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The effect of plasticizers on thermoplastic starch films developed from the indigenous Ethiopian tuber crop Anchote (*Coccinia Abyssinica*) starch

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Abstract

Anchote (*Coccinia Abyssinica*) starch films were prepared by a solution casting method with glycerol, 1-ethyl-3-methylimidazolium acetate, sorbitol or triethylene glycol as plasticizers. The effect of these plasticizers and their concentration on film microstructure, thermal, and mechanical properties was investigated. Scanning electron microscopy revealed that regardless of plasticizer type, films possessing higher plasticizer content had more homogeneous morphologies than those with lower plasticizer content. The FTIR spectra of films plasticized with 1-ethyl-3-methylimidazolium acetate had higher intensity peaks at 3150, 1400 and 1000 cm^{-1} when compared to other film peaks. These data show that 1-ethyl-3-methylimidazolium acetate plasticized films have decreased molecular order which results in less hydrogen bonding. For this reason, films developed from 1-ethyl-3-methylimidazolium acetate were more flexible than the others. The effect of plasticizers on the thermal properties of the anchote starch films was investigated using thermogravimetric analysis (TGA). Films made from 30% (w/w) plasticizer concentration exhibited higher thermal stability for all types of plasticizer. Mechanical testing showed that sorbitol films had the highest tensile strength, approximately 2 times that of the triethylene glycol plasticized film and 3 times that of the film made from 1-ethyl-3-methylimidazolium acetate.

Keywords

Anchote; Starch; Thermoplastic

1. Introduction

Thermoplastic starch (TPS) is a candidate as a naturally renewable thermoplastic material as starch is one of the most abundant and inexpensive biopolymers [1,2]. However, in

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comparison with conventional petroleum-based plastic films, TPS films are hydrophilic, brittle in dry atmosphere, and lose mechanical strength as well as barrier properties in high humidity [3]. Furthermore, recrystallization phenomena or retrogradation of TPS occurs during storage that results in changing functional properties of the film [4]. Various studies have tried to address these limitations through blending starch with natural and synthetic polymers, adding fillers and reinforcing agents to TPS [5,6]. Native starch does not possess thermoplastic characteristics and exists in granular form. TPS is made by applying thermal and mechanical energy on the starch granules in the presence of plasticizers [4]. Plasticizers improve film flexibility by reducing the internal hydrogen bonding between polymer chains while increasing free volume. The effect of the plasticizer depends on their structural similarity with the polymer [1,3]. The functional properties of TPS materials depend on additives used in TPS preparation, and processing conditions including time, temperature, mechanical shear, and plasticizer type as well as amount [2,6].

Glycerol is a commonly used plasticizer for making thermoplastic starch films. There are a number of chemicals used as plasticizers such as glycols, formamide, urea, citric or malic acid, polyols, and others [4]. The most common polyols are glycerol, sorbitol, and polyethylene glycol [7]. Their use is due to their ability to minimize cracking of the films during storage and handling [1]. Different researchers have investigated the effect of polyols as plasticizer in the development of TPS films [8–11]. On the other hand, ionic liquids, which are salts melt below 100 °C, have the ability to dissolve polysaccharides making them excellent starch plasticizers [12].

In addition to using starch for thermoplastic starch or biodegradable materials, it has been utilized for manufacturing of cleaning products, textile sizing agents, food and beverages, cosmetics, adhesives, coating and other applications [13–15]. Due to broad applicability, availability, renewability and environmental advantages there is demand on the market for starch. As such, research to identify “novel” and “underutilized” crops for starch remains important [16–18]. These non-conventional starches were tested for various applications and demonstrated promising results [16]. Anchote starch can be considered as an “underutilized” starch. It is extracted from anchote (*Coccinia abyssinica*) tuber crop which is indigenous to Ethiopia.

No reports are available on the potential use of anchote (*Coccinia abyssinica*) starch to produce TPS films or bioplastic materials. We recently reported the starch physicochemical characteristics of anchote starch which had comparable physicochemical properties but enhanced thermal stability when compared to commercially available wheat and potato starches [18]. Therefore, it is possible to develop thermoplastic starch materials from anchote starch. However, the functional properties of TPS materials depend on the structure of starch which is directly related with the origin of starch [4]. As anchote starch comes from a different origin and it is indigenous to specific area, here we study TPS materials from Anchote starch to investigate the TPS material functional properties. The present study aims to investigate the effects of different plasticizers, such as glycerol, 1-ethyl-3-methylimidazolium acetate, sorbitol, and triethylene glycol as well as their concentration variation on anchote starch films and we report upon the morphological, thermal, and

mechanical properties and the effect of plasticizers on these properties for anchote starch films.

2. Materials and Methods

2.1 Materials

Anchote (*Coccinia Abyssinica*) starch was used in this research. Anchote tuber was obtained from the local market at Nekemet, Oromia Region, Ethiopia. The anchote starch was extracted from the tuber using a modified literature procedure [19]. The plasticizers, such as glycerol, 1-ethyl-3-methylimidazolium acetate, sorbitol and triethylene glycol, were purchased from Sigma Aldrich and used as received.

