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TENSILE PROPERTIES OF WHEAT STARCH FILM WITH THE ADDITION OF SORBITOL AND ALBUMIN

Danuta M. Napierała[1], Jerzy Stangierski[2]

[1]Department of Physics, Agricultural University
ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@.au.poznan.pl
[2]Department of Food Quality Management, Agricultural University
ul. Wojska Polskiego 31, 60-624 Poznań

Abstract. Mechanical properties of wheat starch film with different amount of additives: sorbitol as plasticizer and bovine serum albumin, were investigated in the simple extension test. The concentration of sorbitol in 2.5% filmogenic starch blend was 20 and 40% and the concentration of albumin was 0, 2 and 4%. The data were compared with those obtained for a commercial synthetic film based on polypropylene and polyester. Mechanical parameters: tensile strength, strain at break, stress in relative strain of 0.01 and 0.02, density of elastic energy accumulated at break and Young modulus were determined from the force-deformation curves for all the films studied. The best mechanical performance was observed for the starch films with sorbitol at 40% and albumin below 2%. The presence of globular denaturated protein in higher concentration makes it difficult for the polymer chains to form a strongly entangled network, responsible for high tensile strength.

Keywords: starch film, sorbitol, albumin, mechanical properties, Young modulus

INTRODUCTION

For many years attempts have been made to develop food packaging materials that would replace synthetic polymers characterized by very long time of degradation (Leszczyński 1999). Starch is considered as one of the most promising natural polymers for biodegradable packaging application (Krochta 1997, Lawton 1996, Loudrin et al. 1995, Psomiadou *et al.* 1997). Unfortunately, there are some strong limitations for developing starch-based products, due to its poor mechanical properties and high moisture sensitivity (Chang *et al.* 2006, Garcia *et al.* 2000, Veiga-Santos *et al.* 2005).

Intensive studies have been undertaken on the addition of plasticizers to pure starch-based materials to overcome film brittleness (Chang *et al.* 2006, Mali *et al.* 2005, Myllärinen *et al.* 2002). Plasticizers increase film flexibility because they reduce internal hydrogen bonding between polymer chains. Plasticizers most commonly used in starch films are glycerol, polyethylene glycol, sorbitol. The moisture content in starch films also affects significantly the physical properties of starch-based film (Chang *et al.* 2006, Zięba *et al.* 2002).

It is known that proteins such as collagen, gelatine, wheat gluten, casein are better barriers against humidity than polysaccharides (Lawton 1996, Xu *et al.* 2005), therefore protein and starch films appear to be potential and ecological alternatives for synthetic packaging in food applications.

The study of condensed starch-albumin mixture revealed the existence of specific interactions between starch glucose units and protein amino acid units, dependent on water activity and temperature (Klimek and Poliszko 1998). Therefore, the utilization of albumin as an additive could affect starch film structure and change its mechanical and moisture barrier properties

The aim of the work was to check the effect of bovine serum albumin on the mechanical properties of wheat starch films with sorbitol as plasticizer, at different weight ratios of the components. A comparison between the strength-stress characteristics in simple extension test was made for natural biodegradable starch films and synthetic film based on polypropylene and polyester.

MATERIALS AND METHODS

Materials and film preparation

All the chemicals used: wheat starch, D-sorbitol and bovine serum albumin, were the products of Sigma-Aldrich Chemical Co. The films were prepared according to the casting/evaporation method, described previously for the starch film with sorbitol (Napierała *et al.* 2004). The filmogenic blends were prepared from 2.5% wheat starch solution (5 g per 200 cm^3 of distilled water) with appropriate amounts of additives, according to the experimental design as shown in Table 1. Solutions were heated up to the boiling point with continuous stirring on magnetic stirrer. After 1 hour the hot solution was poured out on glass Petri dishes of a diameter of 14.5 cm, or flat Teflon vessel of the size of 28 x 17.5 cm. Samples were dried in a levelled incubator at temperature of 303 K (solutions with albumin), or at 333 K (solutions without albumin). The drying time, in relation to drying temperature, was 43 and 94 h, respectively. After removing the films from the support, they were stored in closed separate polyvinyl bags for 7 days before testing.

