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Physical Properties of Edible Films Based on Tapioca Starch as Affected by the Glycerol Concentration

Dahiru Adamu AJIYA[1,3,a], Suzi Salwah Binti JIKAN[1,b*], B.A. TALIP[1,c], H. M. MATIAS-PERALTA[1,d], N.A. BADARULZAMAN[2,e] and S. YAHYA[4,f]

[1]Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn, Malaysia.

[2]Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn, Malaysia.

[3]Department of Chemistry, Abubakar Tafawa Balewa University Bauchi, Nigeria.

[4]Department of Physical Sciences, Niger State Polytechnic; Zungeru. Nigeria.

[a]ajiyamt@yahoo.com, [b*]suzi@uthm.edu.my, [c]balkis@uthm.edu.my, [d]azam@uthm.edu.my

[e]yashe46@yahoo.com

ABSTRACT. The aim of this work is to study the influence of different proportions of glycerol on the properties of tapioca starch films. The films were characterized to determine crystallinity by using X-ray diffraction (XRD), thermal property by differential scanning calorimetry (DSC) and mechanical property by tensile test. The DSC thermograms show a decrease in the melting temperature (T_{Peak}) with increase in the glycerol content. According to XRD diffractograms, pure starch exhibits crystallinity, but gelatinisation converts the starch film with 0 (w/w) % glycerol to amorphous, it gains back its crystallinity with the increase in the glycerol concentration. Mechanical properties were also influenced by variation of the percentage ratio of glycerol. The tensile strength was observed to decrease with increase in glycerol concentration whereas the elongation at break sharply increase with increase in glycerol concentration.

Keywords: *Tapioca starch, Glycerol, DSC, XRD;*

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1. INTRODUCTION

Packaging plays important function in maintaining and protecting organic composition of food, it is essential to have a packaging material that protects the value, wholesomeness and safety of the food product with minimum cost and environmental impact. The monumental increase in non-degradable organic solid waste worldwide is championed by synthetic packaging materials [1]. The greater proportion of solid waste goes to food packaging [2]. A rare opportunity to move away from depleting fossil fuel to a replenish-able, environmentally benign material source is found in biodegradable, renewable bio-plastics [3]. Biopolymer potentially used for the production of food package ranges from polysaccharides, protein, lipids, cellulose or combination of both. The most important of polysaccharides for the production of food packaging is starch [4]. This is as a result of its abundance, low cost and processibility [5]. Starch is hydrocolloid substance, produced agriculturally by plants in a granulated form. It consists of about 30% amylose (poly-α-1,4 D-glucopyranoside), a crystalline component and 70% amylopectin (poly- α-1,4- D glycopyranoside and α-1,6-glucopyranoside), a branched of amorphous part of the starch [5].

The gelatinisation is a significant method in starch processing. It involves the breaking of intermolecular links of starch fragments in the presence of water and heat, freeing the hydroxyl groups to interact with more water molecules. The effect of the interaction results to irreversible dissolution of the starch particles in water [5]. The bioplastic starch, when cooled over a period, thickens (or gel) and reorganise its molecules to a more crystalline form [6]. Certain amount of heat will be required to melt the semi crystalline material formed [7].

A specific amount of natural and artificial additives are used to enhance the properties of starch based thermoplastics namely plasticizers [8], antimicrobials [9], stabilizers [10], and antioxidants [11]. The essential function of plasticizers is to increase the elasticity and workability of polymers. Due to the low molecular weight of plasticizers, they tend to dwell in the intermolecular spaces within the polymer chains, reducing stiffness and enhancing intra-molecular hydrogen bonding [12]. Therefore, amount of strength and elasticity of a polymer invariably depend on the nature of the plasticizer including its chemical composition, functional groups and reactivity [3]. Some researchers found that glycerol excellently serves as plasticizer for water soluble polymers [12, 13]. The functional groups in the glycerol promotes molecular hydrogen bonding which become incentive for flexibility and processibility [14].

The main drive of this research work is to evaluate the effect of percentage proportion of glycerol on the features of tapioca starch film by employing the use of tensile analysis, XRD and DSC.

2. MATERIAL AND METHODS

Tapioca starch, was supplied by THC Sdn Bhd, it has the following property [15]: moisture, 13%; amylose, 17%; lipids, 0.1%; phosphorus, 0.01%; soluble sugars, 0.24%; protein, 0.1% and ash, 0.2%. And the glycerol was supplied by R & M Chemicals [16].

Tape casting was the technique employed for preparation of the starch-based films [13]. The formulations were made by 10% (w/w) H_2O, (0, 5, 10, 15, or 20%) (w/w) glycerol and the remaining proportion of the final mixture of 15g was completed by the starch powder. The mixture was heated at 125 °C for 5 min at 50 rpm agitation using mechanical stirrer. The final product was spread on 15 cm x 15 cm glass plates using the doctor blade. Oven was used to dry the film with air circulation at 30 - 40 ºC for 2 hours. Curing of the finished product takes place in an open air at 24 - 48 hours [16].

