ASM Sci. J.Special Issue 2018(1)AiMS2018, 158-165

Mechanical and Physical Properties of Gellan Gum (GG) Biofilm: Effect of Glycerol

M. H. Razali[1]*, N. A. Ismail, U. M. Osman and K. A. M. Amin

[1]*Advanced Nano Materials (ANoMa) Research Group,*

School of Fundamental Science, Universiti Malaysia Terengganu,

21030 Kuala Nerus, Terengganu, Malaysia

The aim of this work was to investigate the effect of glycerol concentration on mechanical and physical properties of gellan gum (GG) biofilm. The biofilm was prepared using solvent casting method and the effective glycerol concentration was found to be within 30-50% w/w (based on GG weight). At 60 and 70 w/w% of glycerol, the films started to distort because the films was flexible and brittle. As glycerol concentration was increased the tensile strength (TS) and Youngs modulus (E) of films decreased. Somehow, elongation at break (EAB), water vapor transmission rate (WVTR) and swelling of films was increased. Glycerol plasticized GG biofilm was thermally stable and flexible, proposed its can be exploited as film-forming material and with optimized glycerol concentration it has good mechanical and physical properties for edible biofilm

Keywords: Glycerol, gellan gum, mechanical, physical, biofilm

I. INTRODUCTION

Gellan gum is a microbial polysaccharide composed of a tetrasaccharide repeating unit of two $\beta -_D -glucose$, one $\beta -_D -glucuronic$ acid and one $\alpha -_L -rhamnose$ [1]-[2]. Among the polysaccharide gels, the gellan gum have better thermal stability and less pH-sensitivity [3]. Due to its properties, gellan gum have been widely utilized in food industry as a thickening agent [4]-[5]. However, it was established that GG gel have poor stability in physiological conditions as well as low in mechanical strength, thus limited their application [6]. Thus, researchers focused on modifying GG film with good mechanical and physical properties to extend their application in food packaging, edible film and coating. Plasticizer is an important additive in film formulation especially for biodegradable films [7]-[9]. Plasticizer such as polyols group are functionalize to increase the strength, flexibility and performance of films. Lately, glycerol was became an appropriate plasticizer due their unique properties. In this research, the effect of glycerol on physiochemical and mechanical properties of the glycerol modified GG was studied. It was found, GG can be exploited as film-forming material and with optimized glycerol concentration it has good mechanical and physical properties for edible biofilm.

*Corresponding author:mdhasmizam@umt.edu.my

II. EXPERIMENTAL SECTION

A. Materials

Low-acyl gellan gum (Kelcogel®, CP Kelco, lot number 5C1574A), Glycerol and Calcium Chloride ($CaCl_2$, lot number K47117278604, M_w 110.98 g/mol) was obtained from Merck, Malaysia. All materials were used as received.

B. Preparation of GG Film

Gellan gum (GG) solution was prepared by dissolving GG (1.00 g) into 100 mL distilled water at 70°C for 2 hours. (0, 30, 40, 50, 60, and 70 w/w%, relative to GG) of glycerol and 5 mM calcium chloride ($CaCl_2$) was added into the gellan gum solution. Then, the mixture was stirred for 15 minutes and the resulting suspension was casted onto an acrylic plate. The samples was dried for 24 h at 50°C in an oven.

C. Characterization

Mechanical properties of film were performed using an instron universal testing machine (model 3366) according to ASTM D882. The thicknesses of film were measured using a micrometer (Mitutoyo). Modified ASTM International Standard method was used to determine water vapour transmission rates (WVTR) according to the Equation 1:

$$WVTR = (m/A \triangle t) \quad (1)$$

where, $m/\triangle$ t is the amount of water gain per unit time of transfer. Swelling was determined by using weighing dried film (W_{dry}) prior to immersion into 50 ml phosphate buffer solutions. The film was removed and weighed (W_{wet}) after 24 h. Water uptake (%) was determined according to the Equation 2 below:

$$Wateruptake(\%) = (W_{wet} - W_{dry})/W_{dry} \quad (2)$$

Where, W_{dry} and W_{wet} are the initial weight and final weight, respectively. Thermogravimetric analysis (TGA) and its derivative (DTG) were carried out using Pyris 6, Perkin-Elmer. Scanning electron microscopy (SEM) images of cross-section of samples were obtained using a JOEL JSM 6360 LA electron microscope.

