Swelling and tensile properties of starch glycerol system with various crosslinking agents

R Mohamed, N Mohd N Nurazzi, M I Siti Aisyah, F Mohd Fauzi
GREEN Polymer Research Group, Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

E-mail: rahmahmd@salam.uitm.edu.my

Abstract. Brittle properties of starch had been overcome by the modification process. In this work, sago starch is being modified with variable amount of plasticiser, namely glycerol at 20 and 40% and crosslinking agent had been added to the system. The film of the modification and characterizations of the starch glycerol system with various crosslinking systems were produced by casting method. The film properties of the starch glycerol system were then characterized by tensile strength (mechanical properties) and swelling (physical properties). The modification of the starch glycerol had improved that system by increasing the tensile strength, modulus however lowering its elongation. The increasing in percentage of the water absorption and also swelling are due to the intrinsic hydroxyl groups presence from the starch and glycerol itself that can attract more water to the system. Upon crosslinking, films casted with chemicals namely, glyoxal, malonic acid, borax, PEG were characterised. It was found that, all the film of sago starch crosslinked and undergoing easy film formation. From this modification, borax and malonic acid crosslinking agent had been determined as the best crosslinking agent to the starch glycerol system.

1. Introduction

Sago is a starch extracted from the pith inside stems of the sago palm metroxylon sagu. It is composed primarily of amylose and amyllopectin. Several minor components such as lipids, protein and phosphates are also present within the granules but at low concentrations. Amylose is an amorphous polymer linkage with chain lengths of 6,000 D-glucopyranose units and molecular weight between 150,000 and 600,000 Da. Amylopectin is a very large and highly branched polymer linked. There are many types of starch especially for commercial use, they are derived from a variety of cereals like rice, wheat, sorghum, corn and tubers like potato, tapioca, sweet potato and etc. Internationally popular forms of starch are mostly derived from corn and tapioca due to their easy availability. However, tapioca starch content of less amylose than sago starch.

Since sago starch is abundant in Malaysia, it can be as an alternative source of material with lower cost [1]. Starch glycerol and system can create variety of products in various field including packaging, medicinal, food and pharmaceutical industries. However, the drawback of starch is having the brittle properties. In order to overcome this problem, the modification process should be used by adding with glycerol as a plasticizer. It can be defined by two purposes, which are to improve the flexibility, extensibility and overcomes the film brittleness. Film forming capacity of different chemical modified corn starches was evaluated by Lopez et al., (2010). The effect of glycerol as
plasticizer on film properties depend on its concentration, low film solubility in water and a more compact structure than those of unplasticized films. In their findings, mechanical behaviour of plasticized acetylated starch films depends on glycerol concentration, being rigid and brittle than the unplasticized ones, more ductile and became very flexible for higher plasticizer content) [2].

Starch had been modified for emulsifiers, as food thickeners while as hydrogels, super absorbents, edible films, adhesive, film forming and packaging in biodegradable packaging industries also exploited modification of starch technology to develop products of high performance. In packaging, interest in environmental friendly products has created a significant market opportunity for starch. The goal has been to increase the amount of starch in thermoplastic composites designed for various packaging materials [3, 4]. Modification of starch are well established using different types of starches and types of crosslinkers and agents [5]. Chemical modifications of starch generally involve esterification, etherification or oxidation of the available hydroxyl groups on the B-D-glucopyranosyl units that make up the starch polymers. Reactions used to produce most commercially modified starches have been reviewed by [6, 7].

Starch that are unplasticized are rigid and brittle [8]. The strength of starch with glycerol is quite low especially in aqueous solution. In order to improve the strength of the film, crosslinker can be added in the system. Crosslinking is common approach to improve the performance of starch. Crosslinking agent concentration, starch content, pH, treatment temperature and treatment time are factors that affect crosslinking. In order to crosslink polymers containing hydroxyl groups, such as starch, the crosslinking agent must be able to react with at least two hydroxyl groups in a single polymer molecule. Crosslinking density affects the gel content and water absorption or swelling of starch molecules. Not only types of crosslinkers and amount of crosslinkers used, the synthesis techniques and pH media with incorporation of other additives and temperature affect final product performances.