Table 1. Characteristics of the starch films and polypropylene-polyester films and design composition of the test piece

Specimen number	Weight ratio (g): starch : sorbitol: albumin	Thickness (mm)	Moisture, $g_{(H_2O)}\ g_{DB}^{-1}$
1	5 : 1: 0.1	0,058 (±0.003)	0.108
2		0,054 (±0.002)	
3	5 : 2 : 0	0,0593 (±0.0004)	0.086
4		0,0637 (±0.0007)	
5		0,0543 (±0.0003)	
6		0,050 (±0.002)	
7		0.055 (±0.003)	
8		0.056 (±0.003)	
9		0.049 (±0.003)	
10	5 : 2 : 0.1	0,099 (±0.002)	0.076
11		0,090 (±0.003)	
12		0,097 (±0.004)	
13		0,077 (±0.001)	
14		0,0767 (±0.0003)	
15		0,081 (±0.0003)	
16		0.0997 (±0.0017)	
17	5 : 2 : 0.2	0.084 (±0.005)	0.073
18		0.079 (±0.005)	
19		0.083 (±0.005)	
20	PP – PE	0.062 (±0.001)	
21	PP - PE	0.062 (±0.001)	
22	PP - PE	0.062 (±0.001)	
23	PP - PE	0.062 (±0.001)	
24	PP - PE	0.062 (±0.001)	
25	PP - PE	0.062 (±0.001)	

Mechanical tests

Film tensile strength and strain at break were measured using a *TA-XT2i* Texture Analyser (Stable Micro System, Surrey, Great Britain) on filmstrips of 15 x 100 mm which were cut with surgical scissors. Each test strip was mounted in tensile grips on the texturemeter in such a way that it would not break at the fixing points on tensile extension. The crosshead speed was 0.5 mm s^{-1}. Measurements were made at temperature of 295 K. Tensile modulus (E, Pa), tensile strength (σ_{max}, Pa), strain at break (ε_B) and tensile energy to break (Φ, J m^{-3}) were calculated from the force-deformation curves.

Film thickness and moisture content measurements

Thickness of each film was measured before mechanical test at six different points along the length with accuracy of 0.001 mm using a GC-31 micrometer (Käfer, Germany). The moisture content in the films was determined with drying at the temperature of 378 K until constant mass. Measurements were performed on the laboratory balance Gibertini E50S with accuracy of 0.1 mg. Moisture content was expressed as $g_{(H_2O)}(g_{DB})^{-1}$.

Polypropylene-polyester laminate (PP-PE) filmstrips were used for mechanical comparison. Six filmstrips of synthetic polymers were designed as numbers 20 to 25. The thickness of all the films was 0.062 mm, the thickness of polypropylene layer was 0.050 mm and the polyester one was 0.012 mm.

RESULTS

Films to be used for packaging should be characterised by elasticity and high tensile strength (Leszczyński 1999). Figure 1 (a, b) shows typical elongation curves of the plasticized starch films with albumin obtained at different amounts of the components. One of the stress-strain curves for PP-PE laminate film is presented for comparison (Fig. 1c). The curve 1a is clearly characteristic of brittle behaviour whereas curve 1b is typical of a ductile material. The behavioural difference is due to the different amount of sorbitol and albumin. The weight ratio of starch, sorbitol and albumin is, in specimen (2): 5:1:0.1, and in specimen (8): 5:2:0, respectively. All the starch films containing 20% wt of sorbitol were easily breakable and crumbled on cutting, irrespective of the albumin content. The force-deformation curves for these films were short and linear in character because of the crushing at relative extension not greater than 2%.