2.2 Film Preparation

Films were prepared using a solution casting method [20]. The film forming solution was made by adding 3 grams of anchote starch powder in 100 mL of distilled water with a plasticizer concentration of 30%, or 40% (w/w) of dry starch. The dispersion of anchote starch and distilled water was maintained for 20 min at 85 °C ± 2 °C under magnetic stirring, and the plasticizer was added and kept for an additional 10 min. The resulting film forming solution was cooled to a temperature of 65 °C. 35 mL of the film forming solution was poured into a 10 cm diameter plastic petri dishes. The films were dried at 50 °C in an oven for 24 h. The dried films were peeled manually and kept for at least 48 h in desiccators containing a saturated solution of Mg(NO₃)₂ prior to the film characterization.

2.3 Film Characterization

2.3.1 Film thickness and density—The film thickness was measured using a digital micrometer to the nearest of 0.01 mm. The film thickness was measured at six random locations in three different samples and is reported as their average film thickness. The film density was determined according to literature procedure [21]. Films were cut into 20 × 20 mm squares, and film thickness was measured with six random measurements. Then the samples were dried at 110 °C for 24 h and weighed. The density was calculated as the ratio of weight to volume.

2.3.2 Moisture content and solubility in water—Moisture content was determined according to the standard method D644–99 (ASTM, 1999). The film was cut into rectangular piece and kept at 105 °C for 24 h in an oven. Then the moisture content was calculated from the weight loss. The water solubility of films was determined according to a literature procedure [22]. Film samples were first dried at 105 °C for 24 h to determine the initial dry weight (W_1). Then the dried samples were immersed in 30 mL of distilled water in a 50 mL beaker with gentle stirring for 24 h. Finally, the samples were dried in an oven at 105 °C for 24 h to determine the final dry weight (W_2). The water solubility (WS) of the sample was calculated as follows:

$$WS(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

2.3.3 Scanning electron microscopy—The cross sectional microstructure of the films was observed using Field Emission Scanning Electron Microscope (JSM-6500F, JEOL Ltd., Japan). The films were cryofractured using liquid nitrogen and then put on the support using double sided adhesive tape. The fracture surface was coated with a 5 nm thick coating of gold using a sputter coater (Desk II, Denton Vacuum) and examined with the acceleration voltage of 5KV and a 10 mm of working distance.

2.3.4 FTIR—The infrared spectra were measured using Fourier transform infrared spectrophotometer (Thermo Scientific Instrument Co., USA) the film sample was placed in the sample holder and the measurements were carried out with 16 scans and 4 cm^{-1} resolution. Absorbances were recorded at wavenumbers ranging from 400 to 4000 cm^{-1} .

2.3.5 Mechanical properties—Instron 5869 Universal Testing Machine (Norwood, MA, USA) was used to test the mechanical properties such as tensile strength, elongation at break and elastic modulus of the films. The specimens corresponded to the Type 5 and the test method was ASTM D638–14 standard test method for tensile properties of plastics. The films were cut using a double blade cutter. Before testing, the thickness of the film strip and width in the thinner dimension of the film strip were measured using micrometer. The film strips were clamped in the testing machine which operated at an initial gap separation of 30mm with cross head speed of 10 mm/min. The tensile strength, elongation at break, and elastic modulus were determined by the computer software. Five measurements were performed for each sample.

2.3.6 Thermogravimetric analysis (TGA)—Thermogravimetric analysis (TGA) of samples was performed by using a TGA instrument (PerkinElmer Ltd., Waltham, USA). The film samples, 10 – 15 mg, were heated from 25 °C to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with flow rate of 20 mL/min.

2.4 Statistical Analysis

Experiments were conducted in triplicate, except for mechanical properties where five measurements were used. For each sample the results are presented as the mean \pm standard deviation (SD). The software SPSS 20 was used for the determination of statically significance between sample comparisons. Differences were considered at significant level of 95% and (p-value of < 0.05).

3. Result and Discussion

Films were produced using a solution casting method for 30% or 40% (w/w) of plasticizer to dry starch ration. Four different kinds of plasticizers (glycerol, 1-ethyl-3-methylimidazolium acetate, sorbitol, and triethylene glycol) were used in this study. The prepared films were transparent, facile to peel, homogeneous, and flexible. The film made from 1-ethyl-3-methylimidazolium acetate was qualitatively more flexible than the others. The sorbitol plasticized film had sorbitol precipitate on the film surface. Similar conditions were reported for a film developed from pea starch using sorbitol as plasticizer [7]. Plasticizer precipitation occurs when the concentration of plasticizer is more than its compatibility limit with the polymer.

The results for film thickness, density, moisture content, and water solubility of prepared films are presented in Table 1. The values of film thickness were between 0.17 and 0.26 mm. All films, except the triethylene glycol plasticized film, had thicknesses which were not significantly affected by the plasticizer identity or their concentrations. A film made from 40% (w/w) of triethylene glycol had the highest film thickness. The density of films ranged from 0.88 to 1.21 g/cm³. In opposite to film thickness, the 40% (w/w) of triethylene glycol film had the lowest density. The films plasticized with 1-ethyl-3-methylimidazolium acetate or sorbitol exhibited increased water solubility with increasing concentration, but in the case of the remaining plasticizers the opposite is true.