According to Singh and Nath (2012) had synthesised and evaluated the physicochemical properties of crosslinked sago starch. The properties were investigated using scanning electron micrograph (SEM), x-ray powder diffractometer (XRD) and thermogravimetric analysis (TGA). It was revealed that crystalline nature of native sago starch was transformed after cross-linking. TGA report exhibited higher thermal stability, which makes it suitable for various industrial applications [9].

There are many types of crosslinking agents that are well established. However in this work the use of selected crosslinkers and chemicals namely malonic acid, borax, glyoxal, dicyandiamide (DCN) and poly(ethylene glycol)(PEG) have been investigated. The different types of crosslinking agent can be analysed according to its ability to crosslink or enhanced flexibility of the polysaccharide chain.
2. Experimental

2.1 Materials

Sago starch (SS) used in this research was supplied by Bor Giap Sdn Bhd of Batu Pahat, Johor. Sago starch supplied by has specification composition states its moisture content in the sago starch varied between 10.6 and 16.0%, ash about 0.1% maximum, fiber about 0.2% maximum while the amylose content varied between 24 and 30%. Its pH is within 5.5 to 6.5. Glycerol, crosslinking agent; malonic acid, glyoxal, was supplied by MERCK (M) Sdn Bhd, while dicyandiamide (DCN), borax, Poly (ethylene glycol) (PEG) was supplied by SYSTERM (M) Sdn Bhd.

2.2 Preparation of Samples

There are two steps of the process:

Step I: Gelatinization of starch

10g of SS was weighed with analytical balance and placed in a 150mL beaker. SS then added with 20% of glycerol that act as the plasticizer based on the weight of SS. The mixture was then added with 100mL of distilled water at 90-100°C to gel the sago/glycerol system. Mixture is kept agitated in water bath at 80°C until it turns sticky. Glycerol SS is then added with crosslinking agent, at 2% based on the weight of SS/glycerol; similar procedure was followed with other crosslinking agents. The procedure is repeated for 40% glycerol and crosslinking done with malonic acid, glyoxal, dicyandiamide, borax and PEG.

Step II: Casting Process

After the gelatinization of the starch, films were fabricated by solution casting method in the aluminium moulds that have been provided. Then, the samples prepared put in the oven about 80°C in order to form film samples.

2.3 Characterizations

Swelling test was performed by immersed the samples in deionized water at room temperature. The initial thickness of all the samples was taken and recorded. The swelling properties of the starch films observation was done within ten days.

\[
\text{Swelling \%} = 100 \times \frac{\text{Final thickness} - \text{Initial thickness}}{\text{Initial thickness}}
\]  

(1)

Tensile properties were performed by using Instron Universal Testing Machine (UTM). The samples were cut with 50mm length and 4.025 mm width of dumbbells shape by using the dumbbells cutter.
3. Result and Discussions

3.1 Swelling Properties

Figure 1 shows the swelling percentage of samples with different crosslinker and percentage of glycerol. From the Figure 4, it found that the malonic acid with 40 % glycerol has the highest swelling percentage at 34.09 % and followed by borax at 30.56 %.

Figure 1. Graph of swelling percentage (%) of starch films with different crosslinker and percentage of glycerol.

According to Mali et al., (2005), the addition of plasticizer provides more active sites by exposing its hydrophilic hydroxyl groups in which the water molecules could be adsorbed. Besides that, higher levels of plasticizer increased the films moisture affinity and these results could be attributed to the hydrophilicity of the plasticizers, which presented hydroxyl groups capable to interact with water by hydrogen bonds. Even though the glycerol molecules are small, they present high capability to interact with starch chains hence enhancing the molecular mobility. This increases the free volume in the film matrix with consequence of increases the water molecules absorbed [8].

3.2 Tensile Properties

Figure 2 shows the tensile strength with various crosslinker and different percentage of glycerol. From both percentage of glycerol, the starch film with 40% of glycerol crosslinked by malonic acid shows the highest tensile strength. High in tensile values indicates the films are stronger with high strength by greater interaction and bonding. According to Mali et al., (2005), the unplasticized starch film represents low value of tensile. According to Sangeeta (2007), the tensile strength will increased due to the crosslinking and/or modification by glycerol [8, 10].
From Figure 3, about similar trend were observed for 20 and 40% addition of glycerol. Film at 20% of glycerol crosslinked with PEG crosslinker has the highest elongation with 10.29 mm and followed by the glyoxal crosslinker with 9.59 mm of elongation. However, film at 40% of glycerol crosslinked with borax crosslinker has the highest elongation with 5.51 mm of elongation and followed by PEG crosslinker with 4.64 mm of elongation, while film that crosslinked by malonic acid still the lowest elongation at break as both 20 and 40% of glycerol addition with 6.77 and 2.22 mm of elongation respectively.