Increase in the sorbitol content in the starch films up to 40% wt significantly improved their tensile properties. It is suggested (Loudrin *et al.* 1995) that if the glass-rubber transition temperature of starch polymer chains in the film is lower than room temperature, the starch will produce a plastic material. Molecular interactions between sorbitol and starch polymer chains decrease the location of glass-rubber transition temperature T_G in starch film, as observed by DMTA (Napierała *et al.* 2004). The decrease of T_G below room temperature in starch–sorbitol film related to high sorbitol concentration may elucidate a cause of plasticizing and antiplasticizing effect of sorbitol (Mali *et al.* 2005).

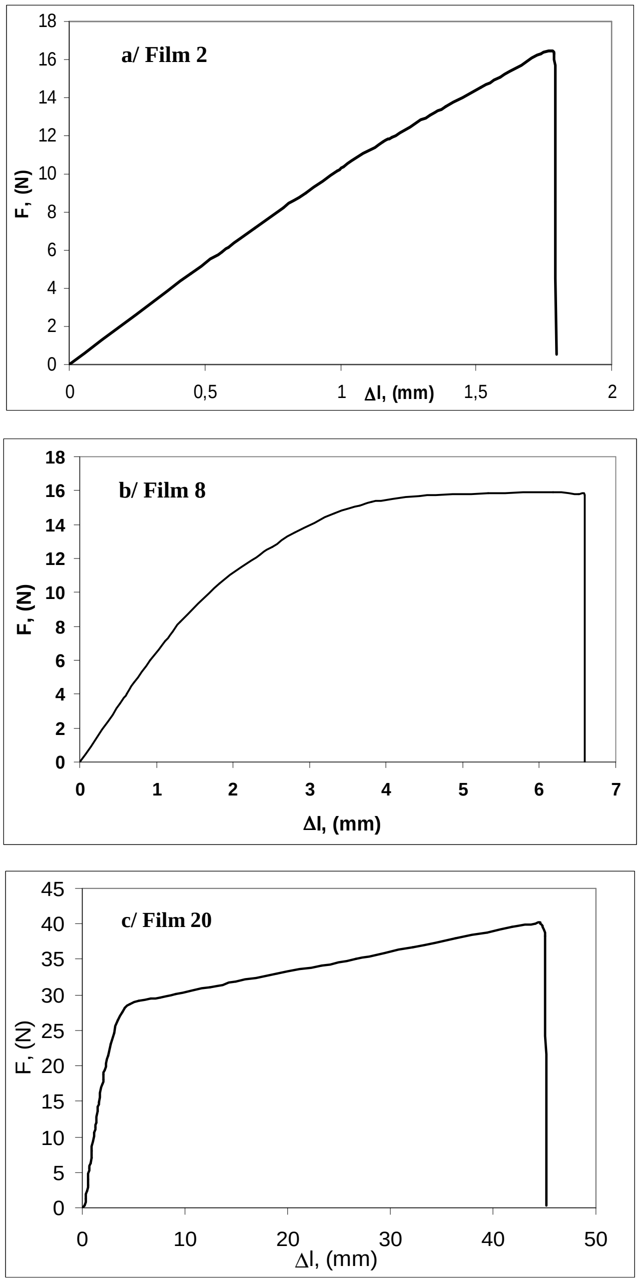


Fig. 1. Experimental force-distance curves of starch-sorbitol-albumin films (a, b) and poly-propylene-polyester film (c). Properties of the films in Table 1

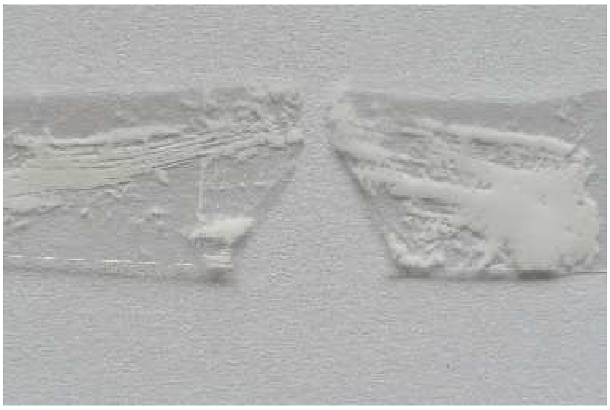


Fig. 2. Photo of the starch-sorbitol-albumin film (specimen 14) ten days after the tensile test with Lüders lines on the surface