The tensile properties were evaluated using Instron 4302 series IX, according to ASTM D 882-02 standard. Five samples, 2.54 cm x 5 cm, were cut from each film. Initial grip separation and crosshead speed were set at 50 mm and 500 mm/min, respectively [16].

The melting temperatures (Tpeak) were found using Differential Scanning Calorimeter (DSC) (TA instrument Q20 V24.10 build 122). The samples were evaluated in triplicate, (± 0.01mg, Mettler Toledo XPE analytical balance). Aluminium pans where impermeably sealed and heated at amount of 10 ºC/min. Moreover, an empty pan was used as a reference. DSC thermograms were presented as exo-up. Therefore, the downward absorption represent endothermic, positive reaction.

The crystallinity of the films and solid starch was examined empirically with an XRD (Bruker D8 Advance) machine. It was operated at 40 kV and 40 mA. Nickel-filtered Cu Kα radiation was used in the incident beam. The square (2mm x 2mm) samples were analysed between $2\theta = 10º - 30º$ with a step size of $2\theta = 4º$, according to [10].

3. RESULTS AND DISCUSSIONS

The presence of glycerol as shown in Fig. 1, has a significant influence on mechanical property of the starch film. Curve (a) in Fig. 1 showed a sharp decrease in the tensile strength as the percentage concentration of the glycerol increases. It has been reported by Bergo et al. [12] that the resistance of starch film reduces with increase in glycerol content. This could be due to less contact between the starch molecules as a result of a barrier created by the presence of glycerol.

Conversely, the elongation at break as shown in curve (b) in Fig. 1 presented a consistent increase as the glycerol content increases. The behaviour of mechanical properties of starch film is widely reported in the literature [4,8,12,17].

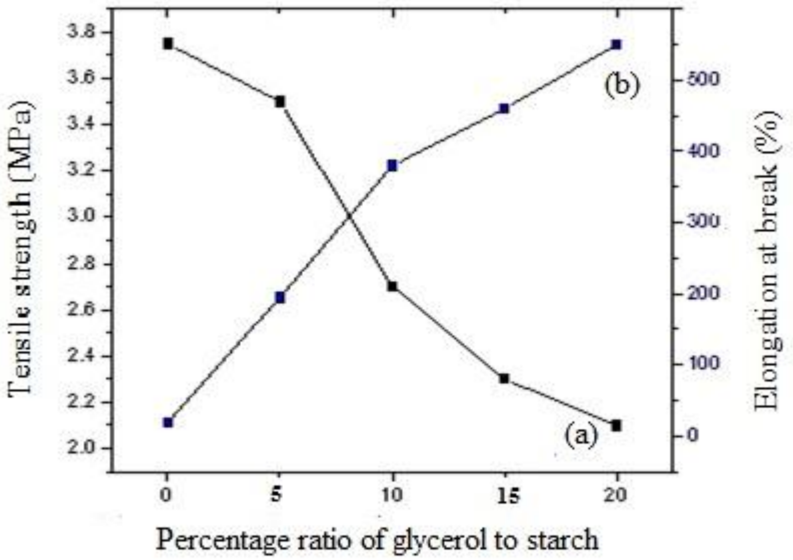

Fig. 1 Effect of glycerol concentration on tensile strength and elongation at break of tapioca starch films

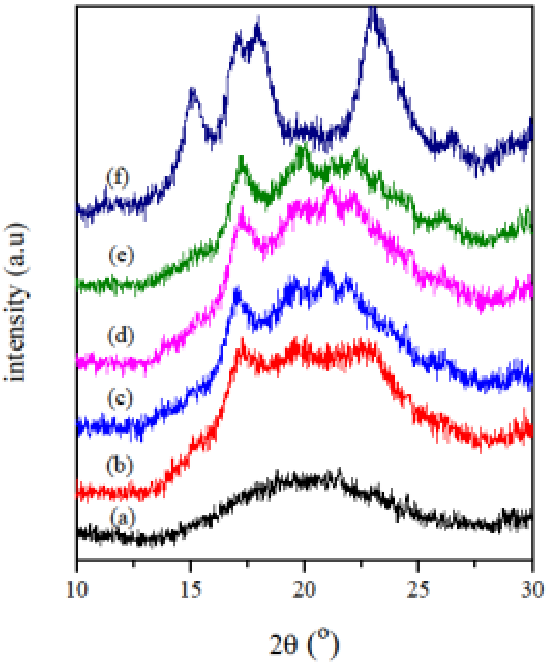

Fig. 2 X-ray diffraction of Tapioca starch containing (a) 0, (b) 5, (c) 10, (d) 15, (e) 20% glycerol and (f) dry starch

Fig. 2 shows the XRD patterns obtained in the starch films as curve (a) to (e) and solid starch as curve (f). The XRD diffractogram of the solid starch indicate peaks around 2θ ≈ 15º, 19º, 24º, which shows high tendency of crystallinity. Whereas, curve (a) for film with 0% glycerol depicted no presence of peak, presenting a fully amorphous characteristic. While, in curve (b) to (e) a crystalline tendency is shown by the presence of peak at 2θ ≈ 17º for films with 5, 10, 15, and 20% glycerol. The peak becomes more conspicuous as the percentage of the glycerol increases. Showing that the crystallinity of the starch film increase with the increase in the glycerol content [17].

