

Effects of the Incorporation of Saturated Fatty Acids on the Mechanical and Barrier Properties of Biodegradable Films

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ABSTRACT: The effects of saturated fatty acids at a concentration of 1.5% on the mechanical and barrier properties of starch-based films were evaluated in films prepared with two concentrations of glycerol, 20 and 25%. The water vapor permeability (WVP) was determined at three ranges of relative humidity, RH, (0–33, 33–64 and 64–97%). In all cases, an increase in WVP values was observed with increasing RH. SEM images showed a more homogeneous and compact structure in the films

with caproic and lauric acids. The films with fatty acids showed higher elongation and maximum stress, and they had Young's modulus values close to those of the control; thus, the addition of fatty acids did not impair the mechanical properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3695–3703, 2012

Key words: fatty acids; biodegradable films; mechanical and barrier properties

INTRODUCTION

Worldwide concern is growing over issues of environmental protection. There is now great interest in developing biodegradable packing made from raw materials, renewable resources, or blends with synthetic polymers to reduce the environmental impact of disposal of nonbiodegradable packaging and possibly to create new markets for raw material films.^{1–5}

Starch is the main reserve polysaccharide of higher plants. It is a low cost, naturally occurring biopolymer. Starch consists of two main polysaccharides, amylose and amylopectin, based on chains of 1–4 linked α -D-glucose. Amylose is essentially linear, while amylopectin is highly branched due to 1–6 glycosidic bonds. The starch granule is partially crystalline depending on the proportion of the two polysaccharides. However, native starch has to be modified and processed to acquire the properties of a thermoplastic because the melting temperature of pure dry starch is close to 220–240°C, and the onset temperature of starch degradation is around 220°C.⁶

The addition of plasticizers to starch films causes a drastic reduction in the glass transition temperature (T_g). The most commonly used plasticizers are

water and glycerol.^{7,8} Heating starch in the presence of a plasticizer causes disruption of the crystalline structure of the native granule. A phenomenon called gelatinization occurs, through which thermoplastic starch (TPS), which has properties of a pseudoplastic, can be obtained.

These biofilms are good barriers to gases such as O₂ and CO₂; however, one of their major limitations is that their mechanical properties are less favorable than those of conventional films, and they possess high water vapor permeability. To solve the limitations of the starch-based films, such as high-cost, biodegradable, and synthetic thermoplastic polymers that are currently available, several studies have been conducted with blends of starch biopolymers and synthetic polymers.⁹

Fatty acids can create effective barriers to water vapor and provide structural support, thus limiting the oxygen and carbon dioxide transfer through the film.¹⁰ According to Gontard et al.,¹¹ the addition of lipids causes a decrease in the water vapor permeability of biopolymers—in addition to the polarity, unsaturation number, and ramification degree—that is dependent on the hydrophobic/hydrophilic ratio provided by their components.

The aim of the present work was to incorporate saturated fatty acids in the development of films made of starch and the biodegradable synthetic polymer poly(butylene adipate-co-terephthalate). We sought to obtain films with better barrier properties

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to water vapor due the presence of fatty acids maintaining the mechanical properties presented by films that do not contain fatty acids.

MATERIALS AND METHODS

Materials

Native starch was extracted from cassava (Indemil, Brazil). Commercial glycerol (Dinamica, Brazil) was used as a plasticizer. The biodegradable polymer used was poly(butylene adipate-*co*-terephthalate) (PBAT), manufactured by Basf (Germany) under the commercial name Ecoflex[®] 701. The fatty acids used were caproic acid (99%, Vetec, Brazil), lauric acid (98%, Vetec, Brazil), and stearic acid (PA, Synth, Brazil).

Preparation of blends of starch and PBAT by blow extrusion

The films were produced by blow extrusion using a pilot extruder BGM (model EL-25, Brazil) with a blowing system made up of a 250-mm diameter screw, four heating zones and an external cooling air ring with a 300–350-mm diameter for film formation. The screw speed was maintained at 35 rpm, and the temperature was kept at 120°C.

Films were produced according to the formulations shown in Table I.

For production of films by extrusion using polymer blends, the components of the blend, starch, glycerol, fatty acids, and PBAT were homogenized and extruded for pelleting in an initial step, and then fed back into the extruder for the pellets to produce the films, that were produced by blown extrusion system, reeled, wrapped in foil, and stored until analysis.

Subjective evaluation

A subjective evaluation of the film was performed to manually verify homogeneity, handling, and tendency to tear.

