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INFLUENCE OF ULTRASONIC TREATMENT ON THE MECHANICAL AND SURFACE PROPERTIES OF POTATO STARCH-BASED FILMS WITH VARIOUS GLYCEROL CONTENT

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Abstract: *Starch-based films are suitable for applications such as single-use food packaging for products with a short shelf life, offering a potential green alternative to certain plastic packaging materials. Although starch-based films offer suitable gas barriers and optical properties for packaging applications, their poor moisture resistance and mechanical strength limit broader use. Ultrasonication presents a promising and efficient solution to these challenges, offering high effectiveness, environmental sustainability, and safety. Selected properties of potato starch-based films with or without ultrasonication were investigated. To explore the impact of glycerol (GLY) content and ultrasonication on starch-based films, a series of films with varying concentrations of glycerol (ranging from 20% to 80%) were developed. The resulting films were characterized by tensile properties, water contact angle (WCA), Fourier Transform Infrared Spectroscopy (FTIR), surface roughness, and Scanning Electron Microscopy (SEM) techniques. It was observed that the application of sonication treatment had both positive and negative effects on the films' overall characteristics. Specifically, the tensile strength values increased by 20% following ultrasonication treatment, particularly in films containing 20% and 40% GLY. Furthermore, the values of WCA increased, indicating slight hydrophobization of the film surface. Finally, the SEM images confirmed the smoothness of the film surface. It was found that ultrasound treatment can improve the overall film performance.*

Key words: potato starch, starch films, mechanical properties, ultrasonic treatment

1. INTRODUCTION

Plastic is widely utilized across many industries, one of the largest being the packaging sector. Since the 1950s, plastic packaging has replaced other reusable materials used for packaging, such as paper, glass, metal, etc. Nowadays, plastic consumption in Western Europe is 150 kg per person, and worldwide, around 60 kg per person (European Environment Agency, 2024). Plastic production has increased from 2 Mt in 1950 to 460 Mt in 2019. It is expected that in 2060, plastic production will almost triple, reaching 1 231 Mt (OECD, 2022). Plastics are highly valued in packaging due to their excellent qualities, including strong mechanical properties and effective barriers against gases and moisture, making them ideal for food packaging. Typically, plastic films are used as single-use packaging, necessitating recycling after use. However, only 38% of plastic packaging waste is recycled in the EU (Eurostat, 2024). Hence, in 2021, each person in the EU generated more than 36 kg of plastic waste, and only about 14 kg per person were recycled.

The primary drawback of traditional plastic materials lies in the recycling process. Plastic films pose a challenge due to their inability to degrade in the natural environment. As a result, the European Union implemented regulations on single-use plastics within the European Green Deal (European Commission, 2019). One of the Green Deal policies is to ensure that all packaging in the EU market is reusable or recyclable by 2030.

Bio-based and biodegradable alternatives have been introduced to reduce the usage of conventional nondegradable plastics based on fossil resources. Some of them are already industrially produced, for example, polylactide (PLA), polycaprolactone (PCL), polyhydroxyalkanoates (PHA), etc. (Żołek-Tryznowska & Cichy, 2018). Polysaccharides like starch derived from potatoes, rice, corn, or wheat are among the most non-toxic and widely used polymers. Starch is seen as one of the most promising alternatives to non-degradable plastics due to its abundance, low cost, biodegradability, edibility, and excellent film-forming properties (Zarski, Bajer & Kapuśniak, 2021). Compared with conventional packaging plastics, starch-based

