

Preparation and Characterization of Enset Starch (ES) Based Films: Plasticized by Glycerol and Sorbitol

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ABSTRACT: Films were prepared using the casting method from enset starch, as a filler material, glycerol & sorbitol as plasticizers at different concentrations (15, 25, and 35%). And glucose, fructose, and sucrose were added to enhance flexibility. The films were characterized and compared with the effect of plasticizer type (glycerol and sorbitol) and the concentration of some physicochemical properties of ES-based films. The films were analyzed for moisture content, film density, and thickness, swelling capacity, tensile strength, and percentage elongation. The study indicated that moisture content, film thickness, film density, swelling capacity, tensile strength, and percentage elongation are dependent on the type of plasticizer and its concentration. Increasing the plasticizer concentration from 15 to 35 % increases moisture content, and film thickness; decreases the film density, water swelling capacity, and tensile strength of films, regardless of the plasticizer type used.

KEYWORDS: 2 Enset starch; Glycerol; Sorbitol; Biodegradable films.

INTRODUCTION

Starch has been considered one of the most promising candidates for the future primarily because of an attractive combination of its large availability and relatively low price [1, 2]. Films developed from starch are described as isotropic, odorless, tasteless, colorless, non-toxic, and biologically degradable [1]. Food packaging is intended to protect food from its surrounding environment as well as preserve the nutritional value of food. Up to now, the packaging materials are still dominated by

non-degradable fossil fuels-based ingredients. Food in particular, has a short shelf life, thus the use of non-degradable food packaging for short-term packaging arises as a serious environmental problem. Bio-based materials which in principle act similarly to regular packaging but are degradable have been widely explored, including edible and biodegradable film from renewable sources. However, it has poor both mechanical and water barrier properties, therefore the industrial applications of this material are still

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limited [3]. Enset (*Ensete Ventricosum*, Family *Musaceae*) is an important traditional Ethiopian staple crop widely distributed in Eastern and Southern Ethiopia to feed about 15 million people through a mixed subsistence farming system. It is often called the “false banana” for its morphologically close resemblance to the domesticated banana plant (*M.acuminata*, Family *Musaceae*). Being different from banana, enset accumulates starch mainly in the pseudostem and underground corm, which is utilized as a starch resource for food products and industrial purposes [3].

The properties of biodegradable films can be enhanced by modification of the starch or by adding different ingredients such as glycerol and sugars as plasticizers and flexibility, Nano clay for reinforcement, and different bioactive materials to be used as active packaging. The development of the starch-based, biodegradable film has been one of the more attractive research topics of starch utilization [4].

Eventually, to study the potential application of Enset Starch (ES) in the development of starch-based biodegradable films, after studying physicochemical and thermal properties of enset starch (ES), biodegradable films were prepared using this Enset starch as a matrix, glycerol, and sorbitol as plasticizers and sucrose, glucose and fructose as flexibility agents. The different concentrations of plasticizers were used to evaluate their effect on the properties of the films. The prepared Enset starch-based biodegradable films were evaluated and characterized by different properties such as film thickness, moisture content, film density, swelling capacity, and mechanical properties like tensile strength and elongation at break. Films' properties are affected by various factors such as amylose and amylopectin ratio, and type and concentration of plasticizers. Amylose and amylopectin composition of Enset starch varies between 21-29 % and 79-71% [5, 6] and is comparable to potato starch. Native starch films are brittle compared with synthetic polymers such as polyethylene, and technology needs to be plasticized. A plasticizer is a substance that is incorporated into rigid materials to increase its flexibility, workability, and dispensability [14]. The addition of a plasticizer to a film produces a film that is less likely to break and is more flexible and stronger [12].

Generally, two types of plasticizers are distinguished. Internal plasticization is a result of modifications to the chemical structure of the polymer. External plasticization

is obtained by adding an agent, which modifies the structure and energy within the three-dimensional arrangement of the film polymer [18].

The plasticizers should be generally compatible with the structure of the polymer that they plasticize and the permeability is present within the solvent-polymer system and under the conditions used. To be compatible, it must be compatible with the polymer, which results in intermolecular reactions. It is important to note that the formulation of the whole film system has a direct effect on the nature and characteristics of the film produced [18]. Nobody has prepared and characterized Enset starch-based biodegradable films.

