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Starch, Glycerol and Acetic Acid-Based Films: Investigating the Impact of Starch and Acetic Acid Contents on Film Properties

WAEL ELHRARI[1,2*], **MOHAMED ELBUZEDI**[1,2], **ASMA ABDALGADER**[3],
ABDULROUF TRISH[1,2], **ABDALAH KLASH**[1,2], **FATHIA ALAHIMER**[1,2],
RABEA ELHABISHI[1,2]
[1] Libyan Polymer Research Center, Tripoli, Libya
[2] Research, Consultation and Training Centre, Sirte University, Sirte, Libya
[3] Department of Chemistry, Faculty of Education, University of Tripoli, Tripoli, Libya

Abstract: *This study investigates the properties and degradability of starch-based biofilms as sustainable, non-toxic, and biodegradable materials, emphasizing the effects of starch content and plasticizers on their performance. Starch biofilms are produced by casting a water solution that utilizes glycerol as a plasticizer and acetic acid as a co-plasticizer. A comprehensive analysis of the films was conducted, assessing various properties such as water absorption, swelling, water vapor transmission rate, water vapor permeability, environmental degradation, thermal decomposition, and tensile strength. The findings reveal that the addition of acetic acid significantly improves the physical properties of the starch biofilms, while the starch content predominantly influences their physical and mechanical characteristics. Notably, all film samples demonstrated excellent soil degradability, with substantial breakdown observed after just one month of burial in the soil garden. This research contributes to the field of biodegradable materials by showcasing the effectiveness of starch biofilms as an eco-friendly alternative, highlighting the role of plasticizers in enhancing their performance and confirming their environmental sustainability through rapid degradation in soil.*

Keywords: *Biopolymers, starch film, glycerol, acetic acid, starch film properties*

1. Introduction

Petroleum-based plastic packaging material remains a popular choice in the packaging industry due to its cost-effectiveness. However, this type of packaging material presents a significant challenge to the environment due to its nonrenewable and non-degradability nature. Besides, the accumulation of plastic waste in the environment leads to a serious threat to human health. As a result, there have been several restrictions placed on the use of petroleum-based plastic packaging materials. To overcome these issues, the adoption of renewable and biodegradable materials as an alternative substitute to traditional plastic packaging materials has gained significant attention at present time. Biodegradable packaging films typically made from natural substances such as polysaccharides, proteins, lipids, and their complexes have been identified as an effective solution to the environmental issues arising from plastic waste [1,2]. Among so many natural materials commonly used, starch-based films are becoming the most promising films in the industry. They provide many outstanding advantages, such as being readily available, cost-effective, and offering superior film transparency compared to other food packaging materials [3,4]. In fact, starch-based biofilms currently account for over 60% of all biodegradable films. Starch is a high molecular weight polymeric substance composed of two α-glucan types: amylose and amylopectin. The linear polysaccharide amylose presents excellent film-forming properties similar to fibers, whereas the α-1,4-glycosidic and α-1,6-glycosidic bonds present in amylopectin are conducive to the thickening effect and freeze-thaw stability. The use of starch as an excellent alternative for edible films and coatings is due to its easy processing, low cost, abundance in nature, biodegradability, and edible character. The

