

The Acidic Deep Eutectic Solvents for Starch Plasticization

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ABSTRACT

For wider use of starch in the production of biodegradable plastics, it is necessary to search for new effective plasticizers. In this study, the effect of seven deep eutectic solvents (DES) based on choline chloride and carboxylic acid (levulinic, lactic, malonic, itaconic, malic, tartaric and citric) on the properties of potato starch were investigated. For this purpose, the thermal and rheological properties of starch/DES mixtures were evaluated. The viscosity of aqueous starch/DES solutions was determined. Subsequently, the starch films were obtained by casting. To determine the plasticization efficiency, mechanical properties, crystallinity and moisture resistance were evaluated. The correlation between the properties of the starch films and the molecular structure of DES acidic component was revealed.

Keywords: starch; deep eutectic solvent; plasticization; carboxylic acid.

INTRODUCTION

Deep eutectic solvents (DESs) are a quite new group of green solvents. They consist of two components: a hydrogen bond donor (HBD) and an acceptor (HBA). Quaternary ammonium salts, such as choline chloride are commonly used as hydrogen bond acceptors. Amines, polyols and carboxylic acids can be used as hydrogen bond donor. The characteristic feature of DES is that the melting point of the mixture is much lower than the melting temperature of the substances forming it. However, they differ from classical eutectic mixtures. Therefore, Martins et al. proposed a slightly different definition - "mixture of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from ideality" [1]. DESs exhibit high thermal stability, low volatility, low vapor pressure, adjustable polarity, and are easy to obtain. Although, depending on the components, they can vary significantly in their properties. The choline chloride : urea system (molar ratio of 1 : 2) was first described by Abbott in 2003 [2]. Since then, numerous DESs and their

applications have been described. It is estimated that there are up to 10^8 binary possible DES systems, making it possible to tailor the solvent for a specific application [3]. The use of deep eutectic solvents in many fields is being explored, among others nanomaterials synthesis, biomass processing, separation and gas capture, pharmaceutical and medical systems, biocatalysis, and polymer chemistry (synthesis and material modifications).

Carboxylic acids are a large and diverse group of compounds, and numerous acidic deep eutectic solvents have been reported so far. Many systems based on oxalic [4], malonic [5], malic [6], tartaric [7], itaconic [8], citric [9], levulinic [10], lactic [11], formic [12], and other acids, have been reported. The effect of HBD selection on the properties of the obtained DES was described. It was pointed out that the formation and properties of DES were significantly affected by the number and type of functional groups in the acid molecule, and using multifunctional HBDs allowed to obtain stable deep eutectic solvents at relatively low temperatures. The decrease in eutectic temperature depended on the molecule size, as well as the number and type of functional

groups [13, 14]. In addition, in the case of DES based on carboxylic acids obtained by mixing at elevated temperatures, the formation of esters is possible, which affects the properties of the solvent [15, 16].

Starch is a widely available biopolymer, that could be a raw material for the production of biodegradable materials. Its extensive inter- and intramolecular hydrogen bonding network results in a high melting point (close to the degradation temperature), which prevents it from being processed by methods typical for thermoplastics. In the presence of low molecular weight substances capable of forming hydrogen bonds with the polysaccharide (such as water or glycerol) at elevated temperatures, the granular structure is destroyed, and the crystallinity and melting are point reduced. The product of such a process is called thermoplastic starch. It is essential to select an appropriate plasticizer that effectively lowers the starch gelatinization temperature, does not tend to migrate on the surface, and limits the retrogradation (recrystallization) of starch [17].

In recent years, there have been publications on the use of deep eutectic solvents for starch treatment. The DES was applied to obtain starch nanostructures [18, 19], study starch solubility [20–27], plasticization [21, 24, 26, 28–44], and obtained films with various fillers [45–49]. Plasticization with acidic DESs was attempted. Zdanowicz and Szychaj tested the plasticization of starch with systems based on choline chloride and acids (citric and succinic) using a hydraulic press – under the test conditions, the starch degraded [21]. In another study DESs based on imidazole and acids (citric and malic) were applied. However, the obtained films were brittle [24]. Sousa et al. investigated using DES (choline chloride : oxalic acid and choline chloride : ascorbic acid) to plasticize cassava starch. They

obtained films with properties similar to glycerol-plasticized starch [37]. The use of a mixture of choline chloride : malic acid (molar ratio 1:1) to obtain starch films by casting was also described, and the effect of plasticization conditions was determined [44].