films have certain shortcomings, including poor mechanical and moisture barrier properties, which limit their further development and application (Mi et al., 2023).
The starch films can be obtained by either extruding and followed by a blowing process or by casting, dipping, or spraying from usually water solution and by a drying process (Lagarrigue et al., 2008; W. Liu et al., 2020; Matzinos et al, 2002; Thunwall, Boldizar & Rigdahl, 2006; Żołek-Tryznowska & Cichy, 2018). Due to native starch's large molecular size and strong hydrogen bonding, it is difficult to dissolve the starch in water, so starch dispersion is prepared at low starch concentrations at elevated temperatures (higher than 90°C) (Chang et al., 2021). In conclusion, the basic recipe for obtaining starch film includes the formation of starch dispersion. Next, the solution is heated to gelatinize the starch dispersion, and finally, it is cast and dried by natural forced air convection to produce a film. Additionally, before the casting process, the starch solution can be treated with an ultrasound. Ultrasound treatment is an environmentally friendly process, and it can be used for dispersion solutions to improve the performance of biodegradable films. The ultrasonic starch treatment was performed as early as 1933 (Kardos & Luche, 2001). Some papers have reported the influence of ultrasonic treatment. Few works in the literature (Abral et al., 2018; Borah et al., 2017; Gaquere-Parker et al., 2018; Huang, Chen & Liu, 2024; P. Liu, 2018a) confirm the effect of ultrasonic treatment on the behaviours of gelatinized starch dispersions and the starch film properties. However, in these papers (Abral et al., 2018; Borah, Das & Badwaik, 2017; Gaquere-Parker et al., 2018; Lima & Andrade, 2010), commercially available ultrasonic baths were used, which work at a limited frequency of ultrasonic 20 or 40 kHz. The ultrasonic treatment can affect starch dispersions and damage the granules (Zuo et al., 2009). Moreover, ultrasonic at 20 kHz frequency can reduce the molecular weight of amylose and amylopectin due to the breakage of C—C bonds, which decreases viscosity (Peres, Leite & Silveira, 2015). The degree of amylose and amylopectin degradation depends on the power and amplitude of the ultrasonics. Ultrasound treatment provides a homogenous starch solution and increases the starch solubility in water. The increase in frequencies of ultrasonic transfers leads to more excellent dispersion and limits the disintegration of C—C bonds. However, the literature research on the influence of ultrasound is not a deeper analysis, despite the usage of commercially available ultrasonic baths at 20 kHz and 40 kHz frequencies and the influence on the limited properties of films.
We apply ultrasonic treatment to improve the properties of starch-based films with various plasticizer contents. Attempts were made in the present paper to investigate the mechanical and surface properties of starch-based composites containing up to 80% of glycerol contents as a plasticizer.

2. METHODS

2.1 Materials

Potato starch (30.3 wt% amylose, 18.1 wt% water content, CAS 9005-25-8) and glycerol (purity ≥ 99%, CAS 56-81-5), as a plasticizer, and diiodomethane (purity ≥ 99%, CAS 75-11-6) were purchased from Sigma Aldrich and used as received.
Amylose content in starch was determined according to ISO 6647 standard at 620 nm with a PerkinElmer Lambda 35 model spectrophotometer.

2.2 Film production

The film production description was shown in our previous works (for example, see (Żołek-Tryznowska & Holica, 2020) or (Żołek-Tryznowska et al., 2024). Briefly, 10 g of starch and 2, 4, 6, and 8 g of glycerol (GLY) were dissolved in water and heated to 95°C at 3°C per minute with continuous mixing. Before pouring, the gelatinized potato starch dispersion solution was placed in an ultrasonic cleaner InterSonic IS-1 ultrasound frequency 35kHz±5% for 15 minutes. Next, the mixture was poured onto Teflon® plates placed using a K Paint Applicator (TMI machines, UK) with an adjustable micrometre spreader gap set at 3 mm after cooling to around 50°C. Obtained starch film sheets had dimensions of approx. 100mm × 150mm. Before analyzing their properties, the films were stored under controlled conditions: at a room temperature of 23±0.5°C and a relative humidity of 50±1% RH, protected from light. All the measurements were conducted one week after film preparation to ensure repeatable measurements.
Table 1 shows the solution formulation. The film abbreviations were coded as S20, S40, S60, and S80, according to their glycerol content (20, 40, 60, or 80 %) in the film-forming solution and sonification process (U for sonicated samples).