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**email: waelelhrari@gmail.com, wael@prc.ly* plasticizers are basically low molecular weight volatile compounds which often added to polymeric films to improve the processing ability and increase flexibility [5–8]. Glycerol content does not affect the physical appearance of the film but has a remarkable role in the mechanical and barrier properties of the films. Glycerol can strongly affect the functional properties of starch-coating films. The addition of glycerol promotes the hydrogen bonding interactions between starch and glycerol molecules. There is no difference in the swelling index and water content with varying glycerol ratios in the film composition. The lower the glycerol content, the better the mass transfer barrier is. The higher the glycerol content, the lower the thermal stability will be [8]. Films plasticized with glycerol, under all relative humidity (RH) conditions, adsorbed more moisture with a higher initial adsorption rate, and films with higher plasticizer contents exhibited higher equilibrium moisture contents [1]. The mechanical properties of starch films were affected by plasticizing content because of the compatibility of glycerol with amylose, which stimulates better mechanical properties resulting in higher strain, Young's modulus, and water absorption for starch films. In all cases, glycerol played a more noticeable plasticization role than acetic acid and other organic acids do [1,6]. The addition of acetic acid as a co-plasticizer [9–11] and also the effect of other organic acids on the physiochemical properties of starch films were investigated by many research studies [12]. Mahsa et al. found that the addition of acetic acid increases the water absorption property of the films [10,13]. Abdul Rasheed-Adeleke et al. studied the effect of acetic acid and citric acid on starch films and found similar results [9]. Zuraida et al. found an increase in tensile strength with increasing citric acid as well as glycerol contents, which reflects the potential role of these components in improving the physical and mechanical properties of starch films which is very promising and could satisfy specific industrial applications [14].

This study investigates the properties and degradability of starch-based biofilms as sustainable, non-toxic, and biodegradable materials, emphasizing the effects of starch content and plasticizers on their performance. Starch biofilms are produced by the solution casting method (SCM) that utilizes glycerol (GLY) as a plasticizer and acetic acid (AA) as a co-plasticizer. The thickness, water content, water vapor permeability, elongation at break, tensile strength, and thermal decomposition were also investigated.

2. Materials and methods

2.1. Materials

Starch used in this study was supplied by a local store, and glycerol (99%) and acetic acid (80%) were purchased from PARK Scientific Limited. Chemicals were used as received with no further treatment.

2.2. Preparation of starch films

In deionized water, a starch film-forming solution was prepared with different starch concentrations (0.05, 0.1, and 0.2 g/mL). The solutions were heated in a water bath at 85ºC for 60 min with continuous stirring to obtain good solubilization and gelatinization of the starch. Then, the plasticizer was added at a constant weight ratio (0.5 % w/w, starch basis) glycerol (SG) and co-plasticizer acetic acid (6 v/v%) at (0.5 % w/w, starch basis) (SGA). The starch solution was cast on a glass plate. The films were dried in the air at room temperature for a week. The films were peeled off the glass plate by hand and kept inside a plastic bag at room temperature. The samples were given codes for distinction purposes based on their compositional contents and starch concentrations. Film samples containing starch and glycerol were coded as SG4, SG8 and SG13. The samples containing starch, glycerol, and acetic acid were coded as SGA4, SGA8, and SGA13.

2.3. Film characterizations

To study the prepared starch films, a couple of measurements and characterization techniques were conducted.

2.3.1 Film thickness measurements

Film thickness was measured using a digital micrometer. The thickness of each film sample was measured in five different places to ensure accurate measurements and an average value was used in the calculations.

2.3.2 Moisture content

A digital weighing scale was used to determine the moisture content for three replicates for each film sample. All film samples were weighed before (W_i) and then dried in the oven at 105°C for 24 h and reweighed (W_f). To calculate the moisture content of each film sample, Eq. (1) was used.

$$Moisture\ Content = \left[\frac{W_i - W_f}{W_i}\right] \times 100 \tag{1}$$

2.3.3 Water absorption analysis

The water absorption analysis was performed by drying the film samples in the oven at 60°C for 24 h. The dried samples were placed in a desiccator to cool down to room temperature to ensure consistent weight measurements. After that, the films were weighed (M_i) and then submerged in distilled water at room temperature for 24 h. A clean piece of cloth was used to wipe off water from the immersed film samples and then reweighed (M_f). The difference between the initial and final recorded masses was calculated using Eq. (2).

$$Water\,absorption\ (\%) = \left[\frac{M_f - M_i}{M_f}\right] \times 100 \tag{2}$$

2.3.4 Film swelling test

The swelling percentage was measured using the hydration method, and it was performed by immersing the disc film samples (10 mm diameter) in distilled water. Samples were withdrawn at different time intervals, and the excess water was carefully removed from the surface using absorbent paper and then reweighed. The film swelling was calculated using Eq. (3).

$$Swelling\ (\%) = \frac{w_s - w_o}{w_o} \times 100 \tag{3}$$

where W_s is the wet mass and W_o is the initial mass of the film.