Scanning electron microscopy (SEM) and optical microscopy

SEM micrographs were taken with a FEI Quanta 200 (EUA) scanning electron microscope. All samples were frozen with liquid nitrogen and fractured before analysis. The samples were coated with a fine gold layer using a BAL-TEC model SCD 050 (EUA) sputter coater, allowing for surface and cross section visualization.

The optical microscopy was performed with a Leica DMLS (Germany) optical microscope with a computer interface using the software Motic Image Plus 2.0. Samples of the films were stained with Lugol reagent and bleached with ethanol 70%.

TABLE I
Formulations Used in the Production of the Films

Film	Name	Starch (wt %)	Glycerol (wt %)	PBAT (wt %)	Fatty acid (wt %)
C20	Control 20	56	14	30	—
C25	Control 25	52.5	17.5	30	—
Ca20	Caproic 20	54.8	13.7	30	1.5
Ca25	Caproic 25	51.4	17.1	30	1.5
La20	Lauric 20	54.8	13.7	30	1.5
La25	Lauric 25	51.4	17.1	30	1.5
E20	Stearic 20	54.8	13.7	30	1.5
E25	Stearic 25	51.4	17.1	30	1.5

Thickness measurements

The thickness of the films was determined using a digital micrometer (Mitutoyo, São Paulo, Brazil) with a resolution of 0.001 mm. The final thickness was the average of 20 random measurements of different parts of the film.

Water vapor permeability (WVP)

Water vapor permeability (WVP) was determined gravimetrically, according to ASTM E-96-95 with some modifications, in appropriate diffusion cells, using three different ranges of relative humidity gradient ($\Delta RH = 0\text{--}33\%$, $\Delta RH = 33\text{--}64\%$, and $\Delta RH = 64\text{--}97\%$). The film was conditioned under 53% relative humidity for 7 days, and then it was fixed in a capsule of permeability with 60-mm diameter. Each test was performed in duplicate. The capsules were weighed 10 times at intervals of 12 h.

Mechanical properties

The tensile properties were determined using a TA TX2i Stable Micro Systems texture analyzer (England) in accordance with ASTM D-882-91. The samples (50 mm x 20 mm) were clamped between pneumatic grips with an initial distance of 30 mm and test speed of 0.8 mm/s. The parameters determined were stress at break (MPa), elongation at break (%), and Young's modulus (MPa).

For each formulation, a total of 16 tests were made: eight samples were cut in the longitudinal direction and eight in the transverse direction. The samples were conditioned under 53% relative humidity for 48 h.

RESULTS AND DISCUSSION

Subjective evaluation

The results of the subjective evaluation, through which homogeneity, handling, and tendency to tear were assessed, are shown in Table II.

TABLE II
Subjective Evaluation of Films Made of Starch, Glycerol,
and PBAT with the Addition of Fatty Acids

Film ^a	Homogeneity ^b	Handling ^b	Tendency to tear ^b
C20	XX	XXX	No
C25	XXX	XXX	No
Ca20	XXX	XXX	No
Ca25	XXX	XXX	No
La20	XXX	XXX	No
La25	XXX	XXX	No
E20	XX	XXX	Yes
E25	XX	XXX	No

^a C20, C25—films with 30% of PBAT, 20 and 25% of glycerol compared to 70% of thermoplastic starch, respectively. Ca20, Ca25, La20, La25, E20, E25—films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric, and stearic acid, respectively.

^b x—deficient, xx—good, xxx—excellent.

Formulations containing stearic acid showed fractures and ruptures during the blow extrusion process and lacked sufficient stability to withstand the air blow at the time of film formation.

The films C20, E20, and E25 were evaluated as being less homogeneous due to the presence of thicker regions, agglomerates, and significant differences in the transmittance of light when observed through a light source.

All of the formulations showed good handling; none of them proved to be brittle during the analysis. The films E20 and E25 showed a tendency to tear the other formulations did not, a characteristic that can be observed by manually applying a minimum force. The other formulations tolerated manual traction relatively larger than that of these films.

Scanning electron microscopy (SEM) and optical microscopy

Figure 1 shows the images obtained by optical microscopy at a magnification of 100×. Lugol is a reagent that blushes starch; thus, the presence of starch can be resolved in the films.

The pattern of the images is the same, regardless the concentration of glycerol in the film. The controls show a more interconnected structure, which represents a kind of alignment, due to the extrusion process. Since the films with caproic acid, Ca20 and Ca25, and lauric acid, La20 and La25, can be observed, the starch was evenly distributed, creating a homogeneous matrix that does not present the same alignment as that of the controls. The structure of the film is made up of granules composed of spherical units.