In this work, the effect of deep eutectic solvents based on choline chloride and seven carboxylic acids (levulinic, lactic, malonic, itaconic, malic, tartaric and citric) was studied. The correlation between the properties of the starch films and the molecular structure of DES acidic component has been determined.

MATERIALS AND METHODS

Materials

In the research the following substances were used: potato starch (S) with the amylose/ amylopectin ratio 26/74 wt% (Zetpezet Piła, Poland), choline chloride (C) (Sigma-Aldrich, China), levulinic acid (Le) (Sigma-Aldrich, Germany) (Sigma-Aldrich, Germany), lactic acid (La) (POCh, Poland), malonic acid (Mo) (Sigma-Aldrich, Germany), itaconic acid (I) (Alfa Aesar, Germany), malic acid (Ma) (Sigma-Aldrich, Germany), tartaric acid (T) (Chempur, Poland), and citric acid monohydrate (C) (Stanlab, Poland). The structure of acids used as DES components was presented in Figure 1.

Sample preparation

DES was prepared by placing choline chloride and carboxylic acid (the molar ratios given in Table 1) in a sealed glass container and mixing with a magnetic stirrer in a water bath at 80 °C to obtain a homogeneous liquid. DES abbreviations are formed as follows: the first letter is taken from

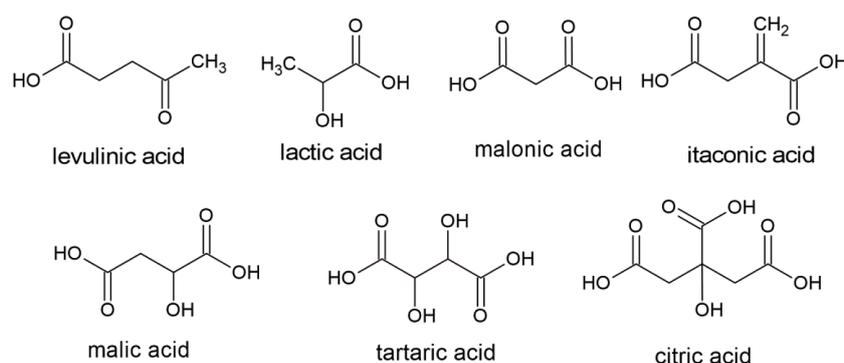


Figure 1. The structure of carboxylic acids – components of DESs

Table 1. The composition of DES and starch/DES systems

HBA	Choline chloride						
HBD	Levulinic acid	Lactic acid	Malonic acid	Itaconic acid	Malic acid	Tartaric acid	Citric acid
HBA:HBD molar ratio	1:2	1:2	1:1	1:1	1:1	2:1	7:3
Number of carboxylic groups in HBD	1	1	2	2	2	2	3
Number of hydroxyl groups in HBD	-	1	-	-	1	2	1
Acid per starch (g)	0.27	0.24	0.18	0.21	0.21	0.15	0.17
Acid/AGU* molar ratio	0.37	0.44	0.27	0.26	0.26	0.16	0.13
pH of DES solution**	2.73	2.18	2.07	2.40	2.30	2.20	2.28

Note: * AGU – anhydroglucose unit; ** 1.5 wt%, i.e. the same as in starch/DES solution.

choline chloride (C), and the second letter is from a carboxylic acid (Le, La, Mo, I, Ma, T or C). The mixture of starch and deep eutectic solvent was ground in mortar, placed in the glass vial, and sealed for 24 hours before testing.

For the film preparation potato starch, and DES (30 wt% per dry starch) were placed in distilled water, and mixed with a mechanical stirrer for 30 minutes at 90 °C (rpm 350). Starch/DES solution (115 ml) was poured into Petri dishes (140 mm diameter) and dried for 24 h at 60 °C. The solutions were marked with “R” in the abbreviation. All films were conditioned in climate chamber (23 °C, RH%) at least 24 hours before testing. The film samples were marked with “F” in the abbreviation.

Methods

Solubility test

Mixtures of starch with DES (5 wt% of polysaccharide) were prepared and sealed in vials. After 24 h, the dispersions were placed in an oven for 60 minutes at 90, 110 and 130 °C. After this time, microphotographs with optical microscope TetraView model #44347 (Celestron) were taken.

Thermal analysis

The modulated differential scanning calorimetry was used to determine the gelatinization temperature and enthalpy of starch/DES mixtures. The system (30 wt% of DES) was placed in the aluminum hermetic pan (ca. 10 mg sample). The tests were performed using DSC Q100 (TA Instruments) in the temperature range from -70 up to 220 °C, and a heating rate of 3 °C/min (1 cycle).