2.3.5 Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was carried out using a Bruker Tensor II, resolution 4 cm^{-1} and performing 16 scans in the range of 4000 to 500 cm^{-1}.

2.3.6 Water vapor permeability (WVP)

10 g of silica gel was filled into a cylindrical cup. After that, the film samples were cut into a circular shape and then stabilized at the opening of the cylindrical cups. Before leaving the cups in a relative humidity chamber (79% RH), at 20°C the test cups were weighed and then the mass was recorded periodically until the equilibrium state was attained. Finally, the test cups with the escalated weight were weighed and used in the calculation of WVP using Eq. (4).

$$WVTR = \left[\frac{\Delta m \times d}{A \times t}\right] \tag{4}$$

where Δm is the increased weight of the test cup (g), d is the film thickness (mm), A is the exposed area of the film (m^2), t is the transmission time interval (s) and the derived unit of the outcome is g day^{-1} m^{-1}.

2.3.7 Thermogravimetric analysis (TGA)

To investigate the thermal decomposition of the prepared film samples, thermogravimetric analysis was carried out by using BAXIT Thermogravimetric analyzer BXT-TGA101. The test parameters were taken as the temperature was raised from 25 to 600°C under a constant heating rate of 10°C/min in a nitrogen gas medium. 2 mg of the film sample was placed and heated in the ceramic tray. The weight loss vs. temperature relation was demonstrated in TGA thermos-curves.

2.3.8 Mechanical properties

The mechanical properties of the prepared film samples were investigated using the ASTM D882-02 (2002) Standard. A METROTEC MTE-25 universal testing machine with a loading cell of 25 kN was used to analyze the mechanical properties of film samples. Initially, the film samples were cut into rectangular pieces with dimensions of (70 mm × 10 mm) and the crosshead speed applied was 50 mm/min. Deformation (mm) and force (N) of the specimens were then recorded. The evaluation of the mechanical properties was carried out using the average value of five replicates.

2.3.9 Soil burial degradation test

The biodegradability test of the film samples in soil was conducted by observing the film surface and appearance after one month of burial in the soil garden under normal conditions and then comparing the obtained results with virgin film samples. The tests were performed in triplicate to obtain reproducible measurements, where each film sample with 20 mm × 20 mm dimensions was buried 100 mm underneath the surface of the soil. The samples were dug up after 30 days prior to visual analysis.

2.3.10 Optical property evaluation

Transparency is one of the most important properties of packaging films. A UV-visible light spectrophotometer was used to determine the opacity of each film. Samples were cut in a rectangular shape and placed directly in a sample holder using a Cintra 2020 GBC. Absorbance was recorded at 560 and 660 nm, and opacity (O) was calculated using the film thickness (x, mm) through Eq. (5).

$$O = \frac{Abs_{660/560}}{x} \tag{5}$$

Measurements were performed in triplicate at ambient conditions. Low values of opacity correspond to high transparency, whereas high values of opacity correspond to low transparency.

3. Results and discussions

3.1. Visual observation and physical properties analysis

Figure 1a–c shows the digital images of starch films placed over the logo of our institute to highlight the degree of transparency of the films. It is noticed that in the case of the film coded as SG4, it exhibits a relatively much clearer image compared to both films coded as SG8 and SG13, respectively. The noticeably much higher transparency for the film SG4 could be linked to the fact that this film contains a much lower moisture content value (11.56%) which contributes to a much-decreased opacity compared to the less transparent film-coded SG13 with moisture content of 15.14% and also the film coded SG8 with moisture content of 15.33% as recorded in Table 1.

This clearly indicates that the preparation method used to produce starch films was convenient and effective, and also exhibits excellent physical and mechanical properties achieved for the prepared starch film samples.