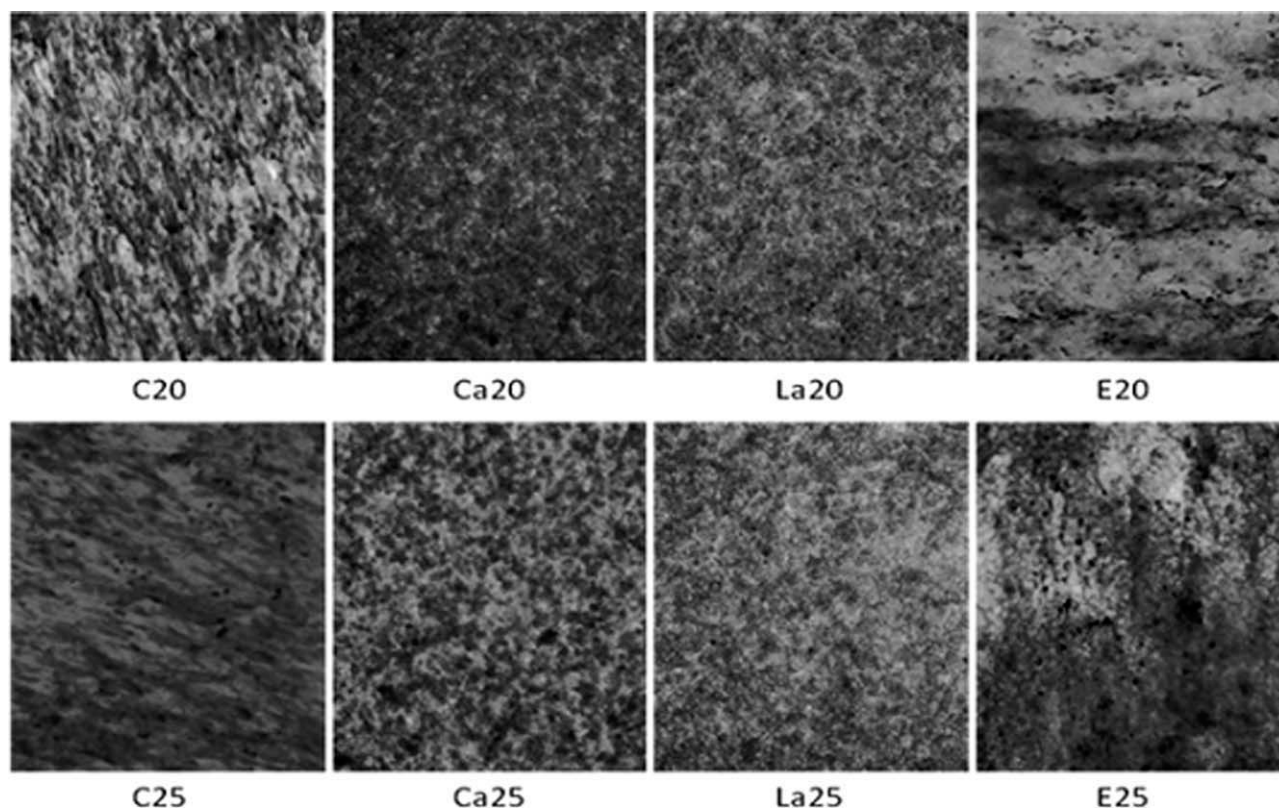


Figure 1 Film images obtained by optical microscopy (magnification 100×). C20, C25—films with 30% of PBAT, 20 and 25% of glycerol compared to 70% of thermoplastic starch, respectively. Ca20, Ca25, La20, La25, E20, E25 – films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric and stearic acid, respectively.