Rheology

Starch/DES mixtures (30, 50, and 70 wt% DES) were prepared and sealed in vials 24 h before testing. The rheological behavior (complex viscosity as a function of temperature) was determined in the air atmosphere, using rheometer Discovery-1 (TA Instruments) equipped with a parallel plate system. The test was performed with a temperature range of 50–220 °C, the heating rate of 10 °C/min, and a frequency 1 Hz.

Viscometry

The viscosity of the aqueous starch/DES solutions after polysaccharide gelatinization (containing 30 wt. % DES based on dry polysaccharide) was tested with Brookfield viscometer, model RVT (Brookfield Engineering Laboratories) at 60 °C. As a reference, a solution of starch gelatinized under the same conditions but without DES was tested (R_S).

Tensile testing

Mechanical properties (maximal tensile strength, elongation at break, Young’s modulus) of starch/DES films were determined using Instron 5982 with Bluehill 3 software (following the standard PN-EN ISO 527-3). The initial gap separation was 50 mm and the crosshead speed was 10 mm/min and with load cell 1 kN. Seven strips (5×100 mm, ca. 0.3 mm thick) of the starch film were tested.

Infrared spectroscopy (FTIR-ATR)

The FTIR spectra of starch/DES mixtures and films were performed with a Nexus spectrometer (Thermo Nicolet Corp., USA) equipped with ATR. Each sample was scanned 32 times in a wave number range from 4000 to 400 cm⁻¹. The spectra were analyzed with OMNIC software.

XRD

The XRD diffractograms of starch/DES films were performed using a PANalytical Empyrean X-ray diffractometer, with Cu K α radiation. Before the test, films were for 24 h in a climate chamber.

Visual evaluation and gloss

The gloss of starch films was measured using a goniophotometer from Rhopoint Instrument, model IQ 20/60/85. Measurement was performed in 3 places for each sample.

Moisture absorption

The film samples (10x20 mm) were dried for 24 h at 60 °C and then weighed (m_0). They were

reweighted (m_w) after 1, 3, 24, 48, and 168 hours of conditioning in a climate chamber (23 °C, RH 50%). The moisture absorption was calculated from the equation (1).

$$\text{moisture absorption} = \frac{m_w - m_0}{m_0} \cdot 100\% \quad (1)$$

Contact angle

The contact angle of starch/DES films was measured with a Dataphysics OCA 15EC optical contact angle analyzer. One drop of distilled water (8 ml) was placed on the film surface and the contact angle was measured using DSA4 software. For each sample, at least three measurements were performed.