Since many potential applications of starch-based films are related to the interaction with water molecules moisture content, swelling percentage, water vapor permeability, and the behavior of film samples upon the addition of glycerol and acetic acid components were analyzed and the results are shown in Table 1.

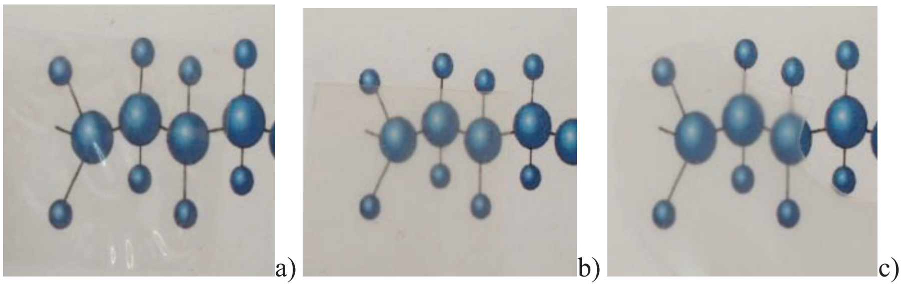


Figure 1. Digital images of the prepared starch films (a) SG4, (b) SG8, and (c) SG13 taken after the placement over the logo of our institute

Table 1. The average percentages of water absorption, swelling, and moisture content of prepared film samples and the standard deviations are written between brackets.

Starch film code	Water absorption (%)	Swelling (%)	Moisture content (%)
SG13	36.82 (0.5)	58.28 (1.3)	15.14 (0.4)
SG8	57.04 (1.2)	92.62 (0.2)	15.33 (0.8)
SG 4	39.12 (0.8)	64.28 (2.3)	11.56 (0.5)
SGA13	50.04 (1.5)	92.89 (2.6)	18.01 (0.5)
SGA8	42.96 (0.4)	71.90 (1.1)	14.63 (1.0)
SGA4	40.58 (1.2)	68.35 (3.4)	13.65 (1.2)

Swelling and water vapor permeability could be related to the hydrophilic nature of starch films since those with greater crystalline starch content are sensitive to moisture and relative atmospheric humidity [15].

The films showed an increase in water absorption, swelling percentage, and moisture content as the starch content in the film composition increased. This can be attributed to the hydrophilic nature of starch molecules. The incorporation of glycerol and acetic acid can form strong interactions with water molecules allowing the films to retain water and form strong hydrogen bonds within the film structure. However, the film containing only starch and glycerol exhibited different characteristics, possibly due to the formation of strong hydrogen bonds between glycerol and starch, which prevented water molecules from interacting with the starch as stated by Tarique et al. [6]. The addition of acetic acid may disrupt these hydrogen bonds between glycerol and starch, leading to an increase in water absorption, swelling, and moisture content [6,16].

Water vapor permeability and water vapor transmission rate are shown in Table 2. WVTR data show that films with medium starch content had the highest value in both films with and without acetic acid contents present. The water molecules easily permeate through the films which results in Permeance values of 0.094 and 0.095 (g/day·m^2·Pa) for SGA8 and SG8 films.

Starch is a semi-crystalline polymer and recent research studies indicate that amylopectin is the main contributor to the crystalline regions in starch molecules [17]. According to García et al. [18], water vapor can easily pass through non-crystalline regions. Additionally, the rate of vapor transmission increases as the starch content decreases. As a result, the film SG13, which has the highest starch content shows the lowest water vapor transmission rate WVTR compared to the other films. Films containing acetic acid exhibit similar characteristics, but with different values, indicating that acetic acid impacts the starch structure, inhibiting water vapor permeation. This may result from the hydrolysis of starch by acetic acid molecules, which causes the structure to become more compact, thereby reducing permeability. Thus, the addition of acetic acid promotes a change in the structure of the film, where starch is considered to be a semi-crystalline polymer and amylopectin is the main contributor to the crystalline domain in the structure. Besides, acetic acid is most likely associated with the non-crystalline region, thus decreasing the space between polymer chains, hindering water vapor permeation through the film, this is clearly observed at low starch content films SGA4 and SGA8 [5,19,20].