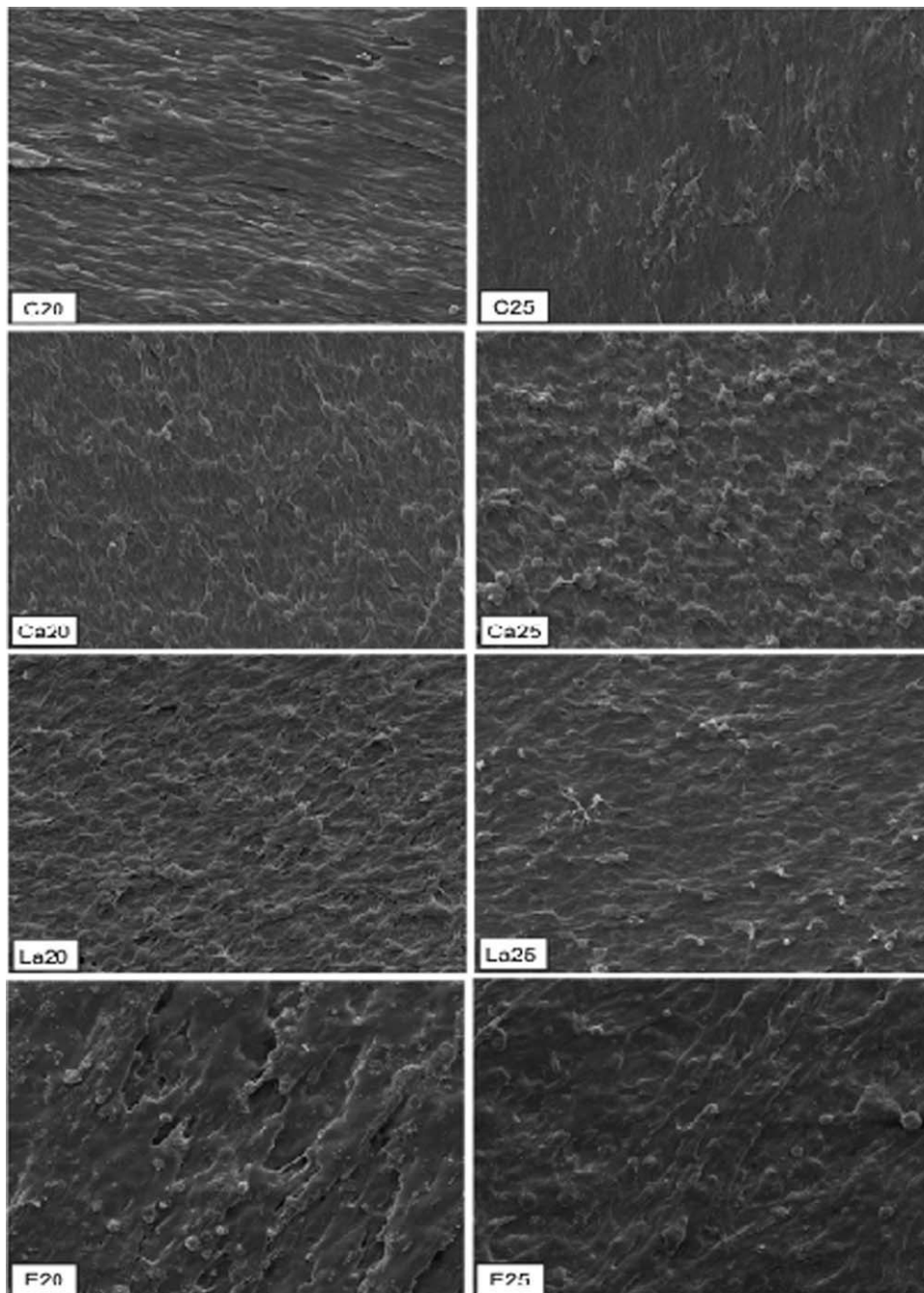


Figure 2 SEM micrographs of the surface of the films at a magnification of 400 \times . C20, C25—films with 30% of PBAT, 20 and 25% of glycerol compared to 70% of thermoplastic starch, respectively. Ca20, Ca25, La20, La25, E20, E25 – films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric and stearic acid, respectively.

The formulations with stearic acid, E20 and E25, showed less homogeneity, with some regions that were quite blushed and others that were lighter, which suggests a nonuniform distribution of starch in the film. The structures continued to appear spherical in shape, showing no alignment.

The micrographs of the films obtained by SEM are shown in Figures 2 and 3. The surfaces showed a homogenous distribution without apparent starch granules, representing a cohesive structure, but they

were not completely smooth. In the films C20, C25, E20, and E25, it is possible to visualize the direction of the extrusion process. The same is also true in the films Ca20, Ca25, La20, and La25, as had been suggested by optical microscopy.