The 40% (w/w) triethylene glycol film had the highest moisture content (23.61%). This observation agrees with the density result. Moisture content of the 1-ethyl-3-methylimidazolium acetate and sorbitol plasticized films was not significantly affected by plasticizer concentration difference or type. On the other hand, films made from other plasticizers were significantly affected by type and concentration of plasticizers (Table 1).

3.1 Film morphology

Morphological characteristics of the cross-section of the anchote starch films were observed by scanning electron microscope (SEM). The SEM images of the cross-section of films are shown in Fig. 1. In Fig. 1 E30 and E40 indicate films made from 1-ethyl-3-methylimidazolium acetate with 30% (w/w) and 40% (w/w), respectively. Generally, in Fig. 1, the letters G, S, and T stand for glycerol, sorbitol and triethylene glycol. The numbers 30 or 40 indicates their weight percentage to dry starch. The micrographs of the fractured surface of the films developed from sorbitol show unmixed starch granules (Fig. 1 S30 and S40), sorbitol plasticizer migrated to the film surface (Fig. 1 S30), smooth fractured surface (Fig. 1 E30, G30, and T30), and irregular fractured surface (Fig. 1 E40 and G40). Regardless of the plasticizer, films with 40% (w/w) plasticizer concentration were more homogeneous than those with 30% (w/w) concentrations. Similar result have been reported for a film made from protein by solution casting using glycerol as a plasticizer with concentrations varying from 1% (w/w) to 9% (w/w), where the 9% (w/w) film had homogeneous cross section [23]. The films containing 1-ethyl-3-methylimidazolium acetate plasticizer showed a more uniform and dense matrix than the glycerol plasticized films. This observation is a good indicator that the plasticization effect of 1-ethyl-3-methylimidazolium acetate is better than glycerol. This result agrees with SEM micrographs of films derived from maize starch and 1-ethyl-3-methylimidazolium acetate using compression moulding [12]. The film plasticized with sorbitol (Fig. 1 S30) more brittle than others; this is due to the migration of plasticizers to the surface of the film. The film made with 40% (w/w) of triethylene glycol had the roughest fractured surface.

3.2 FTIR analysis

The functional groups related with anchote starch and its films were identified using FTIR. The FTIR spectra of the films as well as anchote starch in the range from 4000 to 400 cm⁻¹ region are shown in Fig. 2 and their characteristic absorption bands are presented in Table 3. Anchote starch FTIR spectra showed peak absorptions around the wavenumbers 573, 931, 1000, 1080, 1150, 1350, 1640, 2170, 2920 and 3310 cm⁻¹. The peak observed around 3310

cm^{-1} was assigned to hydrogen bonded hydroxyl groups or the stretching vibration of O-H [24,25]. The peak at 2920 cm^{-1} could be attributed to stretching of C-H in CH_2 , while the peak at 1640 cm^{-1} was associated with O-H bending [26,27]. The peak at 1350 cm^{-1} corresponded to C-H bending [27]. The characteristic peak at 1080 and 1000 cm^{-1} , are related to C-O bond stretching of anchote starch [28]. The D-glucopyranosyl ring vibrational modes and skeletal modes of pyranose ring were indicated at 931 and 573 cm^{-1} , respectively [19].

The film samples, regardless of plasticizers type and concentration, showed similar characteristic absorption bands of anchote starch (Table 2). Regardless of concentration, 1-ethyl-3-methylimidazolium acetate, glycerol, and sorbitol plasticized films for anchote starch exhibited reduced signals at 3310 cm^{-1} to 3290 cm^{-1} indicating they formed stronger bond than the triethylene glycol plasticized film. This observation is attributed to hydrogen bonded hydroxyl group stretch of anchote starch, plasticizer and water [27,29]. Films plasticized with glycerol and sorbitol had higher intensity at 3290 cm^{-1} . This result is related with an increase in hydroxyl group content due to the nature of the plasticizer.

In conclusion, films plasticized with 1-ethyl-3-methylimidazolium acetate exhibited peaks at 3150 , 1400 and 1000 cm^{-1} that were higher intensity when compare to other film peaks. It indicates that 1-ethyl-3-methylimidazolium acetate plasticized films have decreased molecular order, resulting in less hydrogen bonding [24] and a more elastic nature.