Table 2. Water vapor transmission rate and permeability of the prepared film samples

Film Code	WVTR g/day·m^2	WVP g/day·m·Pa	Permeance g/day·m^2·Pa
SG13	314.85 (93.1)	8.9E-6 (2.6E-6)	0.074 (0.02)
SG8	404.26 (16.9)	3.8E-5 (1.5E-6)	0.095 (0.00)
SG 4	393.96 (13.6)	3.9E-5 (1.3E-6)	0.092 (0.00)
SGA13	319.06 (98.6)	6.7E-5 (2.0E-5)	0.075 (0.02)
SGA8	400.04 (18.4)	6.5E-6 (3.0E-7)	0.094 (0.00)
SGA4	305.30 (55.7)	3.2E-5 (5.9E-6)	0.071 (0.01)

3.2. Mechanical properties of starch films

Figure 2 clearly showed a positive effect of starch content on elasticity, strength, total strain energy, and elongation at break (%). Moreover, the addition of acetic acid showed a more noticeable improvement in the properties of the films. The highest value of ultimate strength was 24.31 MPa for SG film, which is similar to the result of 23.06 MPa obtained by Zuraida et al. [14] in their studies for the melt blending process with the extruder.

The results show that as starch content increases, the mechanical properties of the films increase. Besides the addition of acetic acid clearly shows more increment in the mechanical properties of the films. However, films with high starch content showed a decrease in their mechanical properties after the addition of acetic acid. That could be due to the interference of the acetic acid molecules with the starch chains leading to a decrease in the intermolecular bonds between amylose, amylopectin, and amylose-amylopectin linkage which affects the crystalline structure of starch associated with an increase in hydrogen bonding between the acetic acid and starch molecules. Such interference and re-engagement of starch molecular chains lead to a decrease in the elasticity modulus and enhance the flexibility of films by allowing more chain movement. As a result, Young modulus and ultimate strength decrease while elongation at break increases [6,7].

3.3. Thermal decomposition of starch films

TGA was employed to determine the thermal decomposition of starch films. The thermal decomposition of films as a function of temperature is shown in Figure 3. There were two main steps in the thermal decomposition of the films as shown in TGA and DTG curves. These steps are characteristic of starch-based films as reported by Kalendova et al. [21]. The first step of thermal decomposition that occurs below 100°C is attributed to the loss of weak bonded water molecules as well as low molecular weight compounds present in the films. The second step was obtained at 285°C–302°C and indicated by a sharp peak in the DTG curve, which is attributed to the decomposition temperature of polysaccharide rings [21]. The weight loss at this step for the three films SG4, SG8, and SG13 was 52.1%, 57.1%, and 57.3%, respectively. The thermal decomposition of the plasticizer and co-plasticizer was shown at a temperature range of 150°C–250°C. Based on the TGA and DTG curves, a slight decrease in the DTG peak was observed during the second decomposition stage upon the addition of acetic acid. This decrease could be due to the interruption caused by the addition of acetic acid to the intermolecular bonds between the starch crystalline structures. The difference between the two steps could be attributed to the difference between intermolecular bonds formed crystallinity. Similar results of thermal decompositions were observed in other research studies when adding glycerol to starch films [5,6].

