



Research article

Effect of plasticizers on the rheological properties of xanthan gum - starch biodegradable films

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ABSTRACT

The effect of plasticizers, namely glycerol, sorbitol, and citric acid, on the structural and mechanical properties of biodegradable films obtained from xanthan gum (XG) and starch was studied. The plasticizing effect of glycerol, sorbitol, and citric acid on XG-starch films is justified by the destruction of intermolecular contacts between starch and XG macromolecules and the redistribution of hydrogen bonds in the system as a result of the hydrotropic action of plasticizer molecules. The use of glycerol proved to be the most effective for regulating the deformation of films, while the use of sorbitol to preserve strength. The dependence of the film roughness on the type and concentration of plasticizers was characterized. The smallest values of protrusions on the surface of XG-starch films were found in the presence of sorbitol. Considering the effect of the concentration of plasticizers on the stickiness of the surface of XG-starch films and their structural and mechanical properties, 1.5 % concentration of glycerol, sorbitol and citric acid was determined as optimal.

1. Introduction

The accumulation of plastic debris is a well-recognized global emergency, with direct impact not only on the environment but also on human health. In this regard, the development of biodegradable packages is becoming one of the primary tasks of the global community [1].

The utilization of packaging materials in food products is of paramount importance in addressing the global issue of food scarcity. These materials are designed to extend the shelf life of processed foods and to maintain their freshness throughout the extensive steps of storage and transportation [2]. It is generally accepted that unpackaged food products are susceptible to contamination by microorganisms, volatile organic compounds, moisture, and oxygen, particularly when they have been stored for a relatively short period of time. In order to minimize the risk of such contamination, it is essential to select packaging materials that are appropriate for the specific product in question [3].

Biodegradable packaging materials can replace synthetic materials these days [4]. Biodegradable materials are a class of polymers that include substances formed as a result of the vital activity of plants or animals. These include cellulose, protein, starch, nucleic acid, natural resins, and other similar substances [5], furthermore, the process of biosynthesis in the cells of living organisms can result in

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the decomposition of these substances under natural conditions, influenced by factors, such as light, temperature, humidity, and the participation of living microorganisms. This decomposition can result in the formation of substances that are neutral to the environment [6].

Current food and beverage industry is a significant contributor to environmental degradation due to its generation of vast quantities of non-ecological food and plastic waste. This industry's reliance on single-use plastics and unsustainable packaging practices has led to a detrimental impact on ecosystems, marine life, and overall environmental health. Urgent measures are needed to address these issues, such as implementing sustainable packaging alternatives, reducing food waste, and promoting circular economy principles throughout the supply chain to mitigate the industry's environmental [7].

The most crucial quality of films employed in the packaging of foodstuffs is their malleability. The malleability of biodegradable films is enhanced by the minimization of internal hydrogen bonds between polymer chains, which increases the free volume. Plasticizers exert such an influence on films, which can modify and adapt the mechanical properties of the polymer by reducing viscosity, glass transition temperature or modulus of elasticity [7–9]. Furthermore, plasticizers do not alter the intrinsic structure of the polymers [8].

One of the most prevalent plasticizers utilized in the production of biodegradable films is glycerol. It is distinguished by a high boiling point, water solubility, and non-volatility [9]. At the same time, other plasticizers such as sucrose, sorbitol, propylene glycol and citric acid are also highly water soluble and convenient to use. They are also available in solid form, which offers certain advantages over glycerol during transport. However, they are not as widely used as glycerol in the production of biodegradable films. The aim of this study was to compare the effect of glycerol, sorbitol, and citric acid on the structural and mechanical properties of films made from XG and starch. The choice of XG and starch as the basis for the films was motivated by their high compatibility with polysaccharides, which is a desirable property for plasticizers [10].

2. Materials and methods

2.1. Materials

Natural polymers are used to produce films: xanthan gum (XG) (Sigma Aldrich, G1253) and starch (Carl Roth, 4701.1).

Used as plasticizers: glycerol (Sigma Aldrich, G9012), sorbitol (Sigma Aldrich, S1876), and citric acid (Sigma Aldrich, C0759) (Fig. 1).