III. RESULTS AND DISCUSSION

In film formulation, glycerol was used as plasticizer to enhance the film flexibility and decreased brittleness. There are several types of plasticizers are available such as sorbitol, ethylene glycol (EG), polyethylene glycol 400 (PEG), propylene glycol (PG), glycerol and etc . However in this study glycerol was selected as it is the most effective plasticizers for GG film fabrication. Figure 1 shows the photograph of produced GG biofilm at different concentration of glycerol. Good films was produced at low concentration of glycerol (30-50% w/w%) used in film formulation. The films were good in shape

as well smooth surface. However the shape of the films can be altered depends on the casting mold plate. At higher concentration of glycerol (60 and 70 w/w %), a defect can be observed on the produced film as they were distorted attributed to the limited dispersion capability of the GG solution at higher glycerol concentration. When the glycerol concentration exceeds polymer compatibility limits, it will caused the phase separation as well as physical exclusion of the plasticizer [10].

Table 1 shows the thickness of the produced GG biofilms at different concentration of glycerol. Increasing of glycerol concentration during preparation of the GG biofilm from 30 to 70 %, resulted in the increment of film thickness from 60 to 77 μm. The increased of GG films thickness might be due to the restructuring of polymer organisation. This is occurred regarding to the glycerol molecules was disrupted the GG polymer chains through the intermolecular linkage interactions. Thus the structure was expanded proportionally with increased volume of glycerol content and causing the thicknesses of polymer films increased.

The mechanical properties results in Table 1 and Figure 2 demonstrated that the increasing of glycerol concentration resulted in decreased of film tensile strength (TS) and young modulus (E) but increased of elongation at break (EAB). TS and E decreased from 3.70±0.09 to 2.14±0.08 MPa and 58±1.56 to 39±1.38 MPa, respectively, however EAB increased from 12.21±0.36 to 14.98±0.49 when the concentration of glycerol increased from 30% to 70 w/w %. This is due to the hydrophilic nature of glycerol and a high number of hydroxyl groups in glycerol that cause the molecules to enter among the GG polymer. That disruption caused the interaction forces among the polymers matrix became weaker thus altered the mechanical properties of film.

Furthermore, the hydrogen bonds were also increased because of the increase of hydroxyl groups. Hydrogen bonds were established between glycerol and GG chains. It might be has been replaced some of the GG-GG hydrogen bonds due to the interaction of glycerol molecules and GG molecules. Subsequently, the direct interaction between the GG molecular chains itself were reduced, instead increased the chain segmental with the glycerol molecules.

Table 2 shows the WVTR and swelling of produced GG films using different concentration of glycerol. The WVTR and swelling GG of films were found to increase linearly with concentration of glycerol. This is due to the penetration of glycerol into the intermolecular matrix, resulting in reduce GG interactions. For this reason, the WVTR and swelling were promoted to the higher value.

In order to study the thermal stability of biofilms, thermogravimetry (TG) was conducted. Only three samples were selected which are GG biofilms with 30, 50 and 70 w/w% glycerol as well as pure GG film for comparison.