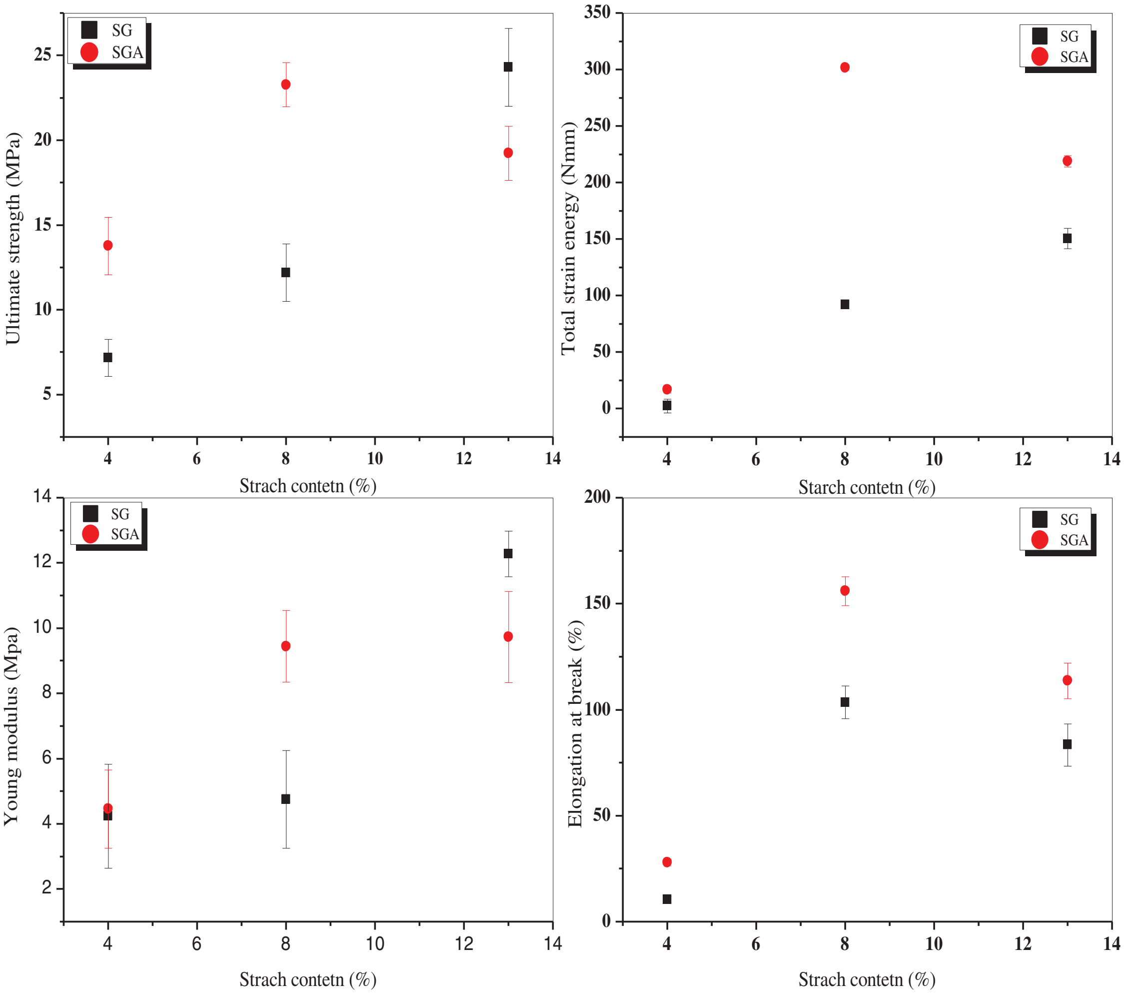
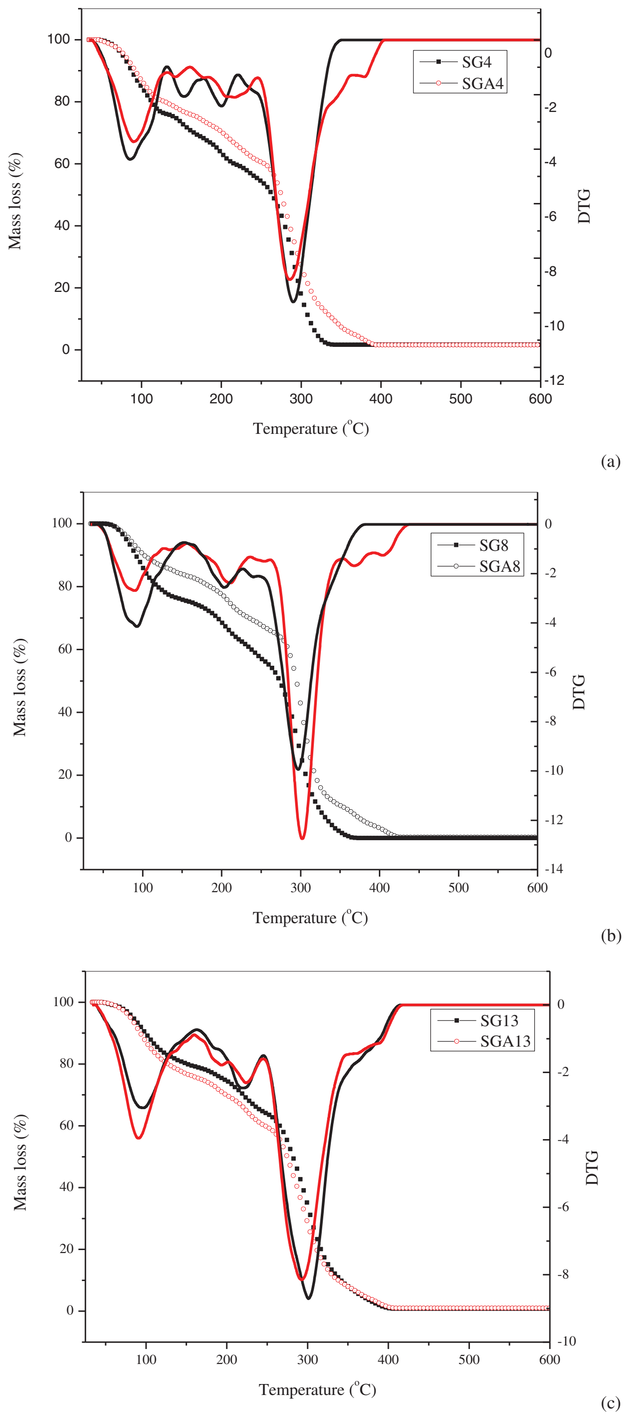