3.3 Thermal Properties

Thermal properties of the anchote starch films were investigated by thermogravimetric analysis (TGA) and derivative of thermogravimetric analysis (DTG). TGA curves of the starch films commonly had three stages of thermal degradation: the first is related with evaporation of free water, plasticizer and molecules with low molecular weight, the second is starch rich phase, there is some plasticizers, decomposition, and the last is oxidation of the partially decomposed starch [5,30]. The TGA and DTG curves of anchote films are shown in Fig 3. These data reveal that films made from 30% (w/w) of 1-ethyl-3-methylimidazolium acetate and sorbitol had comparable weight loss in the temperature range of 30 to $250 \text{ }^\circ\text{C}$. In the same temperature range, triethylene glycol plasticized film had the highest weight loss while the glycerol plasticized film is the most thermally stable film. On the other hand, films made from 40% (w/w) plasticizer concentration show slight differences in their weight loss in the temperature range of 30 to $150 \text{ }^\circ\text{C}$. The film plasticized using 40% (w/w) of sorbitol showed the highest thermal stability in the temperature range of 30 to $325 \text{ }^\circ\text{C}$. Generally, films consisting of 30% (w/w) plasticizer concentrations exhibited higher thermal stability with respect to films plasticized with 40% (w/w) concentration. Particular, films made from 40% (w/w) of triethylene glycol and glycerol showed more than 20% moisture content. Their high weight loss at lower temperature related with their high moisture content.

The DTG curves are shown in Fig. 3. The small peaks in the temperature range of 30 to $150 \text{ }^\circ\text{C}$ correspond with the evaporation of water. The second major peak is at maximum degradation temperature which was allocated for the degradation of the starch rich phase [31]. For different plasticizers; there is slight variation in the degradation temperature

of starch rich phase. Regardless of plasticizer concentration, films plasticized with sorbitol had the highest value for degradation temperature of starch rich phase whereas 1-ethyl-3-methylimidazolium acetate plasticized films had the lowest value. These differences depend on the boiling point difference of plasticizers and their interaction formed with starch molecules [24].

3.4 Mechanical properties

The results from tensile strength, elongation at break, and modulus of elasticity of anchote starch films are reported in Table 3. A film plasticized with 30% (w/w) of sorbitol was not analyzed for mechanical properties. This film was very rigid and brittle when compared to other films, inhibiting analysis. Regardless of the plasticizer type, increasing plasticizer concentration resulted in a decrease in tensile strength and modulus of elasticity. The same trends were reported for thermoplastic starch developed from different starch sources [2,14]. The tensile strength of the films provides insight into their crystallinity. It has been reported that the crystallinity of thermoplastic starch film was inversely related with plasticizer concentration [32].

Films made from sorbitol had the highest tensile strength. Its value is approximately 2 times the tensile strength of triethylene glycol plasticized film, 2.5 times glycerol plasticized film tensile strength, and 3 times tensile strength of film made from 1-ethyl-3-methylimidazolium acetate (Table 3). This result is due to greater number of hydroxyl groups in sorbitol resulting in stronger interactions with the polymeric starch chains [32]. 1-ethyl-3-methylimidazolium acetate plasticized films had the highest elongation at break compared to other films, indicating that 1-ethyl-3-methylimidazolium acetate was an effective plasticizer. This result is in accord with the homogeneous fracture surface observed for 1-ethyl-3-methylimidazolium acetate plasticized film under SEM.

4. Conclusions

Anchote starch films with various plasticizers were produced using a solution casting method and investigated for their morphological, thermal, and mechanical properties. The films plasticized with 1-ethyl-3-methylimidazolium acetate showed higher flexibility than films developed by using polyols (glycerol, sorbitol, and triethylene glycol). The thickness of films was not significantly affected by the plasticizer type and concentration, except the film prepared by using 40% (w/w) of triethylene glycol. For all plasticizers type, films were made by 40% (w/w) plasticizer concentration had more homogenous microstructure than 30% (w/w). All films showed similar characteristic absorption bands of anchote starch. The 40% (w/w) sorbitol film had the highest tensile strength and modulus of elasticity which we attribute to the high hydroxyl group content and its molecular structure. Regardless of plasticizers type, increasing plasticizer concentration resulted in a decrease in tensile strength and modulus of elasticity. This observation resulted from the inverse relationship of film crystallinity and plasticizer concentration. Films made from glycerol and sorbitol had high degradation temperatures. In sum, these results indicate that anchote film properties are a function of both plasticizer concentration and type. Furthermore, the results show that anchote starch is a potential new starch source for the production of biodegradable films

which can be used for different applications, such as packaging films, trash bags, as well as shopping bags to replace conventional plastic materials.