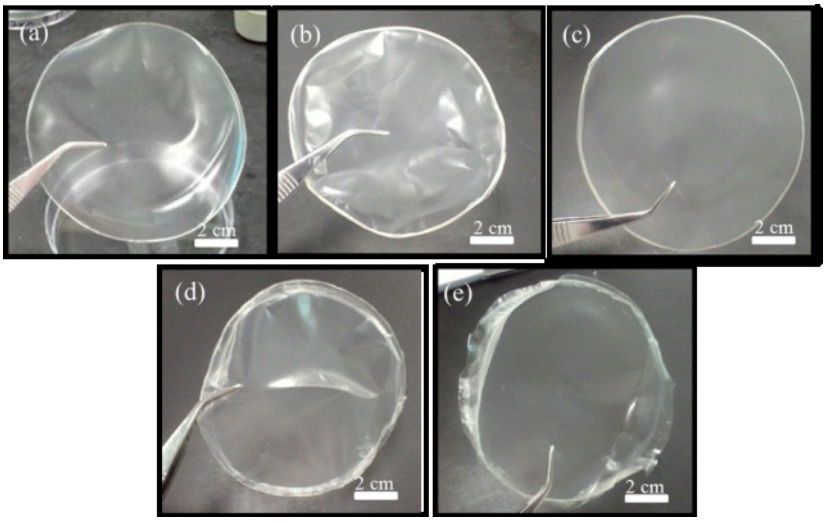

Figure 1. GG biofilm at different concentration of glycerol (a) 30 w/w %, (b) 40 w/w %, (c) 50 w/w %, (d) 60 w/w %, (e) 70 w/w %.

Table 1. The thickness and mechanical properties of GG films at different concentration of glycerol concentrations. Mean ± standard deviation. Tensile strength (TS), Youngs modulus (E), elongation at break (EAB).

Glycerol concentration (w/w %)*	Thick (μm)	TS (MPa)	E (MPa)	EAB (%)
30	60±0.007	3.70±0.09	58±1.56	12.21±0.36
40	63±0.007	3.43±0.05	56±1.74	12.95±0.76
50	67±0.003	3.32±0.08	56±2.63	13.21±0.58
60	70±0.004	2.73±.02	44±0.98	14.32±1.36
70	77±0.011	2.14±0.08	39±1.38	14.98±0.89

*percentage weight relative to GG

The thermograms obtained were presented in Figure 3. Three thermal decomposition for all studies film was observed. The initial stage occurred at temperature less than 100°C associated with the evaporation or dehydration of loosely bound water and low molecular weight compounds in the films [11]-[12]. The plasticized GG biofilms show lower mass loss as compared to pure GG (unplasticized) biofilm at temperature lower than 100°C. At the temperature from 125°C to 290°C, which is second stage decomposition is attributed to removal of plasticizer compounds along with chemically adsorbed water molecules. Heating above 290°C induced the largest thermal degradation rate due to the GG carbon chain depolymerisation.

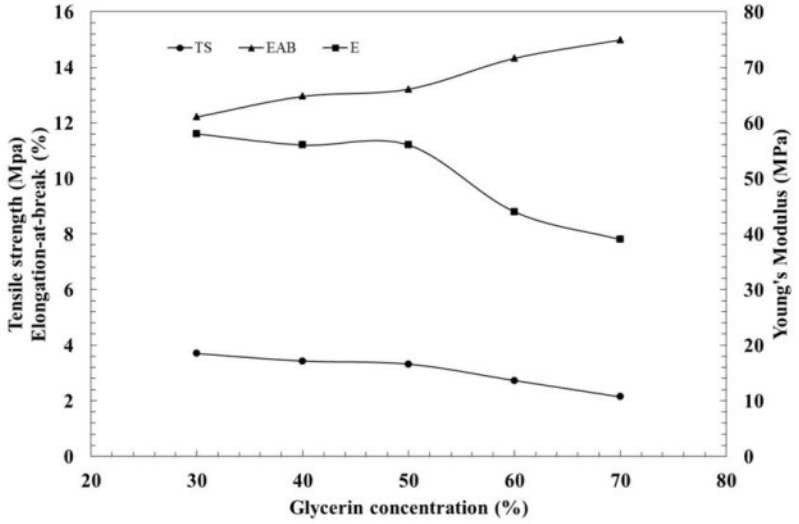

Figure 2. Mechanical properties of GG film as a function of glycerol content. Tensile strength (TS), elongation-at-break (EAB), Youngs modulus (E).

Table 2. TWVTR and swelling of GG films at different concentration of glycerol. Mean±standard deviation.