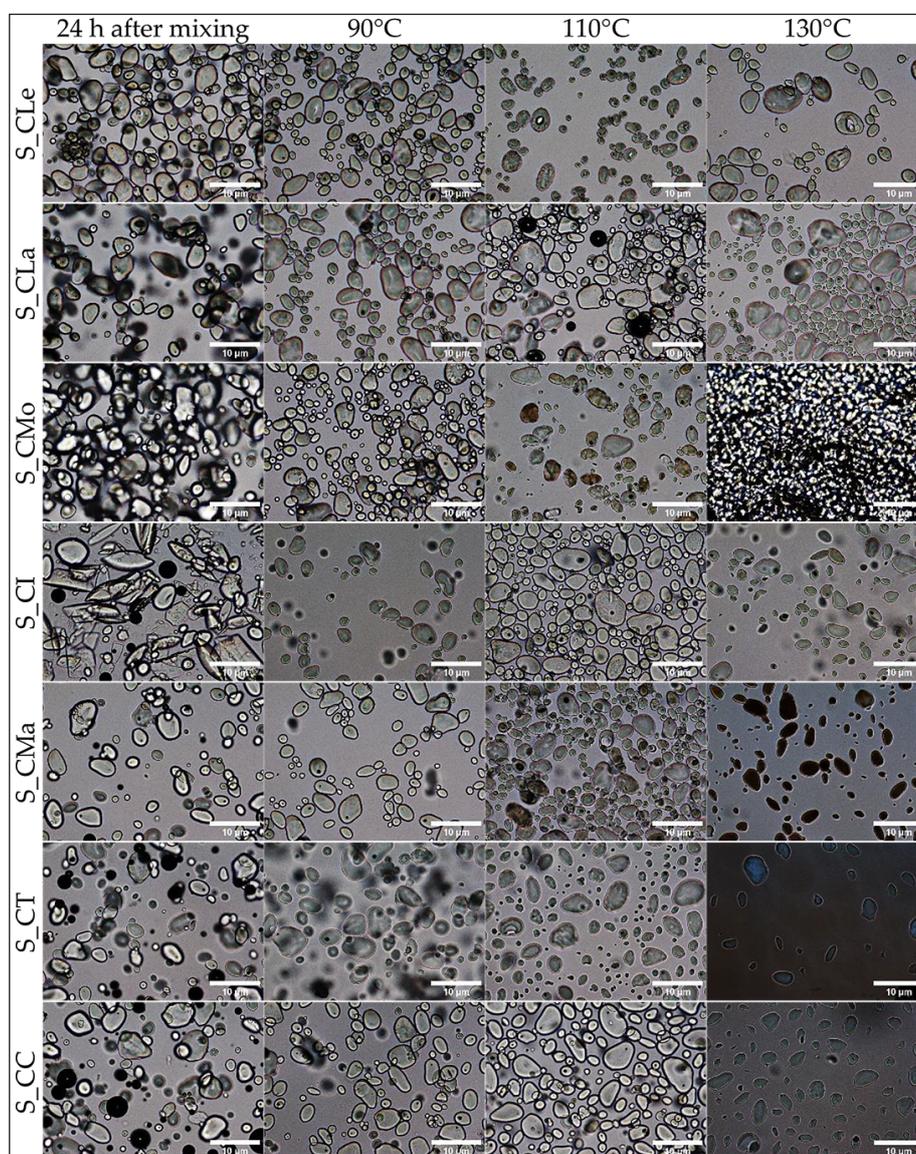


Figure 2. Microphotographs of starch/DES mixtures (95 wt% DES) before the test, and after 60 minutes at 90, 110, and 130 °C

RESULTS AND DISCUSSION

Starch solubility in DESs

Microphotographs of starch/DES mixtures treated at elevated temperatures were collected in Figure 2. For all tested systems, the starch granules did not dissolve in DES at room temperature. In the case of the mixture of starch with DES containing CI, the crystals were observed, indicating that the DES component recrystallized. No major changes were observed at 90 °C, only the crystals of DES with itaconic acid melted. At 110 °C, dark granules were visible in the mixtures containing DES with malonic and malic acid, indicating starch degradation. At 130 °C, the sample containing malonic acid fully degraded, making it impossible to observe granules. In the case of mixtures with malic, tartaric, and citric acids, dark granules (signs of degradation) were observed. None of the selected DES exhibited starch-dissolving ability under testing conditions. Moreover, the DES system with malonic acid showed the lowest thermal stability, which significantly limited its application. In the literature, other systems for starch dissolution have been described. The most effective solvents were urea-based deep eutectic solvents. They led to the full destruction of the granules at the same time without taking out signs of starch degradation (yellowish color of the mixture) [21,28] in contrast to carboxylic acid-based systems.

Rheology

The rheological study of starch/DES with various plasticizer content, as a function of temperature, was presented in Figure 3. In the case of two systems (S_CI_30 and S_CC_30), the test could not be performed because the viscosity of the samples was too high. Generally, the complex viscosity of the 50 and 70% mixtures at lower temperatures exhibited a slight decrease or plateau (except S_CMo_50), but after exceeding ca. 100°C sharply increased, which was probably the result of starch swelling and gelatinization. Moreover, the complex viscosity depended directly on starch content (decreased with DES content increase). The exception was a mixture with levulinic acid - the mixture with the highest starch content exhibited the lowest viscosity. An unusual curve pattern was noted for the systems with DES containing malonic acid. It could probably be the result of acid decarboxylation and

starch degradation, as it was already observed in solubility tests. The differences in complex viscosity values were also apparent. Comparing the peak values of the mixtures containing 50 wt% DES (Figure 4) the lowest viscosity exhibited S_CT_50, and the highest was noted for S_CLa_50.