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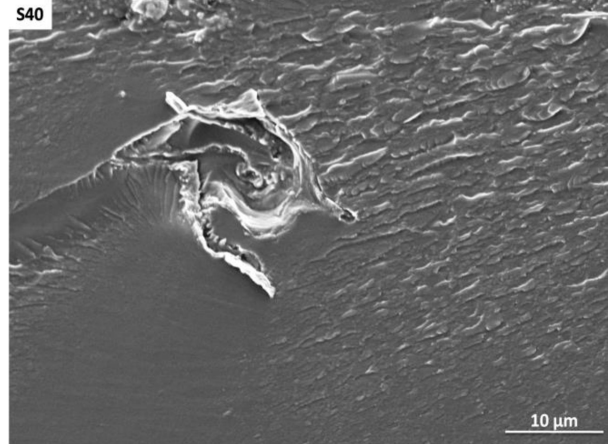
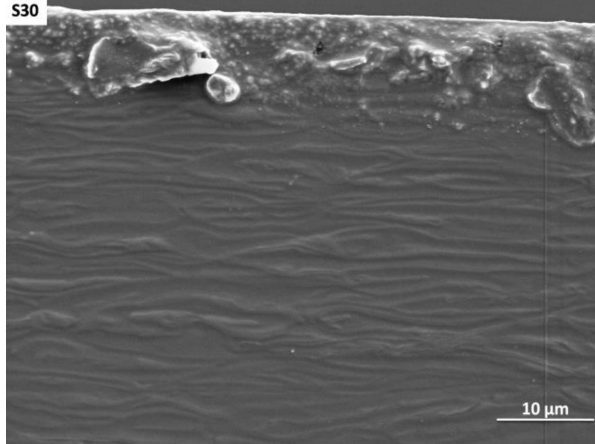
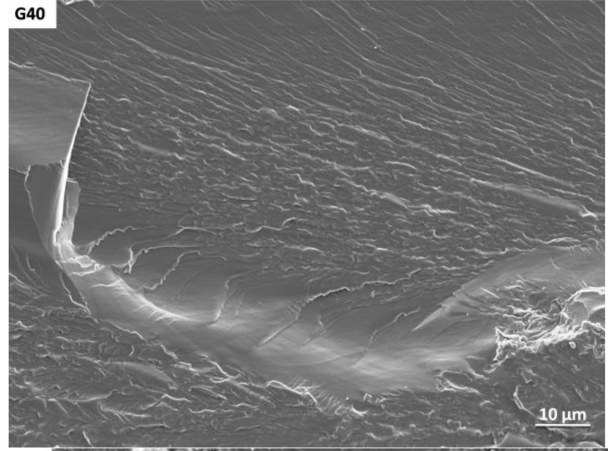
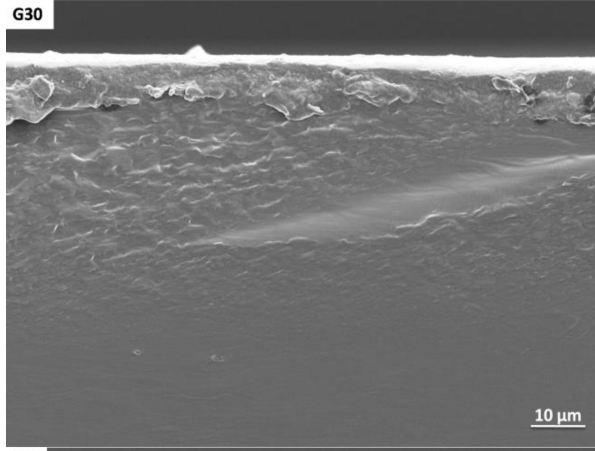
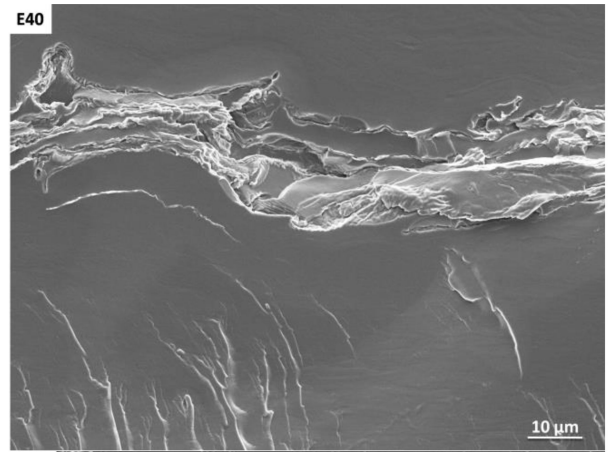
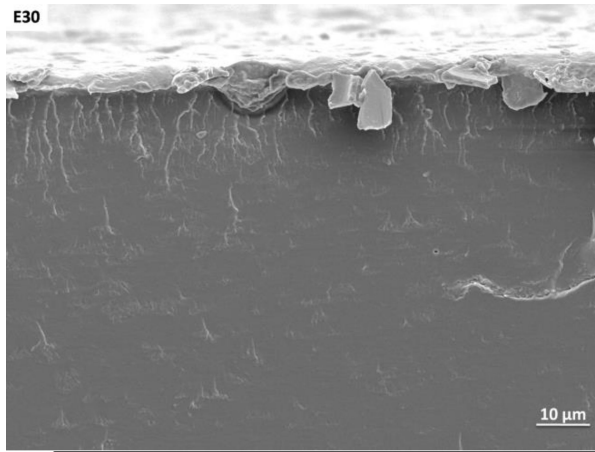
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10.1002/1521-379X(200006)52:4<118::AID-STAR118>3.0.CO;2-0