2.2. Preparation of XG-starch films

To obtain the films, 1 % solution of starch ($C_{\text{starch}} = 1 \text{ mg/mL}$) and 1 % solution of XG ($C_{\text{XG}} = 1 \text{ mg/mL}$) were prepared separately. The starch and XG dissolved by stirring and heating up to 80 °C. Subsequently, the mixtures were combined in varying proportions and plasticizers were incorporated into the resultant blends. The prepared mixtures were agitated on a magnetic stirrer at 1500 rpm/min for 10 min, after which they were transferred to glass cups and stored for 24 h at 25 °C in a thermostat. The resulting films were then separated from the surface of the cups (Fig. 2).

2.3. Characterization of XG-starch film

2.3.1. Moisture content

The moisture content was determined in triplicate from the differential weight before and after drying a film with a surface area of approximately $\approx 1 \text{ cm}^2$ (weight: 0.02–0.03 g) on a hot plate at 120 °C until the sample reached a constant weight. This was calculated in accordance with the methodology outlined in equation (1).

$$\text{Moisture content (\%)} = (M_0 - M_i / M_0) * 100 \quad (1)$$

where, M_0 is initial weight, g, M_i is the final weight, g.

2.3.2. Solubility degree

The samples were excised from the films in dimensions of 2 cm × 2 cm and subjected to drying to a constant weight at a temperature of 60 °C. Subsequently, the dry films were immersed in 50 mL distilled water and maintained in a desiccator at a temperature of 21 °C

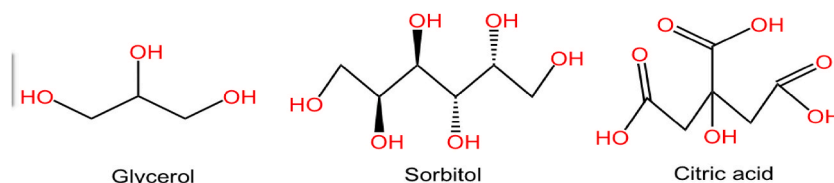


Fig. 1. Chemical structures of glycerol, sorbitol, and citric acid [11,12].

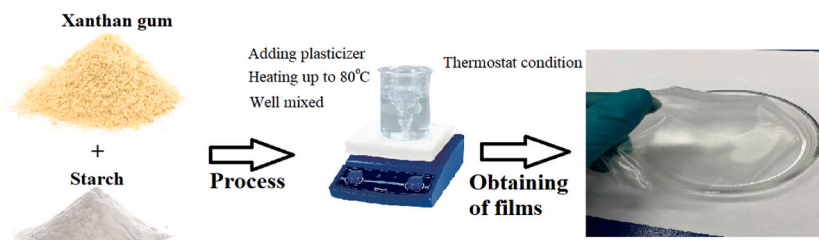


Fig. 2. Schematic representation of obtaining film based on XG-starch

and a relative humidity of 57 % for a period of 24 h. After 24 h, the films were removed from the water and allowed to dry until they reached a constant weight. The solubility degree of the films was calculated in accordance with the following equation (2):

$$\text{Solubility degree (\%)} = (M_i - M_0 / M_0) * 100 \quad (2)$$

where, M_0 is initial weight, g, M_i is the final weight, g.

2.3.3. Tensile strength and elongation at break

The tensile strength (TS) and elongation at break (EB) of the films were determined on the AI-7000S (Gotech Testing Machines) testing machine using the standard test method ASTM D882-97. Rectangular strips of polymer films with dimensions of 5 mm × 25 mm were made for this purpose. The value TS was calculated as the ratio of the maximum load (N) required to rupture the film sample to the cross-sectional area (m²) of the samples. The EB values (%) are calculated as the ratio between the relative elongation of the film and the initial length of the film samples (mm).

2.3.4. Water vapor permeability (WVP)

The water vapor transfer rate (WVTR, g · s⁻¹ · m) through the films was determined gravimetrically in accordance with the ASTM Method E96M – 16 at room temperature (23 ± 2 °C) and relative humidity of 63 ± 2 %. Subsequently, the film specimens were sealed within permeation cups containing distilled water, with a relative humidity of 100 %. The cups were weighed at hourly intervals over a 6-h period. The WVP of the films was calculated according to equations (3) and (4), expressed as g · m / (Pa · s · m²). Three specimens were tested for each film type.

$$\text{WVP} = \text{WVTR} \cdot y / (P_2 - P_1), \quad (3)$$

$$\text{WVTR} = \Delta W / A \cdot \Delta t, \quad (4)$$

where, y – thickness of film,

$P_2 - P_1$ – the vapor pressure difference across the film,

ΔW – the weight of water absorbed in the cup.