Modulated differential scanning calorimetry (MDSC)

Modulated differential scanning calorimetry enables to determination of the effect of DES addition on the thermal properties of starch. Figure 5 shows the temperature (T_{gel}) and enthalpy (ΔH) of starch gelatinization in starch/DES mixtures (30 wt% of plasticizer) and films. For all systems with DES, a reduction of gelatinization temperature was observed (compared to a reference sample, i.e. neat potato starch). The lowest T_{gel} was noted for the mixture with malonic acid, and the highest for levulinic acid. There was a noticeable trend among dicarboxylic acids – with an increase in the number of hydroxyl groups in the acid molecule, the gelation temperature of starch increased. A reduction of gelatinization enthalpy also occurred. The results indicate that the presence of DESs also contributed to lowering the enthalpy of the process. It demonstrates the beneficial effect of DES on starch gelatinization. The highest ΔH values were obtained for CC, and the lowest for CMA. This may be due to two effects - the size of the molecules and the number of groups able to interact with starch macromolecules. Smaller molecules can more easily penetrate the granule and interact with the hydroxyl groups of the starch, which promotes gelatinization.

Viscosity

The viscosity measurement of gelatinized starch/DES aqueous solutions (Figure 6) could allow to determine the interactions between the polysaccharide and plasticizer. Introducing DES resulted in a significant reduction in the viscosity of the solution after gelatinization in comparison with a neat starch solution. The system containing levulinic acid showed the highest viscosity among the tested systems. This DES exhibited the highest pH (Table 1), thus the starch was slightly less susceptible to hydrolysis caused by the acidic medium. Compared to R_S_CLe, the other solutions achieved significantly lower viscosities. The starch solutions with DES