EXPERIMENTAL SECTION

Materials

Enset starch was purchased from a store in Addis Abeba, Ethiopia. Glycerol was purchased from LOBA Chemie PVT.LTD, India, and other chemicals and reagents such as sorbitol, sucrose, glucose & fructose were procured from Sd. Fine Chem. Mumbai, India. Native set starch was used as a matrix, glycerol, and sorbitol as plasticizers, sucrose, glucose, and fructose for enhancing flexibility, and distilled water as solvent film-forming solutions.

Methods

Film preparation

The solution was prepared as follows: 1.25g of Enset starch, 14% of sucrose, 14% of glucose & 14% of fructose were mixed. Then the liquid glycerol at different concentrations (15%, 25% & 35%) with distilled water was added to the above mixture in order to complete 25g of the solution and thoroughly mixed for 5 min. The solutions were heated on the hot plate until gelatinization occurred (at 95°C for 5min.) and allowed to cool at a temperature near 50°C. Finally, the gel was cast on the plastic plate (22 cm x 30 cm) and allowed to dry in direct sunlight (at 33-37°C). Then the film was removed from the plate and sealed in polyethylene bags (21 x 29.7 cm) for characterization. The same procedure was followed when we used sorbitol as a plasticizer instead of glycerol. Both glycerol and sorbitol plasticized films were characterized and compared to evaluate the effect of plasticizer type and concentration on physicochemical properties of the films. The flow chart of Enset starch-based biodegradable film preparation is depicted in Fig. 1.

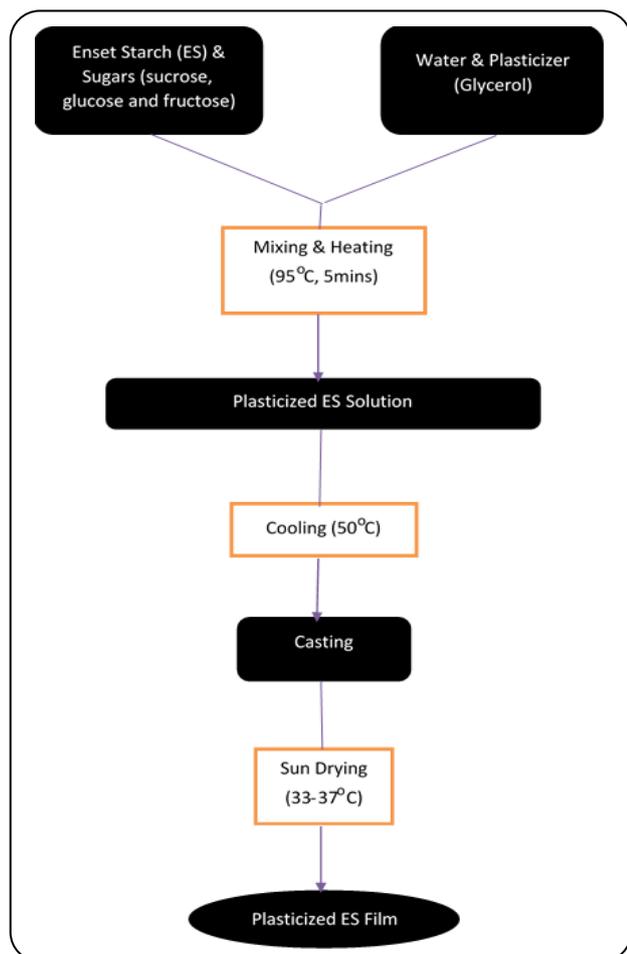


Fig. 1: Flowchart of Enset starch film formation.

Film characterization

Film Moisture Content (MC)

The Films Moisture contents were determined by the gravimetric method, about 35mg of the films were dried at 100°C for 24h (until a constant weight was attained). MC was calculated as the percentage of water removed from the film. It was determined in triplicate and mean values were reported [7].