As was observed in optical microscopy, SEM confirmed that the polymeric matrix of the films C20, C25, E20, and E25 showed no alignment that resembled a stretched fiber, while the matrices of the other formulations appeared to have granules

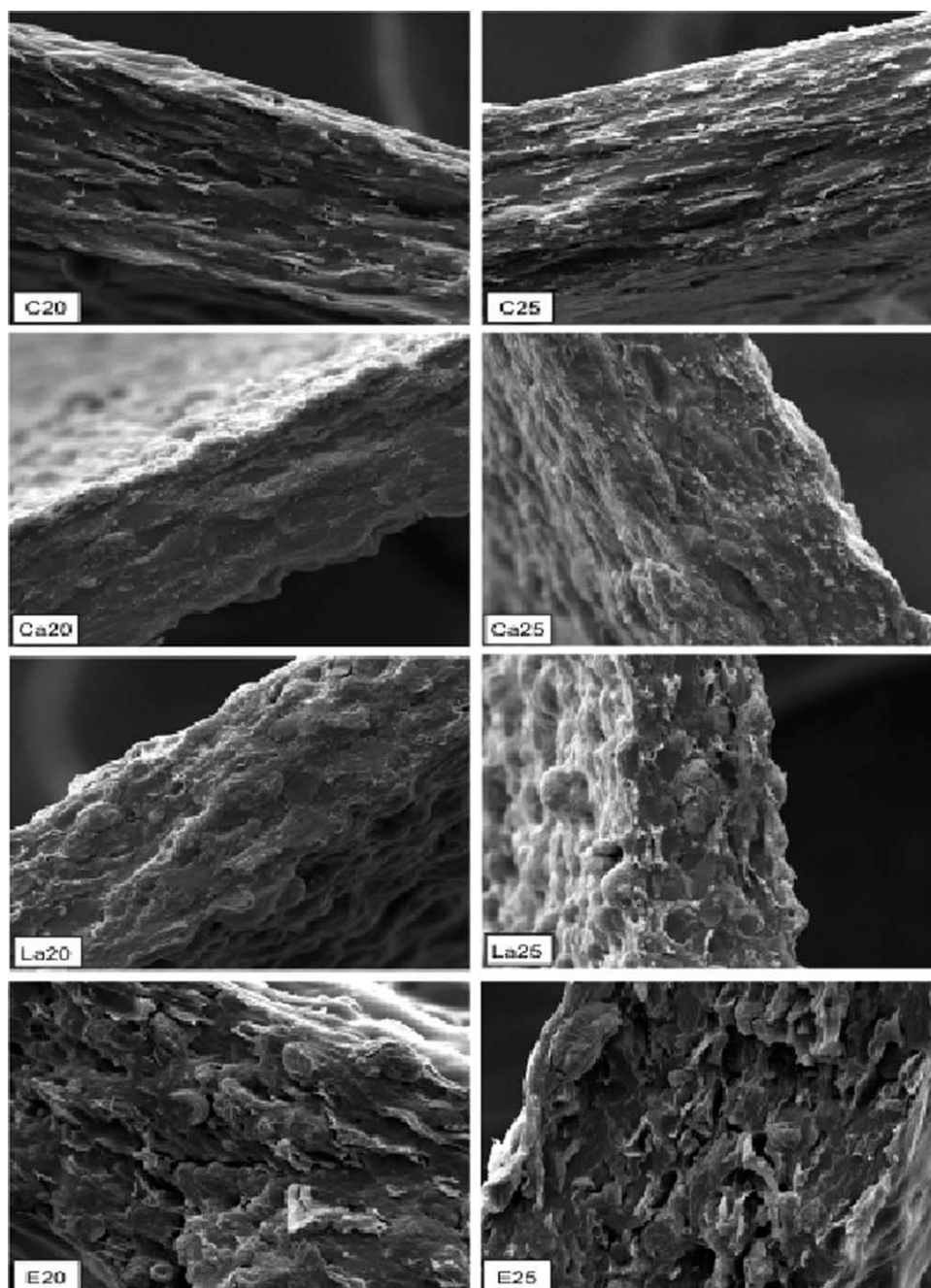


Figure 3 SEM micrographs of cross-sections of the films at a magnification of 1600 \times . C20, C25—films with 30% of PBAT, 20 and 25% of glycerol compared to 70% of thermoplastic starch, respectively. Ca20, Ca25, La20, La25, E20, E25 – films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric and stearic acid, respectively.

distributed all over then. Moreover, they were more homogeneous and compact, which are features that may be better observed by examining the fracture of the films.

Through cross-sectional micrographs, the films containing lauric and caproic acid are shown to be thinner than the control films and films with stearic acid as confirmed by thickness measurements (Table III).

The films Ca20, Ca25, La20, and La25 showed a uniform and compact matrix, no disruption, and

cluster and pore formation. The homogeneous matrix is a good indicator of the integrity of the structure, and therefore, good mechanical properties would be expected, as were obtained in the mechanical tests. This compact and homogenous matrix was also observed by Mali et al.¹² in starch-based films with glycerol produced by casting.