Table 1: Starch film abbreviation and formulation

Sample abbreviation	Starch [g]	GLY [g]	Sonification [min]
S20	10	2	-
S40	10	4	-
S60	10	6	-
S80	10	8	-
S20U	10	2	15
S40U	10	4	15
S60U	10	6	15
S80U	10	8	15

2.3 Film properties

The mechanical properties were determined using a Z010 tensiometer (Zwick-Roell, Germany) according to the ISO 527-1 standard. the following measurement conditions were used: the samples were 15 mm in width and 100 mm in length; the initial distance of the clamps was 50 mm; the stretching speed was 100 $mm \cdot m^{-1}$. The thickness for the mechanical measurements was performed with a hand-held micrometre with 0.001 mm resolution and an error of ± 0.5 mm. The parameters (tensile strength (TS), elongation at break (EaB), and Young modulus (YM)) were obtained from the stress-strain curves. The measurements were repeated ten times, and the average values were taken.
The water contact angle (WCA) was determined using the Drop Shape Analysis System (DSA 30E, Krüss, Germany) in agreement with the ISO 15989 standard.
ATR FT-IR spectra of developed films were collected at room temperature over the 400–4000 cm^{-1} range, with a resolution of 4 cm^{-1}, using a Nicolet iS5 spectrometer fitted with a Platinum single-reflection diamond ATR module. The spectra were analyzed using OMNIC Specta™ software (version 9.12.968).
A digital microscope (Keyence VHX-7000, Japan) and SEM (JOEL JCM-7000) were used to observe the surface structure of developed films. The film's surface roughness (*Sa*) was evaluated with Keyence VHX-7000. The surface morphology was analyzed with SEM. Firstly, the film samples approx. 1 cm^2 was fixed on the sample table with double-sided conductive adhesive. Then, they were covered with a thin layer of gold for SEM image determination. SEM images were received at an acceleration voltage of 15 kV.

2.4 Data analysis

The statistical analysis was performed using the Statgraphics Centurion 19 (v.19.1.3 StatPoint®, Inc., Warrenton, VA, USA). The effect of non-sonicated and sonicated treatment on the mechanical properties of films at a 5% significance level was identified using analysis of variance (ANOVA). The data were expressed as means±SD.

3. RESULTS AND DISCUSSION

3.1 Film appearance

Figure 1 shows the dried film samples. The films were odourless and transparent. The films shrunk during drying, and the edges of the films were brittle. Despite that, they have an acceptable appearance, and they could be peeled from the Teflon plates without damage.

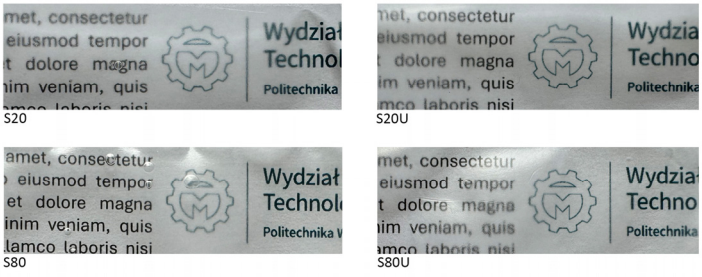

Figure 1: Film samples non-sonicated and sonicated treatment of starch film with 20% and 80% of GLY

3.2 Tensile properties

Average values of Young modulus (YM), tensile strength (TS), and elongation at break (EaB) are summarized in Table 2. The changes of YM, TS, and EaB are shown in Figure 2. The YM and TS decrease with the addition of GLY plasticizer. At the same time, the values of EaB increase, which is related to the higher flexibility of films with higher GLY content.

There is a slight increase in TS and EaB for low GLY values and a decrease in EaB for higher GLY values. For example, values of TS increased by approximately 20% after ultrasonication of starch-based films with 20% and 40% of GLY as a plasticizer. This observation contrasts with (Garcia-Hernandez, Vernon-Carter & Alvarez-Ramirez, 2017). Garcia-Hernadez et al. where the authors observed a decrease in TS and EaB with the sonification time.