On the basis of the data collected it was possible to determine:

- the tensile strength, σ_{max}, (Pa), defined as:

$$\sigma_{\max} = \frac{F}{S_o}$$

where S_0 is the original cross-section area of a film band,

- tensile energy to break defined as the work performed on elongation of the sample per unit volume: Φ (J m^{-3})

$$\Phi = \frac{1}{2}\sigma\,\varepsilon$$

where $\varepsilon = \Delta l/l_0$, l_0 – initial length of a film, Δl – elongation at maximum stress,

- the Young modulus E (Pa), determined as the slope of the linear part of the force-deformation dependence,
- strain at break, $\varepsilon_B = (\Delta l)_B/l_0$

where $(\Delta l)_B$ – maximum of elongation.

The values of the above defined parameters are given in Table 2.

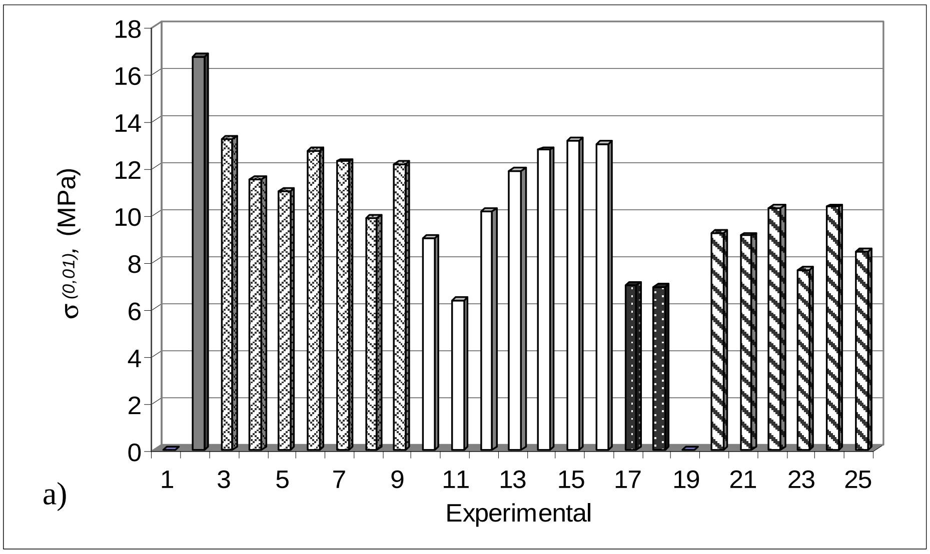
The same mean value of tensile strength, 21.6 MPa, was noted in the starch films with 40% of sorbitol without albumin (specimens 3-9) and with 2% of albumin (specimens 10-16). This value was about twice lower than the corresponding one for the synthetic PP-PE film. In the synthetic PP-PE film used as reference, the average value of tensile strength was 45.4±0.7 (MPa) and the percentage elongation at break was 65±2(%). In both groups of starch films considered and in PP-PE films, the comparable Young modulus value was obtained, about 0.89, 0.87 and 0.87 GPa, respectively. Young modulus for pure starch film without plasticizer is significantly higher, for example for the amylose rich corn starch film it is 3.5 GPa (Bader and Göritz 1994).