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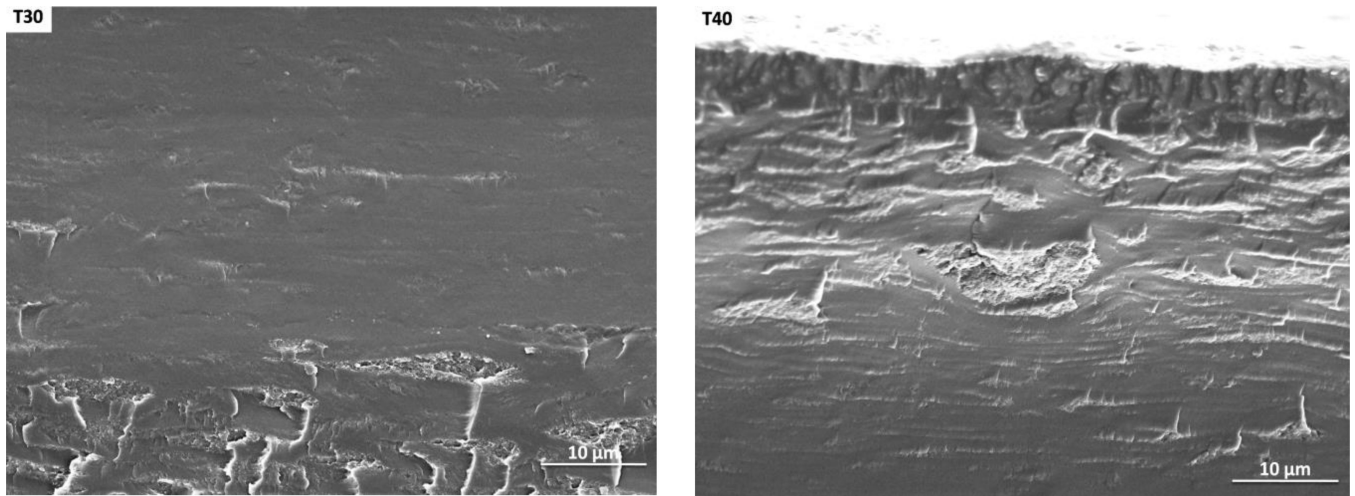


Figure.1. SEM images of E30-film of 30%(w/w) 1-ethyl-3-methylimidazolium acetate, E40-film of 40%(w/w) 1-ethyl-3-methylimidazolium acetate, G30-film of 30%(w/w) glycerol, G40-film of 40%(w/w) glycerol, S30-film of 30%(w/w) sorbitol, S40-film of 40%(w/w), T30-film of 30%(w/w) triethylene glycol, and T40-film of 40%(w/w) triethylene glycol)