Table 2: Mechanical properties of starch-based films: thickness (h), Young modulus (YM), tensile strength (TS), elongation at break (%)

Sample abbreviation	h [mm]	YM [MPa]	TS [MPa]	EaB [%]
S20	0.057±0.016	1313±53	36.4±2.0	4.8±1.1
S40	0.146±0.020	52.5±19.7	4.83±1.08	48±1
S60	0.114±0.007	15.8±2.3	2.66±0.37	70±2
S80	0.157±0.012	8.0±4.1	1.49±0.59	53±1
S20U	0.054±0.005	906±24	42.7±1.2	8.2±0.9
S40U	0.113±0.010	72.8±14.9	5.99±1.18	49±1
S60U	0.134±0.013	19.4±8.3	2.65±0.30	63±2
S80U	0.138±0.010	7.5±0.9	1.35±0.39	45±1

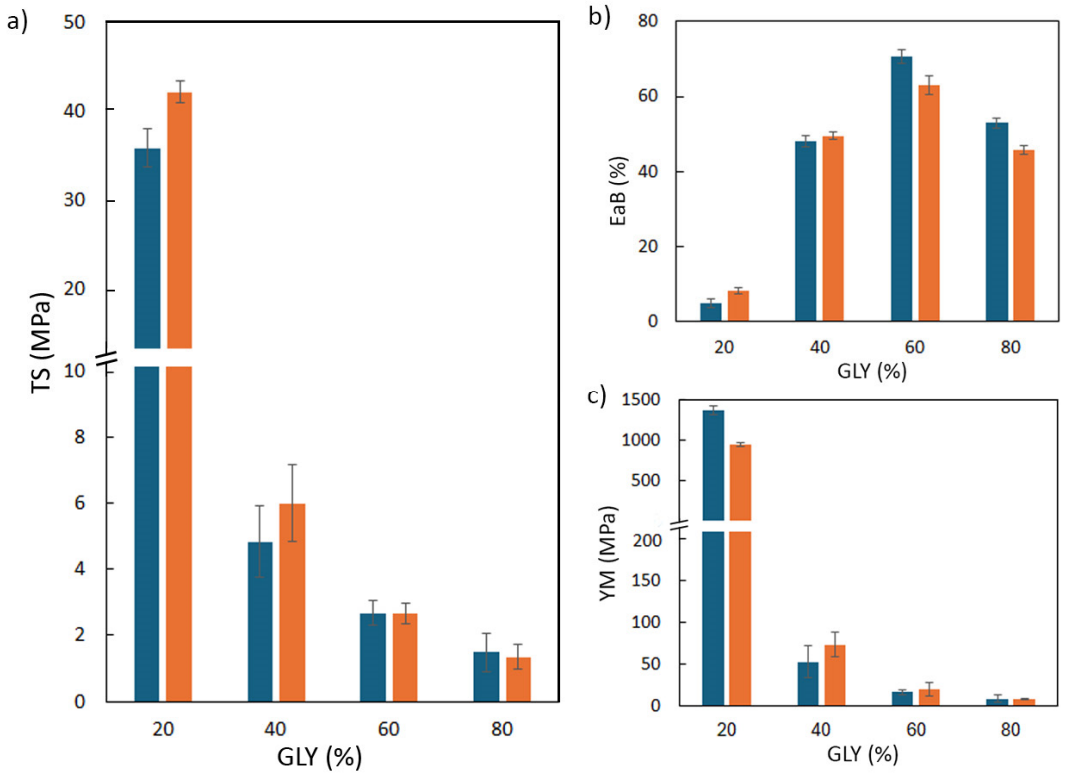

Figure 2: Changes of TS, EaB, and YM prior (blue column) and after sonification (orange column)