A – the exposed area of film.

Δt – the time for weight change.

Analyses were conducted in triplicate.

2.3.5. Atomic force microscopy

Topographic images of XG-starch films with plasticizers were observed using Bruker company, atomic force microscopy (AFM). Dynamic mode at constant forces in air was used for the analysis.

2.3.7. FT-IR spectroscopy

XG-starch films with plasticizers were performed using FT-IR spectroscopy (Shimadzu, Japan). For the analysis, a potassium bromide (KBr) pellet was fabricated with a nanoparticle powder sample. The measurement derived from a spectrum scan ranges from 4000 to 500 cm⁻¹.

2.3.8. Statistical analysis

The results statistically were performed by analysis of 5 % significance level, using Microsoft Excel (2010) and OriginLab Pro 2022 software. The experiments were repeated three times, while the standard deviations corresponded to the condition $p < 0.05$.

3. Results and discussion

Biodegradable films were obtained by mixing aqueous solutions of XG and starch in the presence of various plasticizers, namely glycerol, sorbitol, and citric acid. The external data of the obtained films will now be considered. Films obtained without plasticizers

are XG-starch films are very transparent, brittle and have cracks on the surface. This is likely since the dense network of intermolecular hydrogen bonds limits the mobility of the macromolecular chains of both polymers. Starch-based films obtained in previous studies exhibited similar external characteristics [13,14]. Consequently, these items cannot be utilized as packages.

XG-starch films obtained in the presence of glycerol, sorbitol, and citric acid exhibit minimal differences in appearance. Films with a mass fraction of 0.5 % plasticizer exhibit an inelastic and solid shape, while films with a mass fraction of 3.0 % plasticizer exhibit high elasticity and stickiness.

It is desirable that plasticizers employed to modify plastic polymers should exhibit low toxicity and good adaptability to the polymer in question. Commonly used plasticizers in polysaccharide-based film formations include polyols, mono-, di- and oligosaccharides, which are hydrophilic in nature [15]. The plasticizing effect is contingent upon the dimensions of the plasticizer molecule, its shape, polarity, physical condition, as well as the number of oxygen atoms and the distance between them in the polyol structure [13]. The role of plasticizers in regulating the structural and mechanical properties of biomaterials is to prevent intermolecular interactions between polymer chains. This results in increased flexibility and reduced fragility of the material, which is especially important for biodegradable films and packages. In general, plasticizers should be well compatible with polymers, but they should not chemically interact with them [14].

Compatibility is the formation of a true plasticizer solution in a polymer. When the polymer undergoes spontaneous swelling in the plasticizer, molecular dispersion occurs due to the thermodynamic affinity of the plasticizer for the polymer [16]. In the absence of such affinity, the phenomenon of swelling does not occur. Consequently, the resulting emulsion will be a thermodynamically and aggregately unstable system, which will lead to its stratification [17]. The plasticizer molecules diffuse into the polymer, thereby reducing the strength of the van der Waals interactions between its macromolecules [18]. As stated in Ref. [19] the chemical inertness of plasticizers is evidenced by their inability to undergo chemical reactions with large molecules, even following processing. This results in the plasticizer molecules creating space between the polymer segments, replacing interactions between polymer chains with interactions between polymer and plasticizer. Consequently, the plasticizer increases the available space and decreases the resistance within the polymer structure, serving as a lubricant between the polymer segments [20].

The primary mode of interaction between starch and XG macromolecules is the formation of hydrogen bonds between the $-\text{CH}_2\text{OH}$ and $-\text{OH}$ groups and oxygen atoms, which are further stabilized by hydrophobic interactions between their non-polar sections. Furthermore, plasticizers with an $-\text{OH}$ group in their structure are also capable of forming hydrogen bonds with polymer macromolecules. This facilitates a reduction in intermolecular contacts between the two polymers. Fig. 3 illustrates the interaction between XG and starch in the presence of glycerol.