The micrographs of the films C20 and C25 suggest that they present a homogenous distribution and a compaction of the matrix, despite presenting the higher values of thickness as discussed earlier.

TABLE III
Thicknesses of Starch-Based Films with Glycerol and PBAT with the Addition of Fatty Acids

Film ^a	Thickness (μm) ^b
C20	152 \pm 20 ^c
C25	119 \pm 17 ^a
Ca20	110 \pm 4 ^{a,b}
Ca25	109 \pm 14 ^{a,b}
La20	103 \pm 12 ^{a,b}
La25	89 \pm 8 ^b
E20	277 \pm 66 ^d
E25	205 \pm 31 ^e

^a C20, C25 - films with 30% of PBAT, 20 and 25% of glycerol compared to 70% of thermoplastic starch, respectively. Ca20, Ca25, La20, La25, E20, E25 - films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1,5% of caproic, lauric and stearic acid, respectively.

^b a,b,c,d,e means with different letters are significantly different, Tukey test ($p < 0.05$).

E20 and E25 showed less homogeneity than the other films as well as lower compaction, which led to a greater thickness of these films as evidenced by the thickness measurements. Still, in the matrix of the film it is possible to observe the presence of discontinuities, which suggests that these films will have poor mechanical properties; as was observed, these formulations lead to films with lower tensile strength and elongation.

Thickness measurements

The thicknesses of the films are presented in Table III.

The thickness is determined through the longitudinal tension exerted by the spooler as well as the force exerted by the injected air, which expands the matrix in the transversal direction. The incorporation of both caproic and lauric acid resulted in a decrease in film thickness when compared to that of the control. There was also no significant difference between the films containing these fatty acids; the thicknesses of these formulations ranged from 89 \pm 8 μm (La25) to 110 \pm 4 μm (Ca20).

When a film does not have enough elasticity to undergo expansion, its structure is broken with the air flow, which leads to a thicker film. The films E20 and E25 showed low elasticity as they supported neither the expansion nor the tension of the process, producing larger values of thickness as was confirmed by the subjective analysis of homogeneity and tendency to tear.

The formulations C20 and C25 showed intermediate thicknesses among the films studied. Between the formulations that provided stable films, C20 was about 1.3 thicker than the films with caproic and lauric acid. This can be explained by the lower concentration of glycerol in TPS, which did not provide

good plasticization and resulted in formulations that were slightly more rigid and less elastic.

A correlation between thickness and the amount of glycerol added in the formulations can be observed. An increase in glycerol content leads to thinner films due to the plasticization of the film; thus, the film presents higher tensile resistance and expansion during the extrusion process without breaking or fracture, leading to thinning.

The incorporation of fatty acids with short chains (up 12 carbon atoms) produced a synergistic effect with glycerol on starch plasticization, leading to the formation of films with higher elasticity than those that did not have fatty acids in their composition. When the carbon chain of the fatty acid increases to 18 carbon atoms, this effect is lost and the long chain contributes to a lack of homogeneity, reducing elasticity and leaving the film more susceptible to disruption during the blowing process.

Water vapor permeability (WVP)

The water vapor permeability (WVP) data under different gradients of relative humidity (ΔRH) are shown in Table IV.

For all formulations, water vapor permeability (WVP) increased with the increasing relative humidity used in the diffusion cells. In caproic 25, in which the gradient of relative humidity (ΔRH) varied from

TABLE IV
Water Vapor Permeability (WVP) of Starch-Based Films Containing Glycerol and PBAT with the Addition of Fatty Acids Under Different Gradients of Relative Humidity

Film	ΔRH (%)	WVP ($\times 10^6$) (g/m h Pa)
C20	0–33	4.62 \pm 0.85
	33–64	8.07 \pm 3.78
	64–97	13.74 \pm 4.21
Ca20	0–33	0.19 \pm 0.005
	33–64	1.38 \pm 1.47
	64–97	12.81 \pm 1.95
La20	0–33	0.21 \pm 0.039
	33–64	2.77 \pm 0.29
	64–97	11.02 \pm 0.21
E20	0–33	0.46 \pm 0.21
	33–64	4.76 \pm 0.32
	64–97	18.49 \pm 0.51
C25	0–33	0.24 \pm 0.00
	33–64	3.17 \pm 0.52
	64–97	12.27 \pm 2.74
Ca25	0–33	0.18 \pm 0.08
	33–64	0.28 \pm 0.02
	64–97	11.77 \pm 0.71
La25	0–33	0.16 \pm 0.00
	33–64	2.88 \pm 0.44
	64–97	12.39 \pm 3.53
E25	0–33	0.34 \pm 0.04
	33–64	3.84 \pm 0.18
	64–97	12.51 \pm 0.55