Table 2. Stress at strain σ_{max},, percentage elongation ε_B, tensile energy to break Φ and Young modulus E for the starch-sorbitol-albumin films. Properties of specimens according to Table 1

Specimen number	σ_{max}, (MPa)	ε_B, (%)	Φ (kJ m^{-3})	E (GPa)
1	8.42	0.18	8	1.32 (±0.01)
2	20.10	1.41	180	1.28 (±0.01)
3	21.86	13.14	351	1.14 (±0.01)
4	20.75	10.55	365	0.85 (±0.04)
5	20.53	9.89	753	0.76 (±0.01)
6	19.34	10.61	904	0.89 (±0.01)
7	23.69	3.65	423	0.86 (±0.01)
8	18.94	6.60	585	0.77 (±0.01)
9	26.05	4.53	491	0.94 (±0.01)
10	19.50	3.87	377	0.63 (±0.01)
11	11.84	11.00	524	0.47 (±0.02)
12	16.12	6.12	268	0.81 (±0.01)
13	28.03	5.29	597	0.95 (±0.01)
14	20.21	2.77	257	1.21 (±0.02)
15	29.10	4.60	603	1.12 (±0.01)
16	26.34	5.74	533	0.87 (±0.01)
17	9.83	1.63	80	0.55 (±0.01)
18	12.09	2.48	150	0.59 (±0.01)
19	16.26	2.72	273	–

The greatest percentage elongation, 8.4±1.3(%), and consequently the greatest tensile energy accumulated at failure threshold, 553±80 (kJ m^{-3}), were observed in the sample group of starch films with 40% wt sorbitol and without albumin. In sample group with 2% wt of albumin, average value of elongation was 5.6±1.0(%) and tensile energy was 451±56 (kJ m^{-3}), and in the sample group with 4% wt of albumin, corresponding values were 2.3±0.3(%) and 168±56 (kJ m^{-3}), so the higher the albumin concentration the worse the tensile properties of the film.

After a few days from the uniaxial extension test the starch films with 40% of sorbitol revealed characteristic Lüders lines (Fig. 2), typical of extension of soft steel. The lines appear as a result of unfolding of polymer chains and their recrystallisation along the axis of elongation (Cottrell 1970).



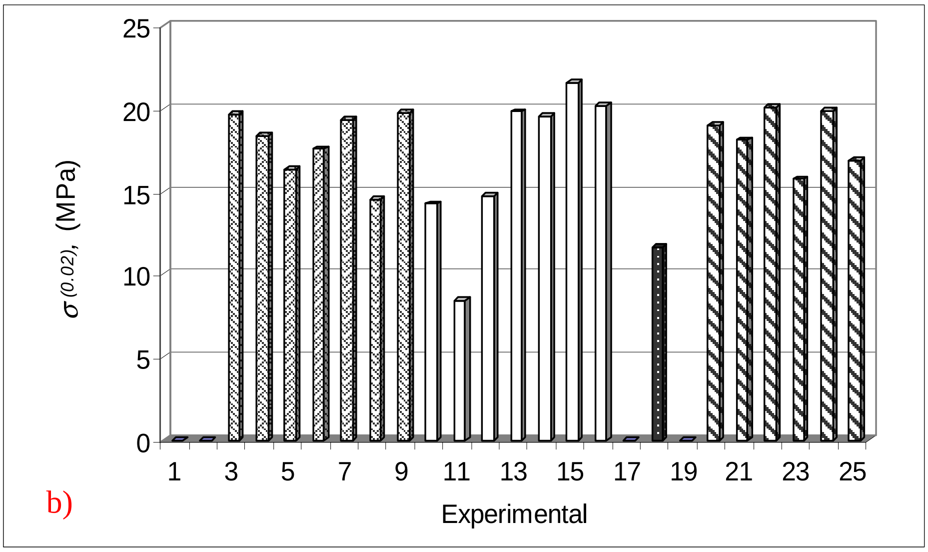


Fig. 3. Tensile stress at relative elongation ε = 0.01 (a) and 0.02 (b) for starch-sorbitol-albumin films (1-19) and polypropylene-polyester films (20-25). Sample labeling as in Table 1