3.1. Solubility and moisture content of films

One of the primary considerations when selecting packaging materials is the solubility of biodegradable films in water. The dissolution rate of biodegradable materials is a crucial factor in determining their suitability for use as packaging materials [20,21]. A high degree of solubility can also be beneficial for coating the surface of food products. However, in some instances, the films must be insoluble in water to maintain the integrity of the product and the water resistance of the packaging materials. The solubility of films in water is influenced by the composition of the material [20]. In this context, the impact of plasticizers on the solubility of XG-starch films in water and the moisture content within them was investigated.

Fig. 4a and b demonstrates that an increase in the plasticizer content of the films results in corresponding enhancement of their solubility in water. The plasticizer exerts a beneficial effect on the solubility of the film by reducing the interactions between the biopolymer chains underlying their structure formation [21]. Concurrently, it can direct H-bonds towards itself, competing with biopolymers to create hydrogen bonds. The highest degree of solubility was found in the case of XG-starch-glycerol films at plasticizer concentrations of 0.5–3.0 %. This is likely due to the lower molecular weight of glycerol, which results in fewer groups capable of forming hydrogen bonds with biopolymers than in the case of sorbitol and citric acid [22]. The sorbitol and citric acid molecules

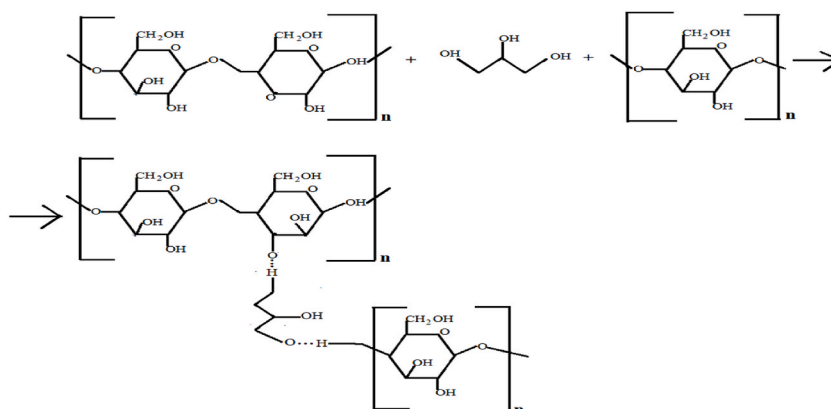


Fig. 3. Schematic interaction of XG and starch in the presence of glycerol

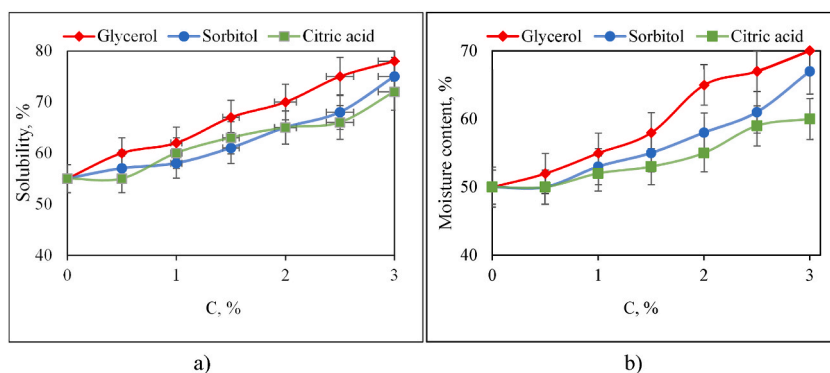


Fig. 4. Influence of plasticizers concentration to solubility degree (a) and moisture content (b) of films based on XG and starch

possess a greater number of groups capable of forming hydrogen bonds with XG and starch, as well as a more developed hydrocarbon chain, which increases the hydrophobicity of the system. In general, an increase in the concentration of plasticizers increases the solubility of films and the moisture content in them. This is probably due to the accumulation of hydrotropic substances between the polymer chains, which contributes to the retention of moisture in the system.

