.4b | 21.14±0.6a | 98.43±0.5a |

*Means within a row with similar superscripts differ did not differ significantly (P < 0.05).

X Xanthan, C Curdlan, G Gelatin. EAB Elongation at break. MC Moisture content.

3.2. Characterization of xanthan/curdlan/gelatin blend films

Mechanical FTIR analysis (4000–400 cm⁻¹) of xanthan/curdlan/gelatin blend films are shown in Figure 1.. As seen in the FTIR spectra, the typical absorption bands of amide-I, amide-II and amide-III were found in the range of 1750–600 cm⁻¹. The bands showing amide A and amide B were also found in the range of 2900-3200 cm⁻¹. These amide bands were found in T3, T2 and T1 but absent in T0 due to the lack of gelatin polymer. In T0, the main adsorption peak was recorded at 3150–3450 cm⁻¹ presenting the axial deformation of bond O-H. Moreover, the peak located at 2750–3000 cm⁻¹ presented the axial deformation of C–H. While, the peak recorded at the region of 1710–1760 cm⁻¹ presented axial deformation of C=O. Moreover, the peak found at 1060–1070 cm⁻¹ exhibited the axial deformation of C–O. In addition, the peak recorded at 1525–1650 cm⁻¹ presented the axial deformation of C=O bonds [8, 10]. Conclusively, the T1, T2 and T3 films shows the same kind of spectra. However, T0 blended film didn’t show the amide peaks which is due to the lack of gelatin polymer. Most importantly, these amide peaks can be seen in T1, T2 and T3 xanthan/curdlan/gelatin blend films which confirms the strong intermolecular interactions between all three polymers.

Figure 1. FTIR spectra of xanthan/curdlan/gelatin blended films.
Scanning electron microscope (SEM) is widely used to study the outer surface morphology of food packaging films. The SEM pictures of all xanthan/curdlan/gelatin blend films are shown in Figure 2. All these novel blend films displayed a uniform, smooth, homogenous and compact outer surface morphology which can illustrate the good miscibility between xanthan/curdlan/gelatin in T0, T2 and T3. On the other hand, all the other blend films displayed dense, even, uniform and smooth microstructure. The results are also in good agreement with the FTIR analysis which confirms its high miscibility between all three polymers.

![SEM pictures of T0, T1, T2, and T3 blend films.](image)

Figure 2. SEM pictures of T0 (50:50:0 X:C:G blend film), T1 (35:35:30 X:C:G blend film), T2 (20:20:60 X:C:G blend films) and T3 (5:5:90 X:C:G blend films).

4. Conclusion
In conclusion, the novel xanthan/curdlan/gelatin blended edible films were successfully prepared from xanthan, curdlan and gelatin polymers. After preparing and optimization, mechanical properties were measured and it was concluded that the T2 with 20:20:60 X:C:G ratio showed excellent mechanical properties. Besides that, the results of FTIR and SEM analysis confirmed the presence of strong intermolecular bonding between 20:20:60 ratio of xanthan, curdlan and gelatin. In summary, the novel xanthan/curdlan/gelatin blended edible films has a potential application in food industries. Conclusively, the environmentally friendly and cost effective food packaging materials can surely be a promising alternative of non-renewable food packaging materials.

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