Figure 2. Mechanical properties of the prepared starch films

3.4. Fourier transform infrared spectroscopy (FTIR) analysis

Chemical analysis performed by infrared absorption spectroscopy suggests a very close conformation among all starch films. All the spectra presented in Figure 4, show a broad band at around 3283 cm^{-1}, corresponding to the free hydroxyl groups (-OH), which are associated with the starch and glycerol components of the films. The intensity of this broadband in the starch-based films could be related to the number of hydroxyl groups [15]. Sharp bands at 2930 and 2890 cm^{-1} are characteristic of the C-H stretch; a significant absorption peak in the range of 1644 cm^{-1} was attributed to the hydroxyl groups of absorbed water within starch films [6,15]. The absorption band at 1548 cm^{-1} could be related to the stretching of the C-H bond. Bands at 1461 and 1237 cm^{-1} are assigned to the bending of water and CH2 and the band at 1337 cm^{-1} could be related to the C-OH bending vibration [22]. The bands in the region between 1200 and 900 cm^{-1} could be attributed to C-O, C-C, and C-OH vibrations [15]. The FTIR analysis has shown that adding glycerol and acetic acid to the starch films had no significant effect on the chemical structure of the starch films. This confirms that the chemical structures of the starch films were completely stable with no considerable chemical reactions having occurred by adding glycerol and acetic acid during film preparation. These findings are consistent with many research studies using both acids in the preparation of films [6].



(a)

(b)

(c)

Figure 3. Thermal decomposition temperatures of starch films (a), SG4, SGA4, (b), SG8, SGA8 and (c), SG13, SGA13

3.5. Soil burial degradation test

Several factors play an essential role in the decomposition of materials including fungi, bacteria, and other biological factors. A Polymer starts to decompose as microbial organisms interact with the polymer molecules resulting in the breaking down of the polymer chains into smaller compounds. In this study, a soil burial degradation test was performed on starch films for 30 days. A complete degradation of all films occurred by then.