Glycerol concentration (w/w %)*	WVTR (g $m^{-2}d^{-1}$)	Swelling (%)
30	352±12	739±73
40	355±09	837±37
50	415±03	902±06
60	458±15	915±12
70	489±07	931±50

*percentage weight relative to GG

In general, glycerol plasticized GG biofilms are possessed higher thermal degradation rate as compared to the pure GG biofilm. For examples the weight loss between 200°C to 400°C was 58%, 60% and 62% for GG+GLY30, GG+GLY50, and GG+GLY70, respectively, while the unplasticized GG biofilm was 30%. It can be concluded that the increment of glycerol concentration from 30% to 70w/w% reduces the thermal resistance of GG biofilms.

Figure 4 shows the cross section SEM micrographs of pure and glycerol plasticised GG biofilms. Pure GG biofilm revealed smooth surface (Figure 4(a), while pores was observed in the cross-section of glycerol plasticized GG biofilms due to emulsification of glycerol. The appearances of pores were more obvious as the concentration of glycerol increased from 30, 50

to 70w/w% as can be seen in Figure 4(b-d). The plasticizing effect from glycerol increased the porosity, thus contributed to the flexibility of plasticized GG films.

IV. CONCLUSION

Based on to the preliminary characterisations, it was showed the glycerol is suitable plasticiser for GG films. Glycerol-plasticized GG films have good mechanical properties based on its hydrophilic nature which increased the moisture content of the film. WVTR and swelling was increased, when the concentration of glycerol increased make the glycerol plasticized GG biofilm was thermally stable and flexible.

V. ACKNOWLEDGEMENT

The authors are grateful to Universiti Malaysia Terengganu (UMT) for providing the facilities to carry out this project and Ministry of Higher Education Malaysia for the financial support vote FRGS 59358 and MyBrain15 (MyPhD) for postgraduate students scholarship.

VI. REFERENCES

[1] Jansson, PE, Lindberg, B, Sandford, PA, 1983, Structural studies of gellan gum, an extracellular polysaccharide elaborated by Pseudomonas elodea, *Carbohydrate Research*, vol. 124, pp. 135-139.

[2] O'Neill, MA, Selvendran, RR, Morris, VJ, 1983, Structure of the acidic extracellular gelling polysaccharide produced by Pseudomonas elodea, *Carbohydrate Research*, vol. 124, pp. 123-133.

[3] Mazen, F, Milas, M, Rinaudo, M, 1999, Conformational transition of native and modified gellan, *International Journal of Biological Macromolecules*, vol. 26, pp. 109-118.

[4] Morrison, N, Clark, R, Chen, Y, Talashek, T, Sworn, G, 1999, Gelatin alternatives for the food industry Physical chemistry and industrial application of gellan gum, *Springer*, pp. 127-131.

[5] Omoto, T, Uno, Y, Asai, I, 1999, The latest technologies for the application of gellan gum Physical Chemistry and Industrial Application of Gellan Gum, *Springer*, pp. 123-126.

[6] Ismail, NA, Razali, MH, Mat Amin, KA, 2017, Mechanical and physicochemical properties study on gellan gum thin film prepared using film casting method, *AIP Conference Proceedings*, vol. 1885, pp. 020045.

[7] Bertuzzi, M, Vidaurre, EC, Armada, M, Gottifredi, J, 2007, Water vapor permeability of edible starch based films, *Journal of food engineering*, vol. 80, pp. 972-978.

[8] Rivero, S, Garca, M, Pinotti, A, 2010, Correlations between structural, barrier, thermal and mechanical properties of plasticized gelatin films, *Innovative Food Science Emerging Technologies*, vol. 11, pp. 369-375.

[9] Vanin, F, Sobral, P, Menegalli, F, Carvalho, R, Habitante, A, 2005, Effects of plasticizers and

their concentrations on thermal and functional properties of gelatin-based films, *Food Hydrocolloids*, vol. 19, pp. 899-907.