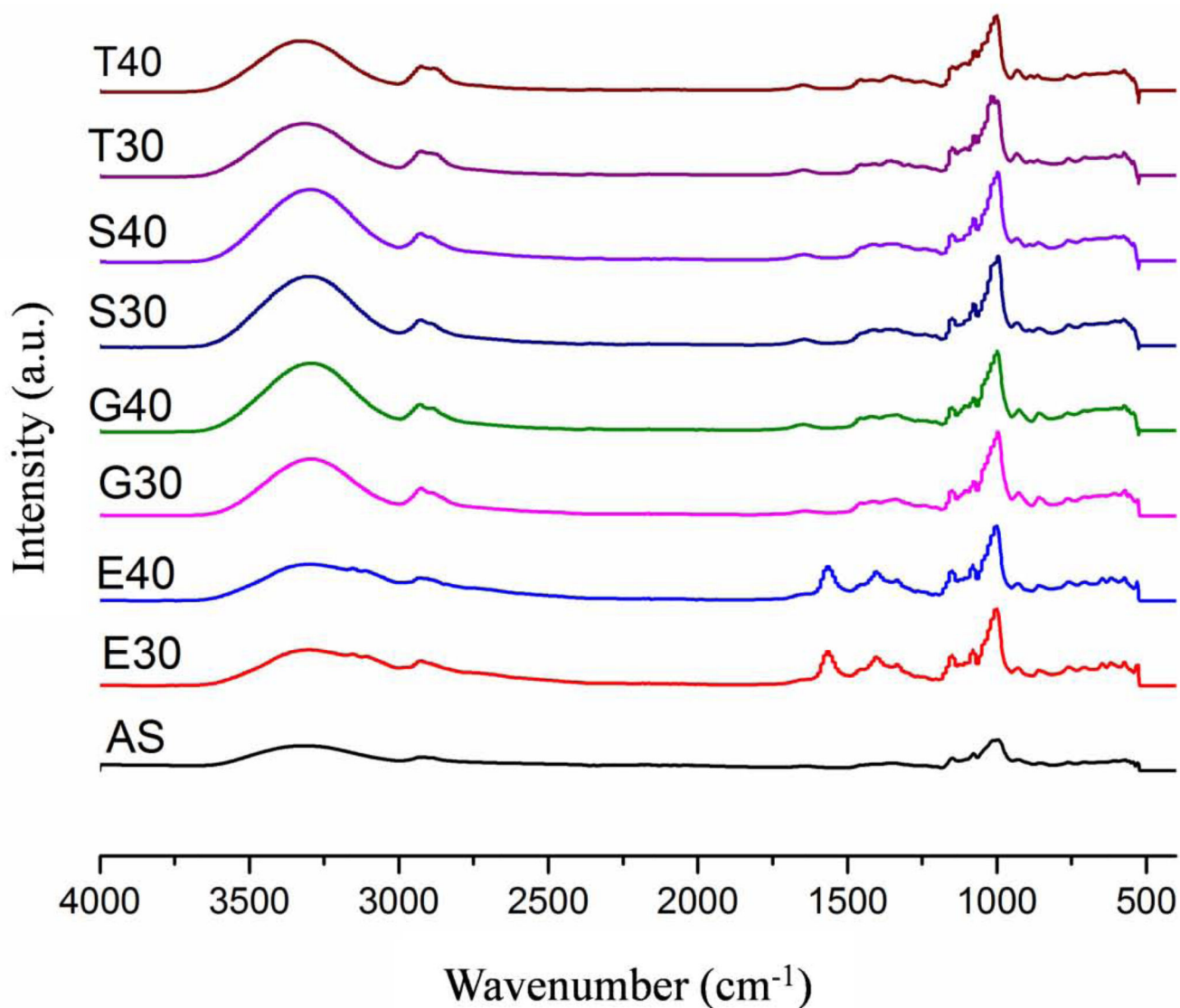
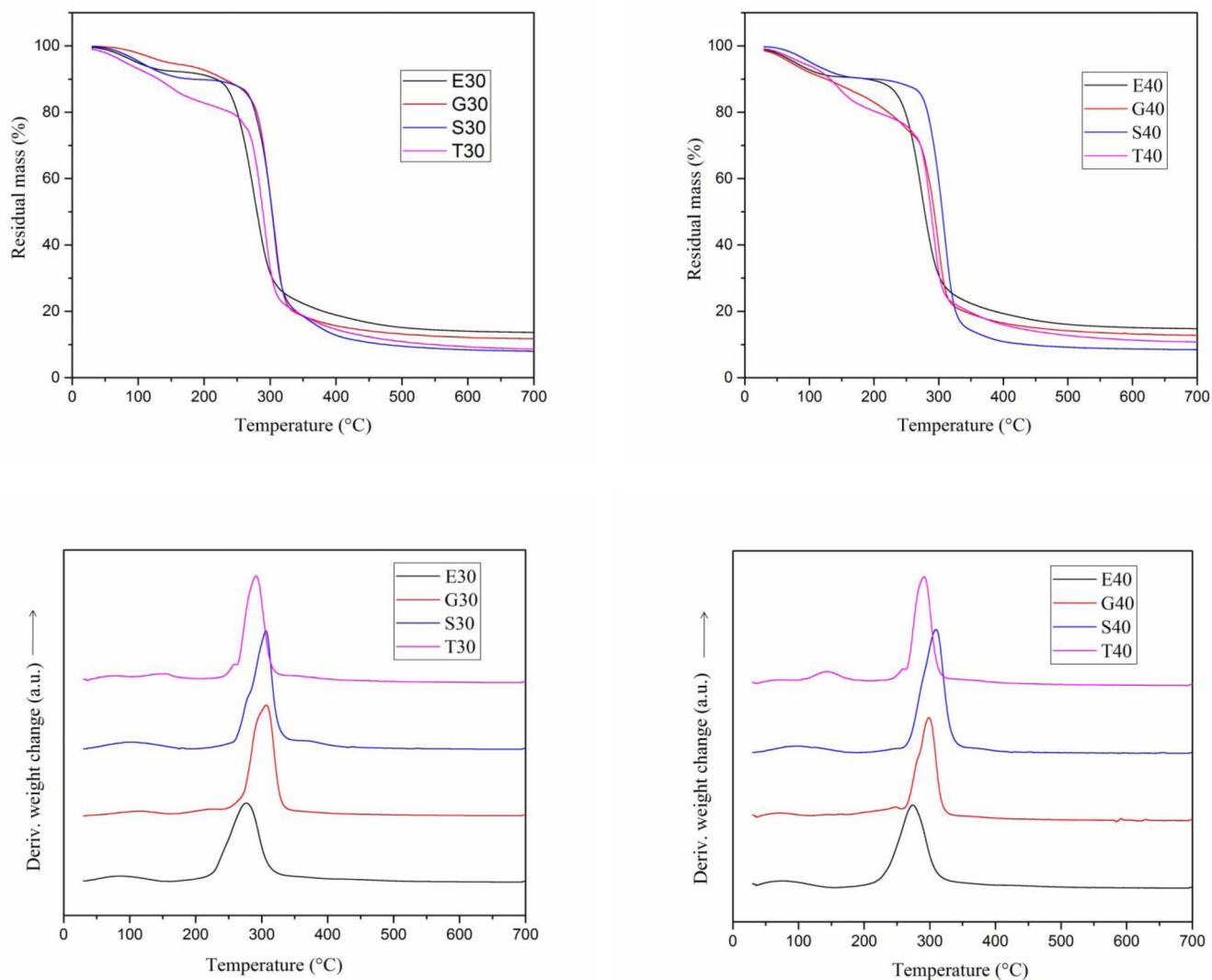


Figure.2.