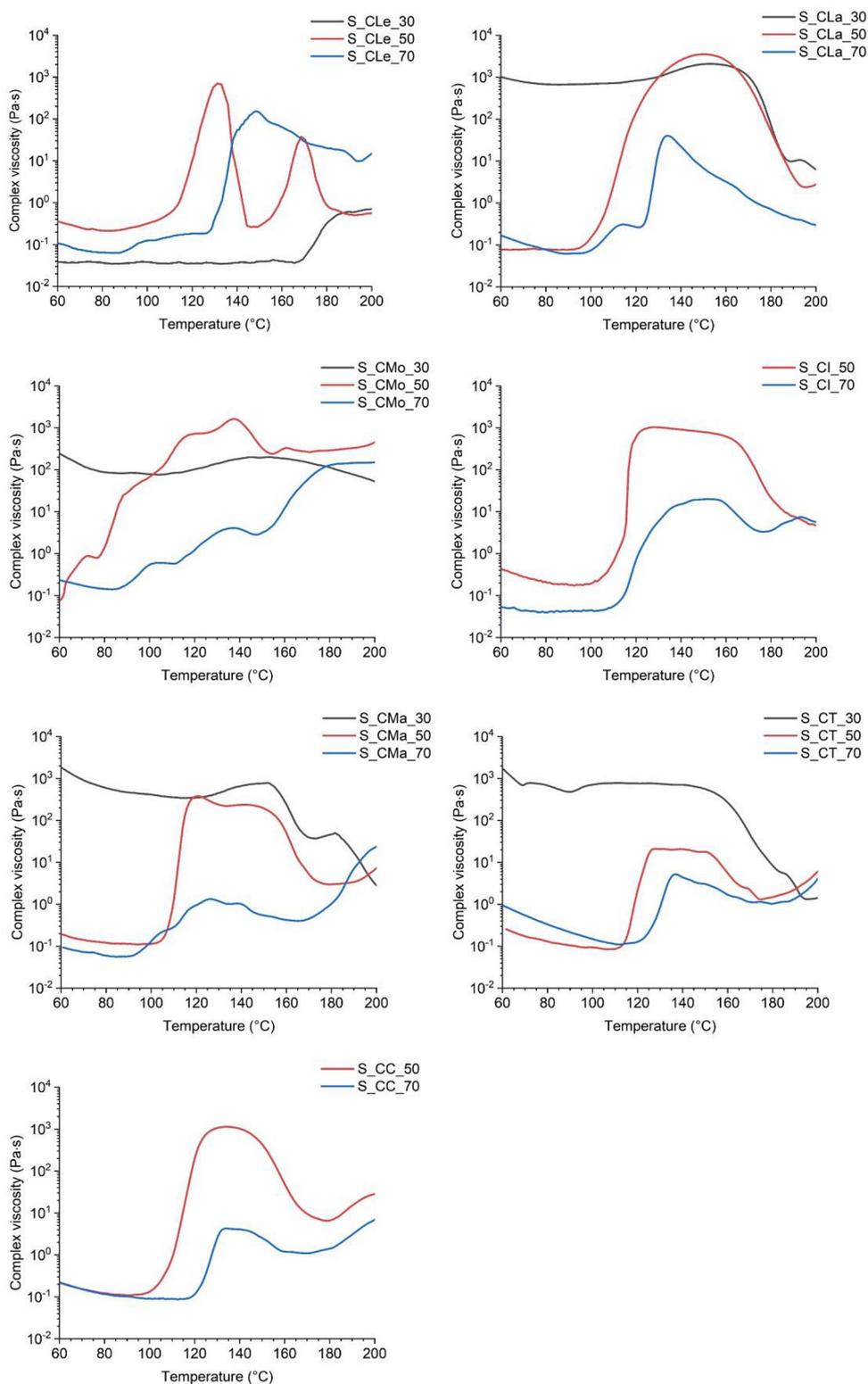


Figure 3. The rheological curves of starch/DES with various plasticizer content (30, 50, and 70 wt%)

containing malonic, citric, and tartaric acids exhibited the lowest and similar viscosity values, although the differences in pH were noticeable. On the other hand, in the case of the solutions with DES containing malic acid or citric acid,

the viscosities were noticeably different despite the pH values differing only slightly. This indicates that acidity (and the resultant possibility of starch hydrolysis) was not the only determinant of starch solution viscosity, and probably other

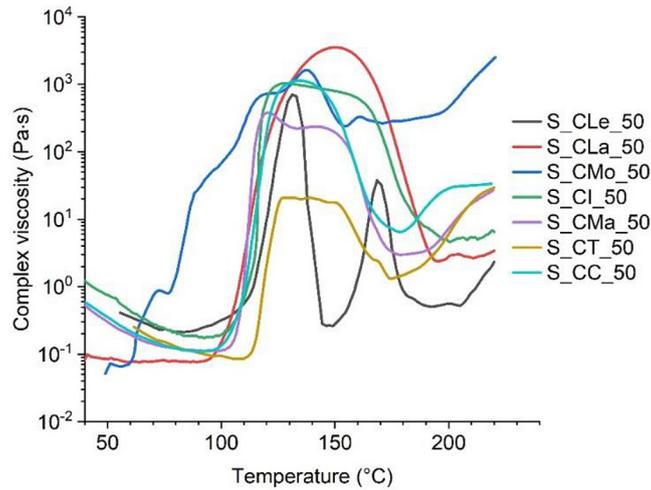


Figure 4. Rheology curves for starch mixtures (50% plasticizer) with various DESs

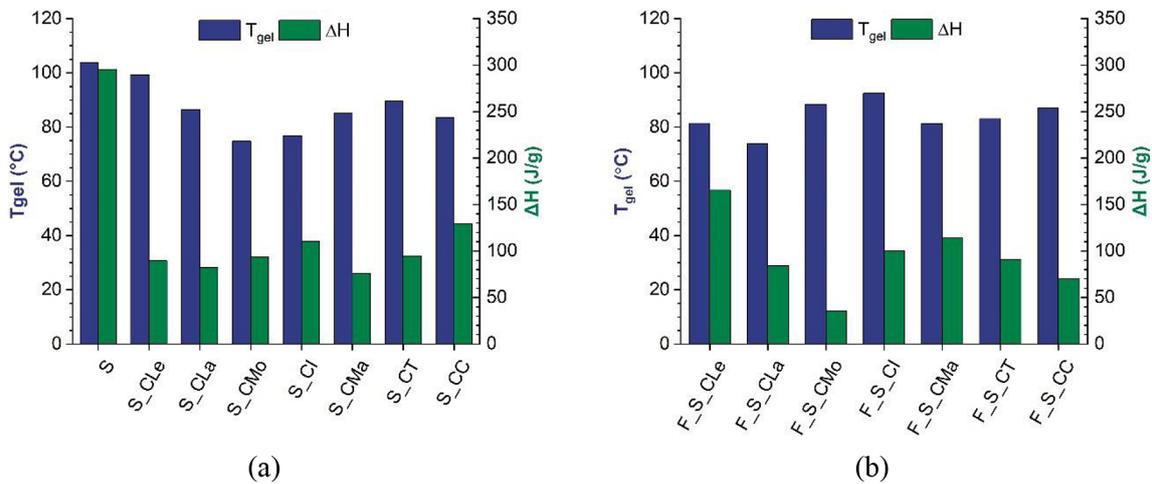


Figure 5. The starch gelatinization temperature (T_{gel}) and enthalpy (ΔH) in starch/DES mixtures (a) and films (b)