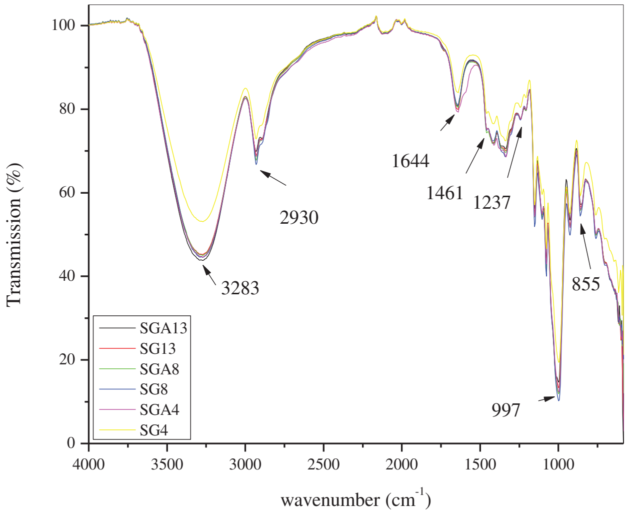


Figure 4. FTIR spectra of the prepared starch films

3.6. Optical property

Opacity is one of the most important properties of packaging films. The opacity test was carried out at two wavelengths 560 and 660 nm which represent the red and green light. The opacity test of the films ranged between 2.2 and 5.1 for red light and 2.4 and 5.3 for green light as shown in Table 3. It was observed that a decrease in the starch concentration yielded films with higher opacity values, which means that SGA13 showed the highest transparency among all the evaluated film samples. Moreover, the film-coded SG8 exhibited the lowest transparency among all film samples. The results obtained in this work showed that the opacity of the films is directly related to the moisture content, which was similar to the behavior reported by Siran et al. in their research studies for edible films [23]. This phenomenon can be related to the intermolecular agglomeration produced by the moisture content increase, raising the turbidity and therefore, the light scattering of films [23,24], which consequently results in less transparent starch films produced.

Table 3. Thickness, absorbance at (560 and 660 nm) and opacity of prepared starch films

Sample code	Film thickness	Absorbance at 660 nm	Absorbance at 560 nm	Opacity (mm^{-1}) at 660 nm	Opacity (mm^{-1}) at 560 nm
SG13	0.15	0.461	0.481	3.0	3.2
SG8	0.10	0.517	0.534	5.1	5.3
SG4	0.10	0.303	0.323	3.0	3.2
SGA13	0.13	0.300	0.317	2.2	2.4
SGA8	0.13	0.350	0.373	2.6	2.8
SGA4	0.12	0.303	0.321	2.4	2.6

4. Conclusions

To explore the influence of starch and plasticizer contents on the film properties, the film's basic properties were investigated such as moisture content, water vapor transmission rate, permeability, optical property, thermal decomposition, and mechanical properties. FTIR results show that no considerable chemical reactions have occurred by adding glycerol and acetic acid components to starch.

Besides, there was an increase in water absorption, swelling, and moisture content as the starch content increased in the composition of films. The addition of acetic acid leads to an increase in the values of water absorption, swelling, and moisture content. Films with medium starch contents showed the highest values. However acetic acid did affect the WVTR values due to the hydrolysis of the starch non-crystalline regions which leads to a decrease in the space between polymer chains in starch molecular structure. Starch content affects the mechanical properties since high starch content is present in the film, and the addition of acetic acid weakens the properties of the starch films. The addition of acetic acid did not change the degradation steps of the starch although a slight decrease in the peak of DTG at the second decomposition temperature was observed which could be due to the interruption in the intermolecular bonds between the starch crystalline structures. All films show complete degradation when buried in soil for 30 days. The opacity of the films was found to be related to their moisture content. This study encourages the utilization of such biodegradable films in the food packaging industry since the films showed excellent mechanical properties and the ability to decompose under natural environmental conditions.

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