In order to compare the deformation process in the starch films with plasticizers and the reference synthetic film, the uniaxial stress at the relative deformation of 0.01 and 0.02 was determined. The results are presented in Figure 3 a,b. At the same deformation the stress in the two types of film is similar. In the polymer material three types of chain deformation are possible: unfolding at the preserved angle of chemical bonds involved, changes in the angle of the chemical bonds, and bond stretching related to changes in the interatomic distances (Wilczyński 1984). The corresponding energy of these types of deformation increases in the above order. Therefore, at small deforming force the film elongation is a result of unfolding of the polymer chains, both in the natural and synthetic films. Elastic deformation of the starch polymer network is a result of flexibility of the long polymer chains. They are able to fold and unfold, and only on significant elongation a natural elasticity limit is reached.

From the above results presented in Figure 3, it can be concluded that the behaviour of starch and polypropylene-polyester polymer chains is similar when considering the small strain range. The presence of small dense spheres of denaturated protein does not enable the chains to form a strongly entangled network, which is generally responsible for the high values of elongation at break. It seems that only a small addition of albumin (below 2% wt) may be beneficial for the mechanical characteristics of the films. The question is whether the presence of albumin at this wt % will have a beneficial effect on the film sorption properties.

CONCLUSIONS

1. Starch films with sorbitol and albumin are structurally heterogeneous and have diversified mechanical properties.
2. The mechanical strength of the starch film is mainly determined by the plasticizer at an appropriate concentration. At a low concentration sorbitol does not enhance the film elasticity and it behaves as a brittle material.
3. An addition of albumin causes a decrease in the elasticity modulus of the starch film but also reduces its durability. Albumin addition resulted in the highest effect observed on wheat starch films elongation at break.
4. Young modulus of the starch film with additions is comparable to or higher than that of the synthetic PP-PE film used as packaging material.

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MECHANICZNE WŁAŚCIWOŚCI FOLII SKROBI Z SORBITOLEM I ALBUMINĄ PODDANYCH JEDNOOSIOWEMU ROZCIĄGANIU

Danuta M. Napierała[1], *Jerzy Stangierski*[2]

[1]Katedra Fizyki, Akademia Rolnicza im. A.Cieszkowskiego
ul. Wojska Polskiego 38/42, 60-637 Poznań
e-mail: dnapiera@.au.poznan.pl
[2]Katedra Zarządzania Jakością Żywności, Akademia Rolnicza im. A.Cieszkowskiego
ul. Wojska Polskiego 31, 60-624 Poznań

S t r e s z c z e n i e. Folie skrobi z sorbitolem i albuminą, otrzymane metodą kastingową z 2,5% kleiku o różnym stosunku wagowym składników poddano próbie jednoosiowego rozciągania. Krzywe rozciągania wykazały niejednorodność właściwości mechanicznych badanych folii. Folie o mniejszym stężeniu sorbitolu, tzn. 20% były zdecydowanie kruche i ulegały zerwaniu przy względnym odkształceniu nie przekraczającym 0,02. Folie skrobi z 40% udziałem wagowym sorbitolu wykazywały cechy materiału elastycznego, co przejawiało się na wykresie naprężenie-odkształcenie większym lub mniejszym odcinkiem trwałych odkształceń plastycznych. Dodatek albuminy o stężeniu 2% nie zmieniał istotnie parametrów wytrzymałościowych uplastycznionej folii skrobiowej. Moduł Younga dla tych folii był taki sam, jak w przypadku folii skrobi bez udziału białka. Przy 4% stężeniu albuminy folie skrobi traciły na elastyczności i ulegały zerwaniu przy względnym wydłużeniu 0,023. Stężenie albuminy powyżej 2% wydaje się zatem niekorzystne dla właściwości mechanicznych folii skrobi pszenicy uplastycznionej 40% udziałem sorbitolu.

Słowa kluczowe: film skrobiowy, sorbitol, albumina, właściwości mechaniczne, moduł Younga