Film Thickness

Films thicknesses (δ) were determined using a digital micrometer (exactness of 0.001 mm, Mitutoyo, Co. Japan). The thickness measurements were obtained from five random film points for each sample. The average value of measurements for each sample was utilized. [13].

Film density (ρ)

For the density (ρ), the average masses of three square samples (20 mm x 20 mm) of film were calculated. Sheet

mass (m) was measured by weighing on a plate balanced with an accuracy of 1 g and its volume (v) was measured by dipping the sheet in a cylinder containing hexane and noting the volume displacement. The density (ρ) was calculated using Equation $\rho = m/v$. [8]

Film Swelling Capacity

The film was immersed in distilled water at room temperature, in order to determine the swelling from water uptake, for 10 minutes and the weight gain was measured every 2 minutes (until a constant weight was attained). The swelling percentage was calculated using the following Eq. (1): [9].

$$\% \text{ Swelling} = \frac{w - w_0}{w_0} \times 100 \quad (1)$$

Where w_0 = initial sample weight (dry sample) and w = final sample (water swollen sample) weight

Tensile strength and Elongation at break

Films' mechanical properties (Tensile strength and elongation at break) were determined from tension tests, using the Brookfield texture analyzer (CS3), in accordance with ASTM-882-00 (2000) [10].

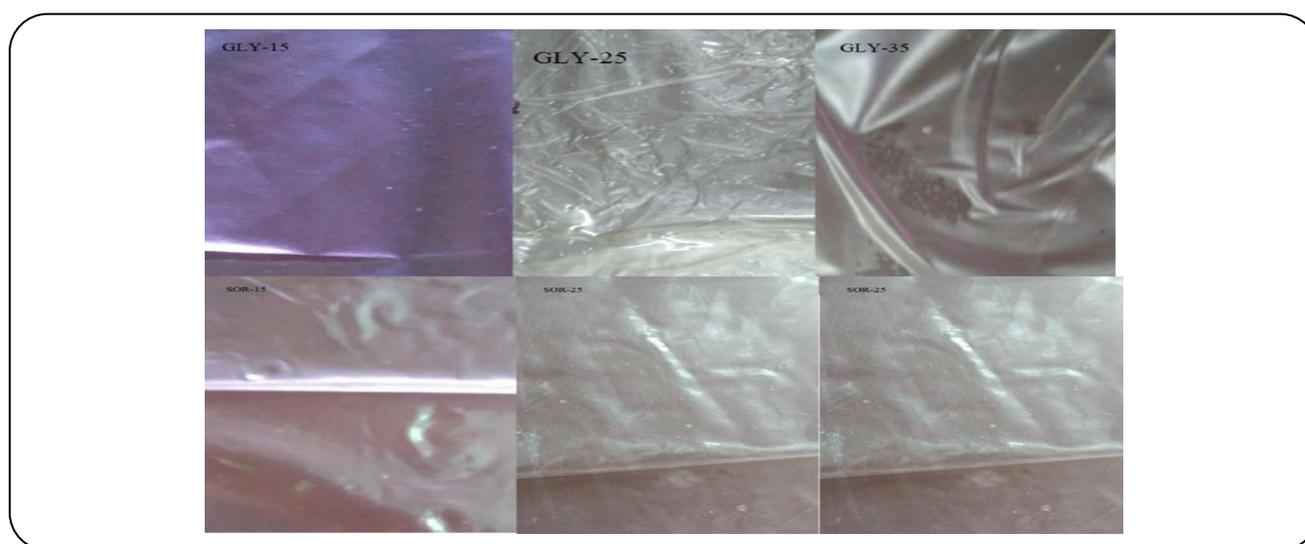
RESULTS AND DISCUSSION

Fig. 2 shows the photographic images of the developed ES-based biodegradable films, plasticized by different concentrations of glycerol (15, 25 & 35%) and sorbitol (15, 25 & 35%). The ES-based films prepared without plasticizers were brittle and rigid. Many cracks were observed on the surface of the films. They were difficult to peel and handle. This observation could be attributed to the strong inter/intramolecular hydrogen bonds of starch which provide less mobility to the macromolecular chains, resulting in brittle and rigid films with surface cracks [4]. The addition of plasticizers to ES-based films rendered them flexible with a smooth and homogeneous surface. The flexibility increases as the plasticizer concentration increases, irrespective of the plasticizer type.