Fig. 3 illustrates the DSC thermograms of the films investigated, having different percentage of glycerol concentration. The graphs of all the films showed an endothermic reaction from 25 ºC to 173 ºC, which indicates the softening of various starch crystals developed during retrogradation [1]. For the different films in curve (a) - (e) in Fig. 3 the endotherms changes in ascending order as the concentration of glycerol increases. Curve (a) shows the highest T_{peak} as 117.8 ºC and enthalpy +1.061 W/g and Curve (e) shows the least T_{peak} as 93 ºC and enthalpy +0.918 W/g. The transition parameters are shown on Table 1. The change in transition enthalpy was due to the occupation of the interstices of the polymer matrix by glycerol keeping the adjacent polymer chains apart, thereby reducing the forces of attraction (i.e. van der Waal's and electrostatic) between the film molecules aiding the molecules glide across each other easily which increases the flexibility of the polymer matrix. This tendency was similarly reported by some other researchers [1,2,7].

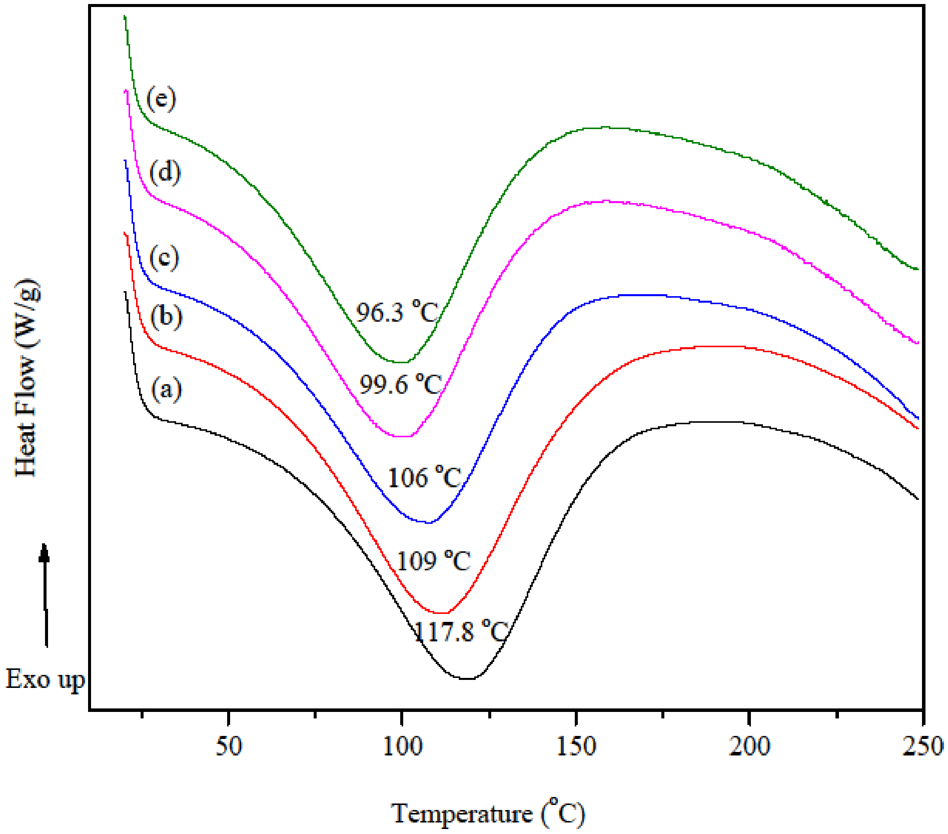

Fig. 3 DSC curves of tapioca starch films containing (a) 0, (b) 5, (c) 10, (d) 15 and (e) 20% (w/w) glycerol

Table 1. DSC transition parameters of tapioca starch films with different glycerol percentage concentration

% Glycerol	T_{onset} (°C)	T_{peak} (°C)	T_{offset} (°C)	ΔT (T_{offset} - T_{onset}) (°C)	ΔH (W/g)
0	25	117.8	172.5	147.5	+1.061
5	34	109.1	175.5	141.5	+1.039
10	27	106.0	136.6	136.6	+1.003
15	26	99.6	160.7	134.7	+0.963
20	25	96.3	158.5	133.5	+0.918

4. SUMMARY

The tensile strength of the tapioca starch film is reduced by the increase in the amount of glycerol, while elongation at break increases with increase in glycerol. The rigidity of TPS film softens with the increase of glycerol content. Thereby, the use of glycerol increases the workability of TPS for food packaging. Though, excessive amount will increase the crystallisation of the TPS molecules leading to fragility as depicted by the XRD results. So also the DSC indicated that higher concentration of glycerol reduces the TPS heat resistance.

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