interactions between DES components and polysaccharides occurred. Another factor worth considering is the amount of acid per starch, which is a result of the different choline chloride/acid molar ratios of DES systems. The acid/starch molar ratio for the solution with DES containing levulinic acid was significantly higher than this for citric acid, however the latter exhibited much lower viscosity. This indicates that the most important factor could not be the acid content, but the amount of (i) hydroxyl groups that could interact with starch via hydrogen bonds and (ii) carboxyl groups that can undergo esterification reactions with the polysaccharide. In both cases, it results in reduced interactions between starch macromolecules (repulsion of starch chains) that can lead to reduced viscosity. In the case of multi-carboxylic acids, there is even the

possibility of starch crosslinking reaction, however, its confirmation requires additional tests (e.g., mechanical properties). In another work [41], the effect of the type of CMA addition, i.e. after or before starch gelatinization was determined. Introducing DES based on choline chloride and malic acid after starch gelatinization resulted in reduced viscosity, indicating the interaction between polysaccharide and plasticizer molecules.

Mechanical test

In Figure 4 the results of mechanical tests were presented. The majority of tested films exhibited similar tensile strength values – ca. 6 MPa (Figure 7a). Only the samples plasticized with DES containing lactic and citric acid distinguished

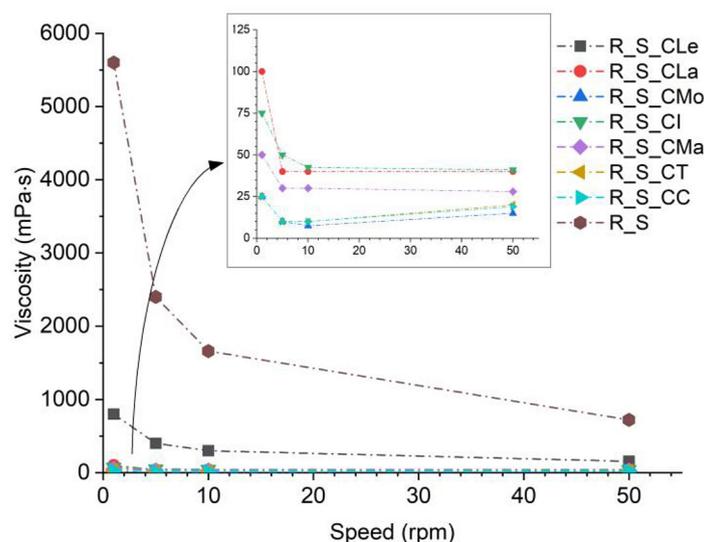


Figure 6. The viscosity of starch/DES solutions

with higher and lower values - ca. 4 and 9 MPa, respectively. In the case of Young’s modulus, the differences were more significant (Figure 7c), however, again the materials with DES containing citric acid exhibited the highest elastic modulus value. The high strength of F_S_CC could indicate the crosslinking of starch with citric acid (which contains three carboxylic groups in a molecule). In a study examining the degree of starch substitution with various carboxylic acids (citric, succinic, malic and 1,2,3,4-butanetetracarboxylic), a correlation between the number of carboxyl groups and the properties of the films was indicated, i.e. the more carboxyl groups, the

higher the degree of substitution and mechanical properties of the materials obtained [50]. Comparing dicarboxylic acid-based DES plasticized films, it can be seen that although they have similar tensile strength values, they show differences in Young’s modulus and elongation at break. The Young’s modulus values are arranged as follows $F_S_CI > F_S_CMo > F_S_CT > F_S_CMa$. In the case of F_S_CI material, its high elastic modulus could be the result of partial plasticizer crystallization, which could act as a reinforcement filler. Interestingly, the materials with DES containing malic acid exhibited tensile strength similar to the others, but significantly higher