[10] Donhowe, IG, Fennema, O, 1993, The effects of plasticizers on crystallinity, permeability, and mechanical properties of methylcellulose films, *Journal of Food Processing and Preservation*, vol. 17, pp. 247-257.

[11] Cyras, VP, Zenklusen, M CT, Vazquez, A, 2006, Relationship between structure and properties of modified potato starch biodegradable films, *Journal Applied Polymer Science*, vol. 101, pp. 4313-4319.

[12] Dang, KM, Yoksan, R, 2015, Development of thermoplastic starch blown film by incorporating plasticized chitosan, *Carbohydrate Polymers*, vol. 115, pp. 575-581.

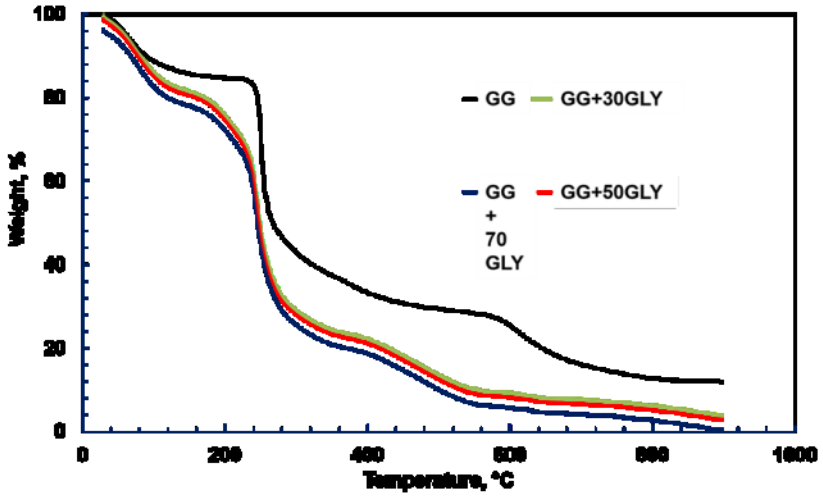

Figure 3. TG thermograms of pure GG and glycerol plasticized GG biofilms.

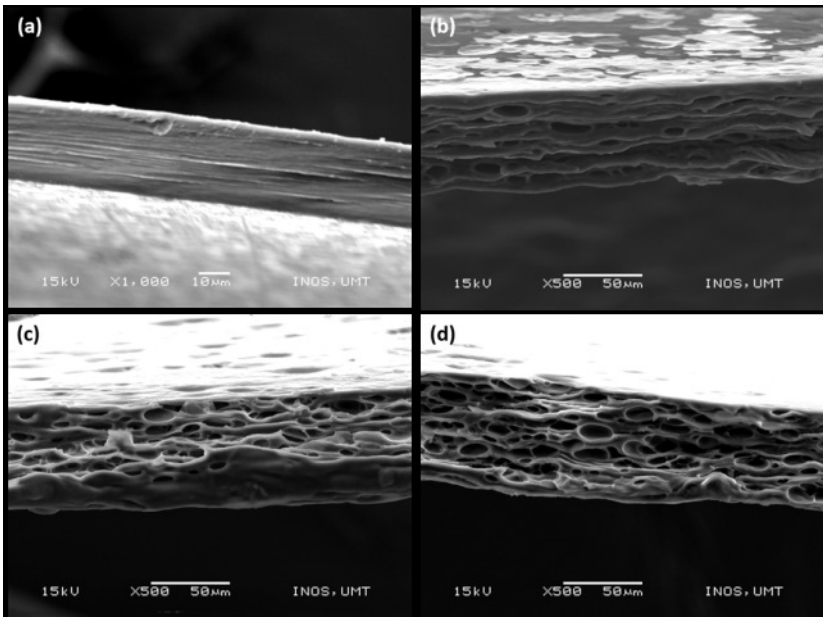

Figure 4. SEM images of cross-sectional of (a) pure GG film (b) GG+30GLY (c) GG+50GLY and (d) GG-GLY70 biofilms.