3.2. Elongation at break, tensile strength and WVP

The rheological properties of films are significantly influenced by plasticizers, which control their strength and elongation [22–25]. Fig. 5a illustrates XG-starch-glycerol films exhibit a higher degree of elongation than films containing sorbitol and citric acid. It can be observed that glycerol, due to its small molecular weight and numerous hydrogen bonding groups, is particularly effective in increasing the volume between two biopolymers and disrupting their intermolecular interactions. Consequently, if glycerol disrupts the structure of the system by increasing hydration, sorbitol and citric acid molecules, with more complex hydrocarbon chains, may also act as cross-linking agents for biopolymer macromolecules. However, the accumulation of these substances in the system also enhances the deformation properties of films because of the enrichment of the system with groups prone to the formation of hydrogen bonds. This is consistent with the data presented in Fig. 5b, which indicates that XG-starch films with the addition of glycerol exhibit the lowest strength. The analysis of the curves demonstrating the effect of plasticizers on the strength of films reveals a significant decrease in the strength of films with an increase in concentration from 1.5 to 3.0%. Consequently, to maintain the strength of films based on XG-starch, additives of glycerol, sorbitol, and citric acid at a concentration of no more than 1.5% should be employed.

It is important to note that the plasticizers used do not differ significantly in their effect on the rheological characteristics of XG-starch films. This is since their molecules are highly similar in structure. Upon examination of the FT-IR spectra of XG-starch films, it becomes evident that all three films exhibit a commonality in their chemical composition. As can be observed in Table 1 and Fig. 6, the FT-IR spectra of all systems exhibit broad absorption bands within the oscillation frequency range of $3500\text{--}3000\text{ cm}^{-1}$, which can be attributed to the presence of O–H bonds. These adsorption bands may indicate the presence of water molecules in the composition of the films, as well as to the $-\text{CH}_2\text{OH}$ and $-\text{OH}$ groups of the starch, XG macromolecules and plasticizer molecules. The intense absorption bands in the oscillation frequency range of 1250 cm^{-1} and 750 cm^{-1} can be attributed to the C–H and C–C bonds of the main hydrocarbon chain of polymers. Furthermore, bands from 2500 cm^{-1} to 1750 cm^{-1} are distinguishable, which indicate the presence of plasticizers in the films [26].

The water vapor permeability (WVP) of a material is also an important criterion to consider when selecting food packaging

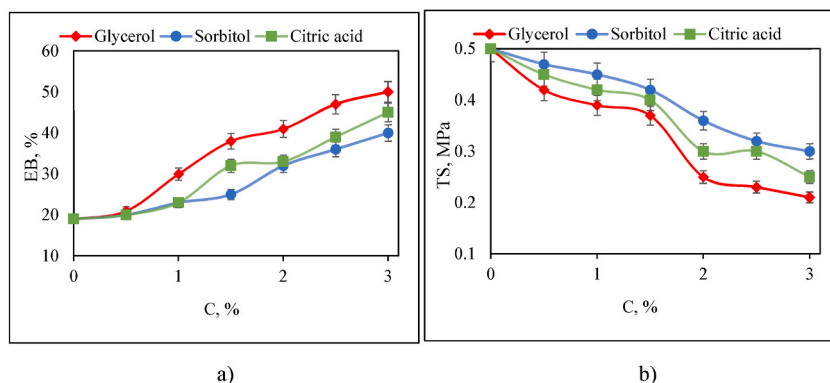


Fig. 5. Effect of plasticizers on the EB (a) and TS (b) of the films based on XG and starch

Table 1
Principal functional groups XG-starch films.

Functional groups	Type of vibration	Wavenumber cm^{-1}			
		XG-starch film without plasticizer	XG-starch film with glycerol	XG-starch film with sorbitol	XG-starch film with citric acid
C-H	bending	2900	2910	2940	2950
O-H	bending	3250	3240	3245	3260
C-C/C-H	bending	990	1000	995	1000
		1040			
		1150	1120	1150	1125

Concurrently, the intensity of vibrations in the FT-IR spectra of the XG-starch-sorbitol and XG-starch-citric acid systems is more pronounced than in the FT-IR spectra of films with the addition of glycerol. This is due to the fact, that sorbitol and citric acid molecules possess a longer hydrocarbon chain and a greater number of functional groups capable of forming hydrogen bonds.