The low molecular size of the plasticizers enables them to creep within the intermolecular spaces of polymer chains, reducing the intermolecular hydrogen bond strength, hence, increasing the molecular mobility [11]. The intermolecular hydrogen bond of ES films weakened as the plasticizer concentration increased from 15 to 35 %.

Table 1: Some properties of enset starch based biodegradable films.

Plasticizer Type	Conc. (%)	Thickness (μm)	Moisture content (%)	Swelling Capacity (%)	Density (mg/mm^3)	Tensile Strength (MPa)	PE (%)
Glycerol	15	39	13.31	120.62	1.56	2.9	16.25
	25	46	14.59	84.53	1.51	2.52	18.56
	35	49	16.43	52.79	1.49	2.33	24.59
Sorbitol	15	53	8.65	93.53	1.60	4.16	44.32
	25	52.5	9.43	94.90	1.58	3.15	37.34
	35	53.5	12.36	97.47	1.55	2.36	34.1

**Fig. 2: General appearance of the films.**

Nonetheless, at the same plasticizer concentration, the change in plasticizer type significantly affected the flexibility of their resulting films. Hence, it was noticed that glycerol plasticized films demonstrated higher flexibility than sorbitol plasticized films when tested physically by handling. When the concentration of glycerol increased the force required to peel was decreased.

It was similar for sorbitol plasticized films but when we compared the two films (glycerol plasticized and sorbitol plasticized) at the same plasticizer concentration glycerol plasticized films were easily peeled from the casting plates. It can be assumed that glycerol is relatively easier to interpose itself within the intra/intermolecular spaces of the starch because of its smaller molecular weight. The strong bond between glycerol and ES reduced the cohesive tension of the starch molecules; thus, glycerol plasticized films became easy to peel [12].

Moisture Content

The moisture content of the enset starch-based biodegradable films plasticized by different plasticizer types are found as shown in Table 1.

The moisture content of both glycerol and sorbitol-plasticized ES-based biodegradable films increased significantly as plasticizer concentration increased from 15 to 35 %. Lower moisture content was observed in the biodegradable films produced by ES that are plasticized by sorbitol when compared to films produced using glycerol as a plasticizer (see Fig 3).

The trend can be explained by the similarity of the molecular structure of glucose units with sorbitol, which caused stronger molecular interactions with glucose units and the formation of intermolecular polymeric chains (Sanyang *et al.*, 2016) [13], further, the retention of water molecules by sorbitol is very low. On the other hand, the hydrophilic nature of glycerol enhances the retention of water by forming a hydrogen bond [12]. The hydrophilic

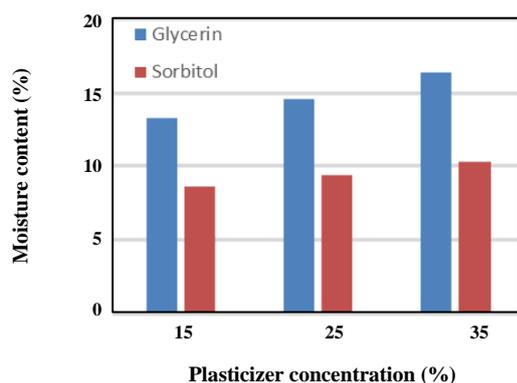


Fig. 3: Moisture content of ES-based biodegradable films with different plasticizer types and concentrations.

The nature of starch-based films is generally enhanced with an increase in the concentration of plasticizers.

Film thickness

The Thicknesses of ES-based biodegradable films at different concentrations of glycerol and sorbitol are found to be as shown in Table 1 and Figure 4. As shown in the results the thickness of the film plasticized by glycerol is significantly increased as plasticizer concentration increases however, there is no significant increment for sorbitol plasticized film. The increasing effect of glycerol is because of the activity of plasticizers in disrupting and restructuring of intermolecular polymer chain networks, creating more free volumes which translate into higher film thickness [14]. A similar effect of plasticizer concentration on film thickness was reported by M. L. Sanyang et al. [9].