0–33% to 33–64%, there was an increase in WVP of 55%, and when the Δ RH varied from 33–64% to 64–97%, the increase was 420%. This behavior of permeability with respect to the gradient of relative humidity is related to the thermoplastic starch in the film. WVP increases with increasing Δ RH due to excessive absorption of water from the polymer matrix, which increases the diffusion of water molecules, thereby decreasing the barrier properties as has been reported by Bilck et al.⁴ and Müller et al.¹³

The addition of caproic and lauric acids decreased considerably the WVP values in formulations with 20% glycerol considering the Δ RH of 0–33% and 33–64%. This behavior can be explained by the fact that these fatty acids have shorter carbon chains than stearic acid, facilitating their incorporation into the film matrix and allowing greater interaction with other components that are present. Moreover, this prevents the formation of heterogeneous regions that are more brittle and that would create discontinuity in the film matrix. Wong et al.,¹⁴ studying the effect of addition of fatty acids in chitosan films produced by casting, observed that the incorporation of lauric acid reduced the water vapor permeability to 49% when compared to control.

For the Δ RH of 64–97%, with the exception of E20 that presented some cracks, the values of all samples were very close, it can be explained by the fact that at high humidity occurs the saturation of the film and the permeability is almost totally due to solubility coefficient, once that were observed by Muller et al.¹⁵ that the diffusion coefficient did not change considerably when the Δ RH passed from 2–33% to 64–90%.

The effects of these two fatty acids in formulations containing 25% glycerol were less pronounced. Nevertheless, the incorporation of fatty acids with lower carbonic chains showed an absolute value of WVP about 20% lower than that of the control with 25% glycerol. The WVP value is directly related to the thickness of the specimen; thus, the incorporation of caproic and lauric acids resulted in thinner films, and this reflected in the values of WVP.

The addition of stearic acid did not reduce the value of WVP in the films, probably due to a lack of homogeneity, and, although the tendency-to-tear test did not show a less homogeneous matrix, it facilitated the passage of water vapor. Fakhouri et al.,¹⁶ using a casting technique, added 15% fatty acids to films of lipophilic starch and gelatin and obtained higher values of WVP in films with palmitic acid (16C) when compared to films with caproic (6C) and lauric (12C) acid.

Cheng et al.,¹⁷ studying the incorporation of palm oil in carboxymethylcellulose and glucomannan films produced by casting, observed that the addition of a hydrophobic material in the film-forming

TABLE V
Stress at Break (T), Elongation at Break (ϵ), and Young's Modulus (Y) of films with Different Concentrations of Glycerol and Cutting Direction

Film ^a	Glycerol (%)	T (MPa)	ϵ (%)	Y (MPa)
Longitudinal direction				
C	20	5.1 \pm 0.3	41 \pm 4	38 \pm 3
	25	7.4 \pm 0.3	137 \pm 11	40 \pm 2
Ca	20	7.6 \pm 0.2	203 \pm 14	36 \pm 3
	25	5.7 \pm 0.1	171 \pm 22	34 \pm 1
La	20	5.9 \pm 0.2	73 \pm 7	56 \pm 6
	25	4.7 \pm 0.2	226 \pm 20	20 \pm 1
E	20	3.8 \pm 0.2	24 \pm 1	44 \pm 2
	25	3.2 \pm 0.1	28 \pm 2	35 \pm 2
Transverse direction				
C	20	4.0 \pm 0.1	94 \pm 8	23 \pm 1
	25	5.8 \pm 0.1	64 \pm 6	45 \pm 2
Ca	20	7.0 \pm 0.1	188 \pm 20	34 \pm 2
	25	5.8 \pm 0.3	126 \pm 16	37 \pm 3
La	20	5.6 \pm 0.2	80 \pm 7	47 \pm 4
	25	3.6 \pm 0.1	184 \pm 13	18 \pm 1
E	20	2.0 \pm 0.0	11 \pm 1	32 \pm 3
	25	2.4 \pm 0.1	22 \pm 2	32 \pm 1

^a C—films with 30% of PBAT, 20 and 25% of glycerol compared to TPS. Ca, La, E—films with 30% of PBAT, 20 and 25% of glycerol compared to TPS and 1.5% of caproic, lauric, and stearic acid, respectively.

solution does not guarantee a reduction in the amount of WVP because the permeability is influenced by the existence of steric hindrance and "tortuosity" for the diffusion of water molecules, which decrease the WVP and by the presence of pores, plumbing and cracks, which cause an increase in WVP.