According to Lopez et al. (2008), unplasticized starch is brittle and by the addition of the plasticizer (glycerol), tensile strength was decreased but increase in the elongation at break. This is due to the plasticizer interfering with the polymeric chain associating their slipping and thus enhances the film flexibility [2]. However Malonic acid decreases in flexibility of starch/glycerol system while PEG showed opposite trend. Effect of glycerol on physical and mechanical properties of wheat starch edible films had been studied by Farahnaky et al., (2013), they found glycerol did not change X-ray patterns
of starch films; however, the degree of crystallinity were reduced [11].

![Figure 4](image_url)

**Figure 4.** Tensile modulus of starch film against varies of crosslinker.

Figure 4 shows the film crosslinked by malonic acid give the highest rigidity through tensile modulus. When compared 20 % of glycerol with the 40% of glycerol, film crosslinked by borax has reduced its tensile modulus by 300 % or three times reduction upon increasing glycerol content from 20 to 40 %. Film that crosslinked by malonic acid does not affect significantly on starch modulus compared to film with borax crosslinker. It only decreased by 23 % from 20 to 40 of glycerol.

With glycerol content, the strain at break increased considerably, however the breaking stress and elastic modulus decreased. However, with an increase in the glycerol content, was shown to results in decrease of the tensile modulus as happens with plasticizers used with synthetic polymers in general (Briassoulis (2004)) [12]. When considering on the ability of the plasticizer, according to Mali et al., (2005), the plasticizer can increase the film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular space. The most effective plasticizers will generally resemble most closely the structure the polymer they plasticized, thus, the most commonly plasticizers used in starch-based films are polyols, such as sorbitol and glycerol. They avoid cracking of the film during handling and storage, affect of gas, water vapor and solute permeability and sorption characteristic [8].

4. **Conclusions**

In conclusion, SS/glycerol system with various crosslink agents had increased tensile, modulus but decrease in elongation; meaning SS system is less flexible. Considering the characterization from swelling test, the highest percentage of swelling for 20% glycerol with a crosslinker DCN and 40% glycerol with a crosslinker malonic acid. Higher levels of plasticizer increased the films moisture
affinity and these results could be attributed to the hydrophilicity of the plasticizers, which presented hydroxyl groups capable to interact with water by hydrogen bonds. While the best crosslinking agent which highest performance in terms of tensile and modulus are borax and malonic acid. Lastly, it can be conclude that, crosslink agent can be easily modified to obtain desired strength, rigidity for specific drug delivery application based on the variable of glycerol percentages and also variable types of crosslinker of =C–H out of plane bend is appeared.

Acknowledgements
The authors thank Faculty of Applied Sciences (FSG), Universiti Teknologi MARA (UiTM) Shah Alam, Malaysia for providing good facilities. Highly appreciation is conveyed to those involved in completing this work.

References
[1] Ahmad F B and Williams P A 1998 Journal of Agricultural and Food Chemistry 46 4060-4065.
[2] López O V et al 2008 Carbohydr. Polym. 73 573-581.
[3] Doane W M 1994 Cereal foods world (USA) 39 556-563.
[4] Poutanen K and Forssell P 1996 Trends in Polymers Science 4 128-132.
[5] Chiu C and Solarek D 2009 Starch: Chemistry and Technology 3 629-655.
[6] Shah U et al 2016 Comprehensive Reviews in Food Sci. and Food Safety.
[7] Ashwar B A et al 2016 Food Hydrocolloids 56 108-117.
[8] Mali S et al 2005 Carbohydr. Polym. 60 283-289.
[9] Singh A V and Nath L K 2012 Int. J. Biological Macromol. 50 14-18.
[10] Sangeeta G and Asim Kumar J 2007 Eur. Polym. J. 43 3976-3987.
[11] Farahmy S et al 2013 J. Texture Studies 44 176-186.
[12] Briassouls D 2004 J. Polym. Environment 12 65-81.