The ES-based biodegradable film thickness is significantly influenced by the plasticizer type as shown in Fig. 4. The sorbitol plasticized ES-based biodegradable films exhibited thicker films than glycerol plasticized films. The differences in film thickness of various plasticizers may be ascribed to their molar mass because the film-forming solution formulation was constant. Low film thickness expressed by glycerol-plasticized films at constant concentration can be possibly ascribed to its smaller molar mass compared to sorbitol plasticizer [15]. Research on Enset Starch (ES) based biodegradable films is scanty and hence the data produced could not be compared with other films. However, Sanyang et al (2016) reported that sugar palm starch-based films using sorbitol as plasticized produced films with higher thickness when

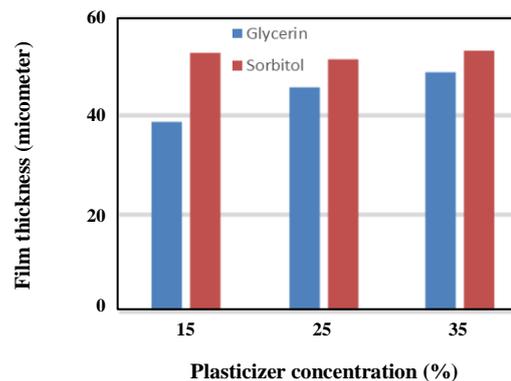


Fig. 4: Thickness of ES-based biodegradable films with different plasticizer types and concentrations.

compared to films based on glycerol as a plasticizer.

Film density

Increasing the concentration of plasticizers from 15 to 35 % causes a slight decrease in the density of glycerol plasticized film (1.56–1.49 g/cm³) and sorbitol plasticized film (1.60–1.55 g/cm³), regardless of plasticizer type (see Table 1 and Fig. 5). This phenomenon may be ascribed to the differences in molecular weight and density of the plasticizers. The molar weight of the plasticizers also follows a similar trend as the aforementioned density reduction. [15]. The starch crosslinking of ether or ester linkages amongst hydroxyl (-OH) clusters in starch molecules improved mechanical properties, due to the density increased by crosslinking.

The influence of the varying amount of dialdehyde starch solution on the physical and mechanical properties of bitter yam starch-based biofilms was investigated. The proportional increase in film thickness (0.20–0.26 mm), density (1.15 to 1.43 g/cm³), and opacity (0.92 to 1.04%) were observed from the neat film (Film₀) to film with the highest dialdehyde starch content (Film₃) respectively [16].

Swelling capacity

As shown in Table 1 and Figure 6, the swelling capacity of glycerol plasticized ES-based biodegradable film was decreased with increasing plasticizer concentration from 15 to 35%. However, in sorbitol plasticized film there was no significant difference with increasing of plasticizer concentration (less affected

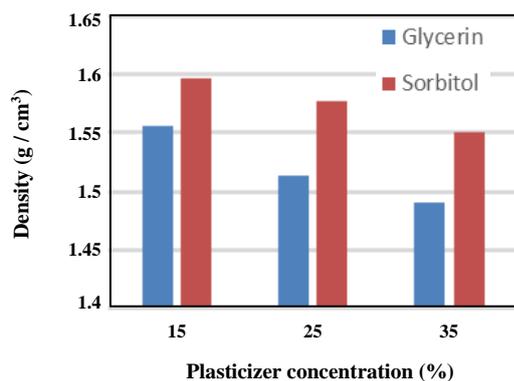


Fig. 5: Density of ES-based biodegradable films with different plasticizer types and concentrations.

by plasticizer concentration). For all concentrations, sorbitol plasticized films were more water-resistant and less hygroscopic than glycerol plasticized films, due to their strong hydrogen bond formation with the starch intermolecular [15].

According to *Mali et al.*, (2005) [17], 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 film's 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 a high capability to interact with starch chains hence enhancing the molecular mobility. This increases the free volume in the film matrix as a consequence of increases in the water molecules absorbed.