The FTIR spectra of AS-anchote starch, E30-film of 30%(w/w) 1-ethyl-3-methylimidazolium acetate, E40-film of 40%(w/w) 1-ethyl-3-methylimidazolium acetate, G30-film of 30%(w/w) glycerol, G40-film of 40%(w/w) glycerol, S30-film of 30%(w/w) sorbitol, S40-film of 40%(w/w), T30-film of 30%(w/w) triethylene glycol, and T40-film of 40%(w/w) triethylene glycol)

**Figure.3.**

TGA and DTGA curves for anchote starch films E30-film of 30%(w/w) 1-ethyl-3-methylimidazolium acetate, E40-film of 40%(w/w) 1-ethyl-3-methylimidazolium acetate, G30-film of 30%(w/w) glycerol, G40-film of 40%(w/w) glycerol, S30-film of 30%(w/w) sorbitol, S40-film of 40%(w/w), T30-film of 30%(w/w) triethylene glycol, and T40-film of 40%(w/w) triethylene glycol,

Table 1.

Thickness, density, water solubility and moisture content of anchote starch films made from different kind and concentration of plasticizers

Films	Thickness (mm)	Density (g/cm ³)	Water Solubility (%)	Moisture Content (%)
E30	0.17 ± 0.01 ^{aA}	1.21 ± 0.04 ^{cD}	26.70 ± 1.25 ^{fB}	8.66 ± 0.25 ^{dC}
E40	0.19 ± 0.04 ^{aA}	1.20 ± 0.05 ^{cD}	32.85 ± 1.23 ^{eB}	7.40 ± 0.55 ^{dF}
G30	0.18 ± 0.00 ^{bA}	1.07 ± 0.02 ^{dB}	32.57 ± 0.82 ^{aAF}	14.92 ± 1.52 ^{aB}
G40	0.19 ± 0.02 ^{bA}	1.03 ± 0.00 ^{dB}	20.97 ± 4.41 ^{bB}	21.42 ± 1.25 ^{bD}
S30	0.18 ± 0.02 ^{cA}	1.20 ± 0.06 ^{aD}	28.07 ± 1.82 ^{dBF}	7.45 ± 0.56 ^{fF}
S40	0.19 ± 0.01 ^{cA}	1.20 ± 0.03 ^{aD}	31.34 ± 0.51 ^{dB}	7.29 ± 0.56 ^{fC}
T30	0.18 ± 0.01 ^{dA}	1.06 ± 0.19 ^{bB}	34.19 ± 6.72 ^{cAF}	18.53 ± 0.75 ^{cA}
T40	0.26 ± 0.02 ^{eB}	0.88 ± 0.02 ^{fA}	18.92 ± 0.60 ^{cB}	23.61 ± 1.21 ^{cD}

^aData (mean ± SD), The letters E, G, S and T indicate to 1-ethyl-3-methylimidazolium acetate, glycerol, sorbitol and triethylene glycol, respectively. The number next to them

^bDifferent superscript letters in a column indicate that there are statistically significant differences ($P < 0.05$) between samples. Lower caseletters show statistically analysis for a plasticizer with different weight percentage and capital letters indicate statistically analysis between plasticizers

Table 2.

FTIR absorption band of anchote starch and its films

Samples	Wavenumber (cm ⁻¹)									
AS	3310	2920	1640	1350	1150	1080	1000	931	573	
E30	3290	3150	1570	1400	1150	1080	1000	930	575	
E40	3290	3150	1560	1400	1150	1080	1000	930	573	
G30	3290	2920	1640	1340	1150	1080	997	926	571	
G40	3290	2925	1650	1350	1150	1080	997	926	571	
S30	3290	2930	1640	1350	1150	1080	997	933	575	
S40	3290	2930	1645	1340	1150	1080	997	931	575	
T30	3310	2930	1650	1350	-	-	997	933	575	
T40	3330	2925	1650	1350	-	-	997	931	573	

AS stands for anchote starch. The letters E, G, S and T indicate to 1-ethyl-3-methylimidazolium acetate, glycerol, sorbitol and triethylene glycol, respectively. The number next to them indicates the percentage (w/w) of plasticizer to dry starch ration

Table 3.

Effects of plasticizers on mechanical properties of anchote starch films

Films	Tensile Strength (MP ^a)	Elongation at Break (%)	Modulus of (MP ^a)
E30	6.18 ± 0.65	49.10 ± 7.76	105.00 ± 32.66
E40	4.19 ± 0.67	42.83 ± 9.44	50.20 ± 13.50
G30	6.45 ± 1.19	34.26 ± 12.42	341 ± 68.00
G40	6.35 ± 0.55	48.95 ± 4.22	133 ± 29.00
S30	-	-	-
S40	15.30 ± 3.91	25.43 ± 8.90	1200 ± 260.00
T30	8.53 ± 1.25	17.40 ± 1.94	727 ± 117.04
T40	7.01 ± 0.57	38.71 ± 5.70	447 ± 29.41

^aData (mean ± SD). The letters E, G, S and T indicate to 1-ethyl-3-methylimidazolium acetate, glycerol, sorbitol and triethylene glycol, respectively. The number next to them indicates the percentage (w/w) of plasticizer to dry starch ration

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