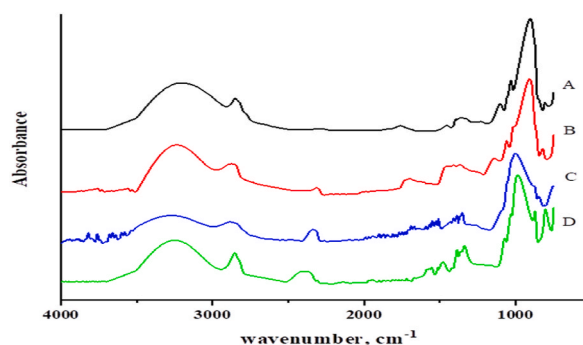


Fig. 6. FT-IR spectrum of XG-starch films without plasticizer (A) and with 3.0 % glycerol (B), sorbitol (C) and citric acid (D) plasticizers

materials. Given that the majority of natural biopolymers are highly susceptible to water absorption, it is essential to minimize their vapor permeability in order to maintain the freshness of packaged foods [27]. As illustrated in Table 2, a study of the WVP of films demonstrated that the incorporation of plasticizers into the XG-starch mixture resulted in a reduction in this indicator, thereby enhancing the moisture-proof properties of the films. A comparison of the effect of three plasticizers on the vapor permeability of films reveals that sorbitol is the most effective in this case. Films containing 3.0 % sorbitol exhibited minimal vapor permeability, with a value of $3.31 \cdot 10^{-11} \text{ g m}/(\text{P.s.m}^2)$. Note that films with the same starch-carrageenan content in Ref. [26] have $3.01 \cdot 10^{-8} \text{ g.m}/(\text{P.s.m}^2)$, which suggests that XG also affects the results of WVP.

The observed reduction in WVP can be attributed to the high strength of the films obtained in the presence of sorbitol. As illustrated in Fig. 5b, the XG-starch-sorbitol system exhibits the highest strength values. Conversely, this can be attributed to the sorbitol molecule's extensive array of functional groups capable of binding and retaining water molecules from the surrounding environment. To substantiate this, it is notable that microbial cells retain compounds on their surface that are prone to forming hydrogen bonds with polysaccharides of their walls, and that they pass only those compounds or ions that do not interact with them inside themselves [28].

A reduction in the values of WVP of films with an increase in their concentration indicates that for films intended for food packaging, the content of the studied plasticizers in the amount of 3.0 % is sufficient.

Additionally, topographic images of the films were obtained using an atomic force microscope (AFM). Fig. 7 illustrates that the introduction of a plasticizer into the composition of XG-starch films results in the emergence of surface roughness. Furthermore, an increase in the concentration of the plasticizer from 1.0 % to 3.0 % is accompanied by a corresponding increase in the surface roughness of the films.

The increased roughness of the films is a consequence of the reduction in intermolecular interactions between the macromolecules of the two polymers as the concentration of the plasticizer increases. This results in a greater absorption of moisture by the plasticizers, which are easily hydrated [29]. The data presented in Fig. 7e and f demonstrate that sorbitol-based films exhibit a reduced degree of roughness in comparison to glycerol-based films (illustrated in Fig. 7a and b) and citric acid-based films (illustrated in Fig. 7c and d). This is since sorbitol effectively interacts with polymer macromolecules, thereby reducing the number of groups prone to water binding. Furthermore, the surface of the films can be endowed with hydrocarbon chains derived from sorbitol molecules, which renders it more hydrophobic than the surface of other films. It can be concluded that the use of glycerol, citric acid, and sorbitol as plasticizers in the production of XG-starch films proved to be highly effective. Glycerol molecules exert the most significant effect on the flexibility of films, while the presence of sorbitol results in the production of more durable films. It is important to note that the addition of all three plasticizers to the composition of films results in a reduction in the strength of the films. The greatest reduction in the strength of the films is observed when the concentration of the plasticizers is greater than 1.5 %. In consideration of the impact of plasticizer concentration on the surface stickiness of XG-starch films and their structural and mechanical properties, the 1.5 % concentration of glycerol, sorbitol and citric acid is recommended as optimal.

Table 2
Effect of plasticizers on the water vapor permeability of the XG-starch films.