The mass increase in all of the blank TPS samples increased by about 200%. However, spraying a waterproof spray on the surface of the TPS products reduced the water uptake by more than half for all samples. Moreover, waxing prevented the starch-based plastics from swelling. The advantage of covering thermoplastic starch with a bio-based adhesive laminate or wax is that they can be removed after use, giving the bio-adhesive, wax, and TPS the chance to degrade under natural conditions.

Tensile strength

The textural properties of the ES-based biodegradable films were measured using a Brookfield texture analyzer and the double layer (one fold) film samples were taken.

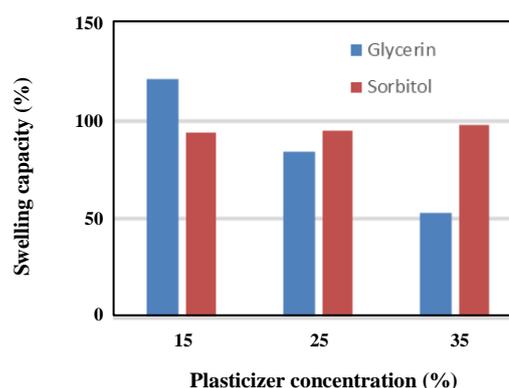


Fig. 6: Swelling capacity of ES-based biodegradable films with different plasticizer types and concentrations.

Thus, we have taken this into consideration when we evaluate and calculate the films for peak load, tensile strength, and elongation. As shown in Table 1, we found a tensile strength value of 2.9MPa for 15% glycerol plasticized film and 4.16MPa for 15% sorbitol plasticized film. However, increasing the plasticizer concentration caused a significant reduction in the tensile strength of films, regardless of plasticizer type. As we increased the glycerol concentration to 25% and 35% the tensile strength decreased to 2.52MPa and 2.33MPa, respectively. The tensile strength of sorbitol plasticized films also decreased to 3.15MPa and 2.36MPa, respectively. The possible reason for the high tensile strength at low plasticizer concentration is the domination of strong hydrogen bonds produced by a starch–starch intermolecular interaction over starch–plasticizer attraction [10]. This phenomenon can be explained through the role of plasticizers in diminishing the strong intra-molecular attraction between the starch chains and promoting the formation of hydrogen bonds between plasticizers and starch molecules. Thus, it reduces the tensile strength of ES plasticized films by subsequently weakening the hydrogen bonds between starch chains. The sorbitol-plasticized films were more resistant to breakage than films plasticized with glycerol at the same concentrations (Fig. 7).

Elongation at break

Elongation at break is the extendibility of film length from the initial length to the point of the break. This parameter (E %) helps to determine the flexibility and stretchability of films. Increasing glycerol concentration from 15% to 35% increased the elongation from 18.6% to 24.6% (Table 1).

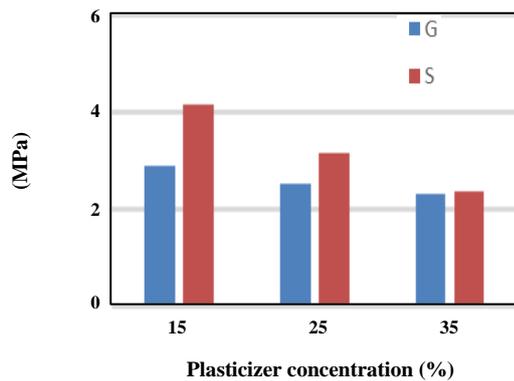


Fig. 7: Effect of plasticizer type and concentration on tensile strength of ES based biodegradable films.

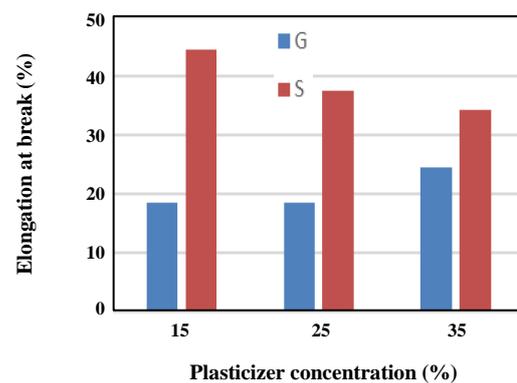


Fig. 6: Swelling capacity of ES-based biodegradable films with different plasticizer type and concentration.