Mechanical tests

Tensile tests were performed in longitudinal and transverse directions of the films to verify possible anisotropic behavior in the mechanical properties. This behavior can occur because of two parameters of the extrusion process: the speed of the winders, which guides the film in the longitudinal direction, and the pressure of blowing air, which expands the film across the transverse direction.

Table V shows the results of the mechanical tests in terms of stress at break (T), elongation at break (ϵ), and Young's modulus (Y) of the films.

The maximum stress of the films ranged from 2.0 to 7.6 MPa. Among the various films studied, the film Ca20 showed the highest values for both the longitudinal and the crosscut directions. Caproic acid has six carbons in its chain, which causes its hydrophilicity to be small and allows for the interaction with other components present in the film. Moreover, its small size allows it to be inserted into the starch chains and give greater strength to the polymeric matrix.

With the exception of Ca20, the incorporation of fatty acids reduced the maximum stress values. Studying emulsified films based on wheat gluten, Gontard et al.¹¹ showed that an increase in the concentration of lipids resulted in the loss of mechanical properties, as lipids make the film more brittle. Bourtoom and Chinnan,¹⁸ studying films of rice starch and palm oil, oleic acid, and margarine produced by casting, showed that films containing lipids had lower values of maximum strength than those of controls.

The differences between the values of T presented by different types of incorporated fatty acids can be related to the physical state, structure, and chemical nature of these saturated fatty acids. The films with stearic acid (18C) showed lower values than those with lauric (12C) and caproic (6C) acid. The increase in the size of the carbon chain causes greater reduction in the maximum stress. This may be due to the fact that longer chains hinder the formation of the polymeric matrix during processing, leading to discontinuous and fragile regions.

In synthetic polymers, the anisotropic behavior is attributed to the orientation of the molecules in the amorphous phase during the extrusion process when values of stress at break are higher in the longitudinal direction.¹⁹ For the films studied in this work, this molecular orientation affects the results: the films showed higher values of maximum stress when analyzed in the longitudinal than in the transverse direction.

The difference in the amount of elongation (ϵ) of the films could be observed by comparing the direction of processing. The films generally showed higher values of ϵ in longitudinal tests compared to transversal tests.

The increase in glycerol concentration from 20 to 25% compared to starch contributed to the increase in the plastic character of the films. The formulations with 25% showed higher values of ϵ ; glycerol acts as a plasticizer, weakening the intermolecular forces between polymer chains and allowing them to increase their mobility and the flexibility of the film.

The addition of caproic and lauric fatty acids increased the elongation of the films when compared with controls with the same concentration of glycerol. Within the range of concentrations studied, these fatty acids showed plasticizing properties and acted in synergy with glycerol in the plasticization of starch. Cheng et al.,¹⁷ studying emulsified films of carboxymethylcellulose, glucomannan, and palm oil, showed lower elongation values in the films with palm oil when compared to the control. In these samples, the plasticizing role of lipid was reinforced as the lipid acted as a lubricant that facilitated the mobility of the polymeric chains.

The film with stearic acid showed values of ϵ lower than those of the control because this fatty

acid has a hydrophobic portion of 17 carbon atoms joined by single bonds, and it decreased the mechanical strength of the film when it was incorporated into the hydrophilic matrix of starch, glycerol, and PBAT.

The Young's modulus (Y) showed no differences with respect to the direction along which the samples were cut. Increasing the concentration of glycerol had a tendency to decrease the value of the elastic modulus due to the higher starch plasticization and higher concentration of glycerol.

The value of Young's modulus of the film C25, 40 ± 2 MPa, was very similar to that achieved by Bilk et al.⁴ in their study films for strawberry production; these authors obtained a value of 48 ± 4 MPa for the same formulation.

The Young's modulus ranged from 18 to 56 MPa, but physically the film showed no difference in stiffness. The values are close to those obtained by Mali et al.,⁷ who studied different concentrations of plasticizers in starch-based films by casting. These values ranged from 2300 MPa for films without plasticizer up to 400 MPa for films with 28.5% plasticizer.

CONCLUSIONS

The incorporation of saturated fatty acids until 12 carbon atoms reduces the permeability to water vapor and improves the mechanical properties of films made of starch, glycerol, and PBAT produced by extrusion. Saturated fatty acids with chains shorter than 12 carbon atoms contribute to the formation of a cohesive and homogeneous polymeric matrix. This does not occur with fatty acids with longer carbon chains.

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