3.3 Surface properties

The results of the water contact angle, WCA, measurements are shown in Figure 3. The WCA values indicated the hydrophilicity (CA < 90) or hydrophobicity (CA > 90) of the surface (Sganzerla et al, 2020). Strach-based materials are mostly hydrophilic with great water affinity due to hydroxyl groups in the starch molecules. The values of WCA are in the range of 79.7±2.0 and 95.6±1.3° for S20 and S60U, respectively. The sonification treatment influences the hydrophobic character of the surface. After the sonification process, the WCA values of films with 20%, 40%, and 80% GLY content exceeded slightly 90° and amounted to 94.8+2.5, 95.6±1.3, and 91.4°, respectively. This observation agrees with (Abral et al., 2019). On the other hand, Gracia-Hernandes et al. reported decreased wettability and reduced WCA with the sonification treatment time (Garcia-Hernandez, Vernon-Carter & Alvarez-Ramirez, 2017).

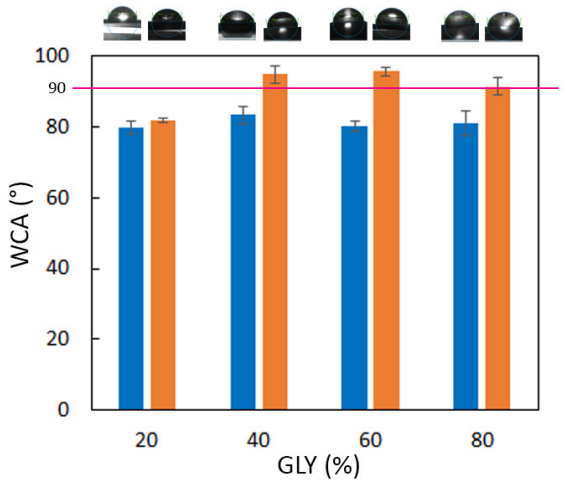

Figure 3: Changes of WCA prior (blue column) and after sonification (orange column)

The FTIR spectra in the range of 500 to 4000 cm^{-1} and the fingerprint region of the developed film are presented in Figure 4. Generally, the film spectra seem similar, and sonification does not affect the FTIR spectra of films. In terms of band shapes and intensity, slight changes may be observed. The typical characteristic peaks of native starch are also revealed in starch-based films. A broadband around 3300 cm^{-1} is attributed to O—H stretching vibrations. The peak near 2910 cm^{-1} is attributed to the C—H stretching vibration present in the starch molecules (Bergo, Sobral & Prison, 2010). The bands in the fingerprint region can be assigned to C–O bond stretching (Vicentini et al., 2005). Two peaks might be observed in this region: at 1015 and 994 cm^{-1}. The peak observed at 1015 cm^{-1} appears as a shoulder lower GLY concentration (S20 and S20U films) and becomes more prominent and presented for films with higher GLY content.

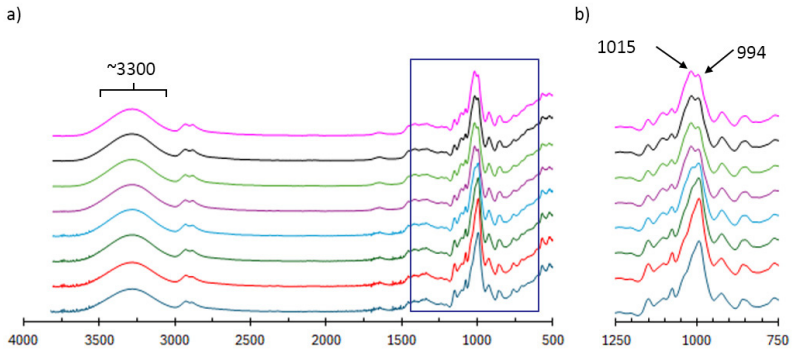

Figure 4: FTIR spectra for a) S20 (blue line), S20U (red line), S40 (dark green line), S40U (light blue line), S60 (violet line), S60U (light green line, S80 (black line) and S80U (pink line); b) fingerprint region

Table 3 summarizes the roughness profiles of the developed film surface, Sa. *S*a indicates the average roughness of a surface – the difference in height of each point compared to the arithmetical mean of the

surface. The *Sa* parameter decreases with the addition of GLY from 2.88 µm to 4.04 for S20 and S60, respectively. The *Sa* parameter is lower for S80 and equals 2.77 µm. The sonification treatment reduces the *Sa* values and the SEM analysis confirmed this observation.