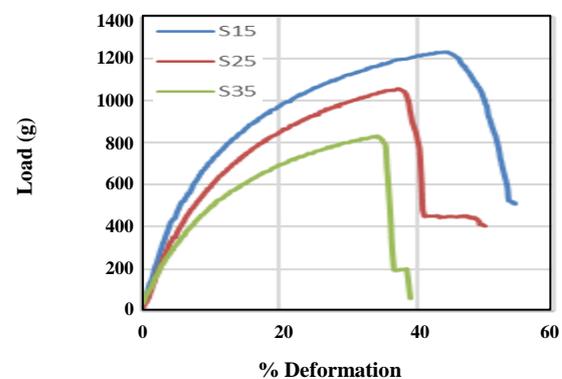
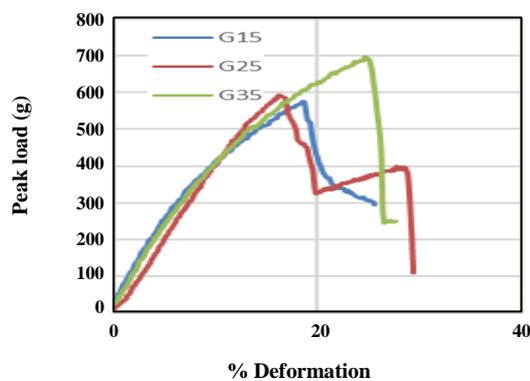


Fig. 9: Tension test of glycerol (A) and sorbitol (B) plasticized films: 50% deformation at speed of 0.5mm/s.

The observed increase in film elongation is because plasticizers decrease the intermolecular bonds between starch molecules and thus, substitute them with hydrogen bonds formed between plasticizer and starch molecules. Such disruption and reconstruction of starch molecular chains reduce the rigidity and promote flexibility of films by allowing more chain mobility [10]. However, the elongation of sorbitol plasticized films significantly decreased from 44.3% to 34.1%, when the sorbitol concentration increased from 15% to 35%. This occurrence can be explained by the anti-plasticization behavior or phase separation of highly plasticized starch films [7]. The sorbitol plasticized film elongations, for all similar concentrations, were higher than the glycerol plasticized films (As shown in Fig. 8).

As shown in the Figure 9A (the peak load–%deformation) curves, the glycerol plasticized film peak load was decreased as plasticizer concentration increased

whereas the percentage deformation (flexibility) was increased as plasticizer concentration increased. Sorbitol plasticized films (Fig 9B) peak load and percentage deformation were decreased as plasticizer concentration increased.

CONCLUSIONS

This study confirmed that Enset starch has the potential for developing biodegradable films, however, it needs a plasticizer and optimized film-forming procedures to obtain good-quality films.

Many visible cracks were observed on ES-based biodegradable films, which are hard and brittle when no plasticizer was used. They were hard to separate from the casting surface. Thus the application of plasticizers helped to improve their flexibility and peelability. It is also clear that the addition of sugars (sucrose, fructose & glucose) had an effect on the increase of the flexibility of the films

and help, specifically fructose and glucose, to preserve their flexibility because they are inverted sugars that would not crystallize at room temperature. Thus, this might affect the tensile strength, in turn, the elongation of the films.

The type of plasticizer and concentration was varied to study their effect on various physicochemical and mechanical properties of ES-based biodegradable films. It was found that increasing the concentration of plasticizer from 15 to 35 % resulted in enhanced moisture content, film thickness, reduced film density, water swelling capacity, and tensile strength of films. It was also noticed that type of plasticizer had a minimum effect on the above parameters.

Lower moisture content and swelling capacity were observed in sorbitol-plasticized films than in glycerol-plasticized films. However, glycerol-plasticized films exhibited lower film thickness and density compared to sorbitol-plasticized films. The percentage elongation of glycerol-plasticized films were increased with plasticizer concentrations (15 to 35%). In contrast, in sorbitol plasticized films percentage elongation was decreased with increasing plasticizer concentrations. It is attributed to the antiplasticization effect at the increased plasticizer concentration.

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