Concentration of plasticizers, %	Glycerol, g.m/(P.s.m ²)·10 ⁻¹¹	Sorbitol, g.m/(P.s.m ²)·10 ⁻¹¹	Citric acid, g.m/(P.s.m ²)·10 ⁻¹¹
0.0	5.33 ± 0.02	5.33 ± 0.02	5.33 ± 0.02
0.5	5.28 ± 0.02	5.29 ± 0.01	5.30 ± 0.02
1.0	4.90 ± 0.01	4.20 ± 0.01	4.72 ± 0.05
1.5	4.72 ± 0.03	3.91 ± 0.03	4.61 ± 0.03
2.0	4.45 ± 0.05	3.66 ± 0.02	4.29 ± 0.04
2.5	4.22 ± 0.01	3.53 ± 0.04	4.13 ± 0.04
3.0	3.90 ± 0.03	3.31 ± 0.04	3.72 ± 0.02

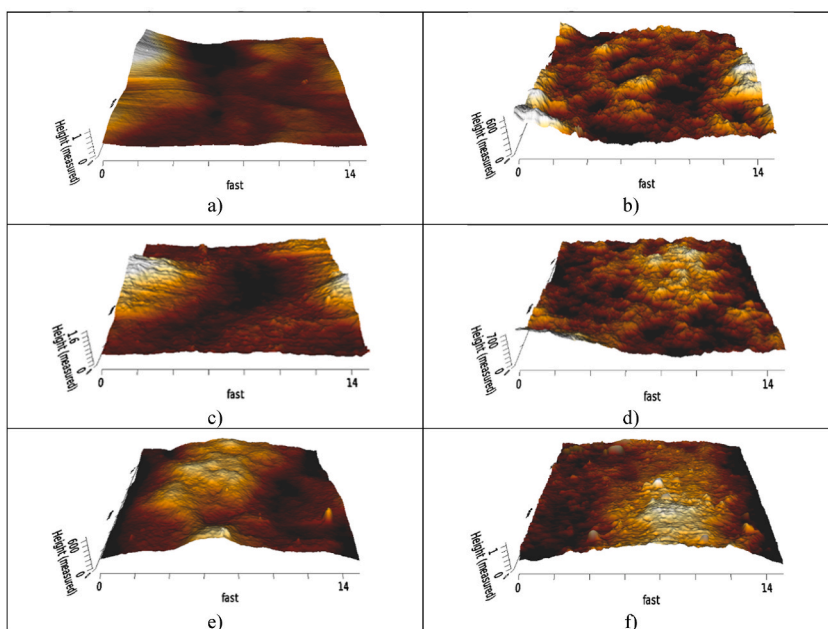


Fig. 7. Topographic images by AFM of XG-starch films without plasticizer (a) and with 3.0 % glycerol (b); XG-starch with 1.0 % citric acid (c) and 3.0 % citric acid (d); XG-starch with 1.0 % sorbitol (e) and 3.0 % sorbitol (f)

4. Conclusion

The present investigation demonstrated that incorporating glycerol, sorbitol, and citric acid plasticizers into XG-starch-based biodegradable films enhances their solubility and moisture content. This plasticizing effect is attributed to the disruption of intermolecular contacts between XG and starch macromolecules and the rearrangement of hydrogen bonds within the system, facilitated by the hydrotropic interaction of the plasticizer molecules. As the concentration of plasticizers increases, there is a gradual rise in the elongation values of the films accompanied by a reduction in their strength. Notably, sorbitol-based films exhibit the highest durability owing to the potential formation of intermolecular contacts between XG and starch macromolecules, along with the presence of a relatively long hydrocarbon chain in the sorbitol molecule. Furthermore, the increased hydrophobicity of sorbitol molecules contributes to decreased surface roughness of the films through hydration. In conclusion, optimizing the concentration and type of plasticizers, particularly sorbitol, presents a promising approach to enhance the mechanical properties and surface characteristics of XG-starch-based biodegradable films, thereby improving their applicability in various packaging and environmental protection contexts.

Data availability statement

No data was used for the research described in the article.

CRediT authorship contribution statement

A.D. Yermagambetova: Writing – original draft, Conceptualization. **S.M. Tazhibayeva:** Writing – review & editing, Conceptualization. **B.B. Tyussyupova:** Project administration, Investigation. **K.B. Musabekov:** Project administration, Funding acquisition. **Laura Pastorino:** Methodology, Investigation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yermagambetova Aigerim reports administrative support and writing assistance were provided by Kazakh-British Technical University. Tazhibayeva S.M. reports a relationship with Al-Farabi Kazakh National University that includes: board membership, non-financial support, and speaking and lecture fees.

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