Table 3: Surface roughness parameters of developed films

Sample abbreviation	***Sa*** **[µm]**
S20	2.88
S40	3.06
S60	4.04
S80	2.77
S20U	2.56
S40U	2.94
S60U	2.92
S80U	2.98

Figure 4 presents the samples' scanning electron microscopy (SEM) images. All the films showed smooth surfaces without cracks, breaks, or pores, indicating the excellent integrity of starch films. In the non-sonicated films, some impurities can be observed. This is related to the presence of partially gelatinized starch (Abral et al, 2019). This agrees with Liu et al, who reported continuous and uniform texture of the potato starch films after ultrasonic treatment (Liu et al., 2018b). Liu et al. suggested that the film-forming components become more compatible after ultrasonication treatment – ultrasonication results in a more regular, smothered surface without pores, cracks, and agglomerates.

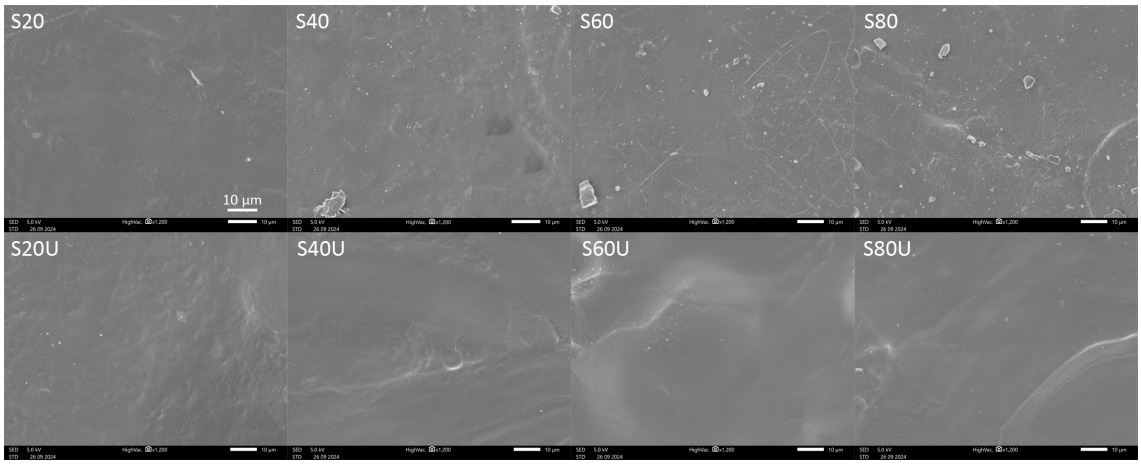

Figure 4: SEM structure photos of the films before (upper row) and after sonification (bottom row)

4. CONCLUSIONS

The study explores the effects of GLY content and sonification treatment on the properties of potato starch films. Adding GLY enhanced the films' flexibility, as evidenced by increased elongation at break, but decreased both tensile strength and Young's modulus. Sonification positively impacted mechanical properties for low GLY concentrations, increasing tensile strength and elongation at break.

The sonification treatment influences surface properties and increases hydrophobicity for treated films with higher GLY content. While the FTIR spectra remained largely unaffected by sonification, surface roughness (*Sa*) decreased, suggesting that sonification causes microstructural change. SEM images revealed smoother, more uniform film surfaces post-sonication.

In conclusion, the study demonstrates that ultrasonication can be a valuable tool for optimizing biodegradable starch-based films' mechanical, structural, and surface properties, particularly when combined with glycerol as a plasticizer, making these films potential candidates for packaging applications.

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