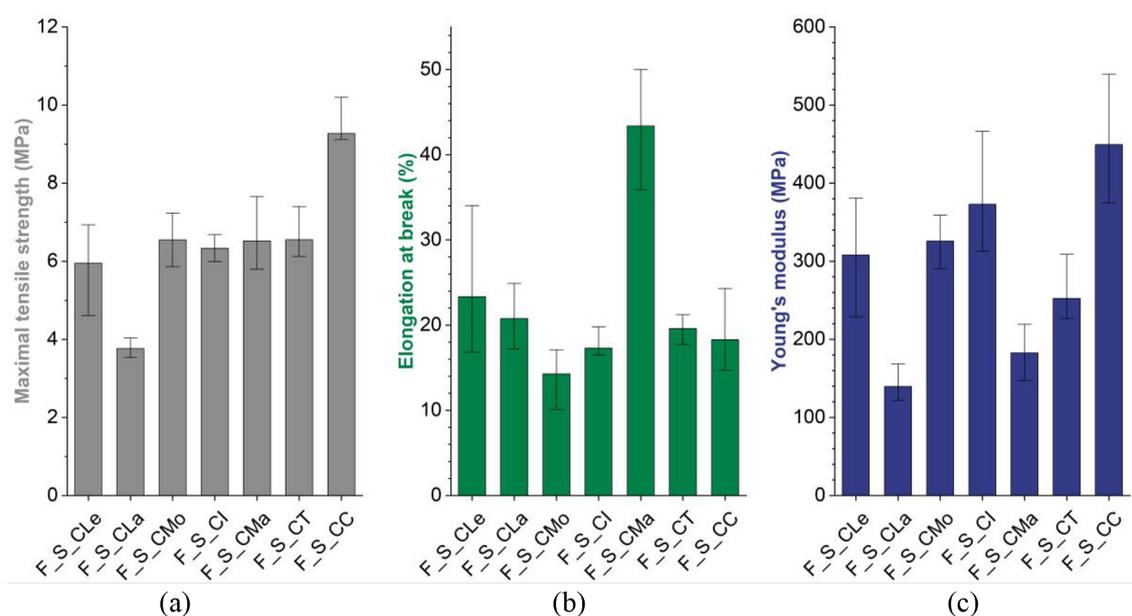


Figure 7. Mechanical properties of starch/DES films

(doubled) elongation at break (Figure 7b). That indicates effective plasticization.

FTIR

Infrared spectroscopy was used to determine the reaction between plasticizer and starch. Choline chloride, organic acids and DES spectra were performed first (Figure 8). Shifts in the

bands corresponding to carboxyl groups toward higher wave number values were observed. Such a trend has also been reported in other publications [51,52]. DES was prepared by mixing at elevated temperatures. Other studies [15,16] have indicated that using this method results in partial esterification of organic acids with choline chloride and the observed shifts may confirm this. For the sake of clarity in Figure 9 the full

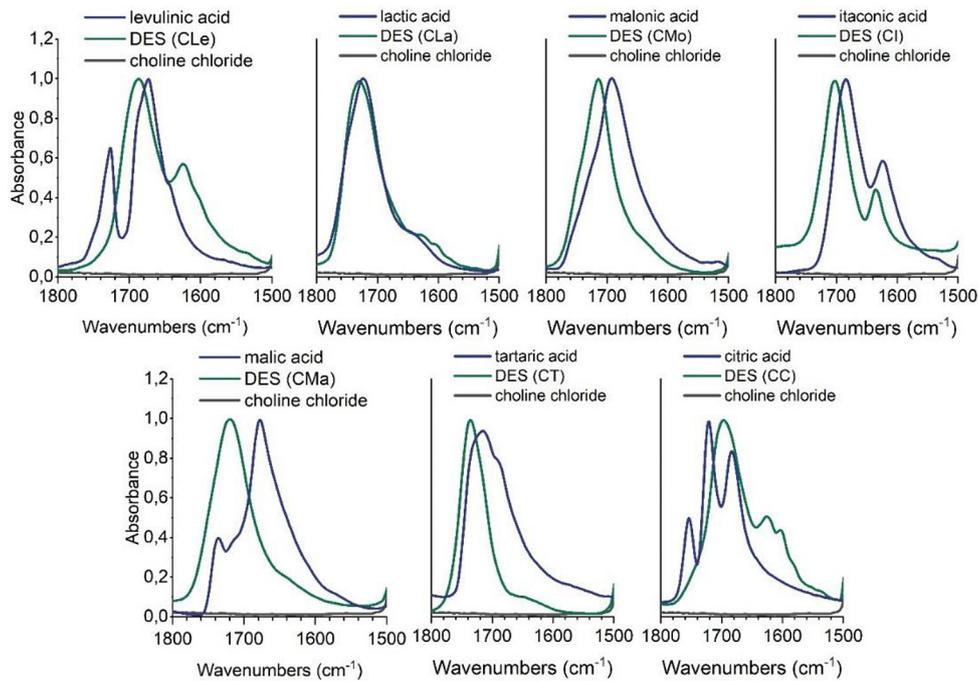


Figure 8. The FTIR-ATR spectra of choline chloride, organic acids and DESs

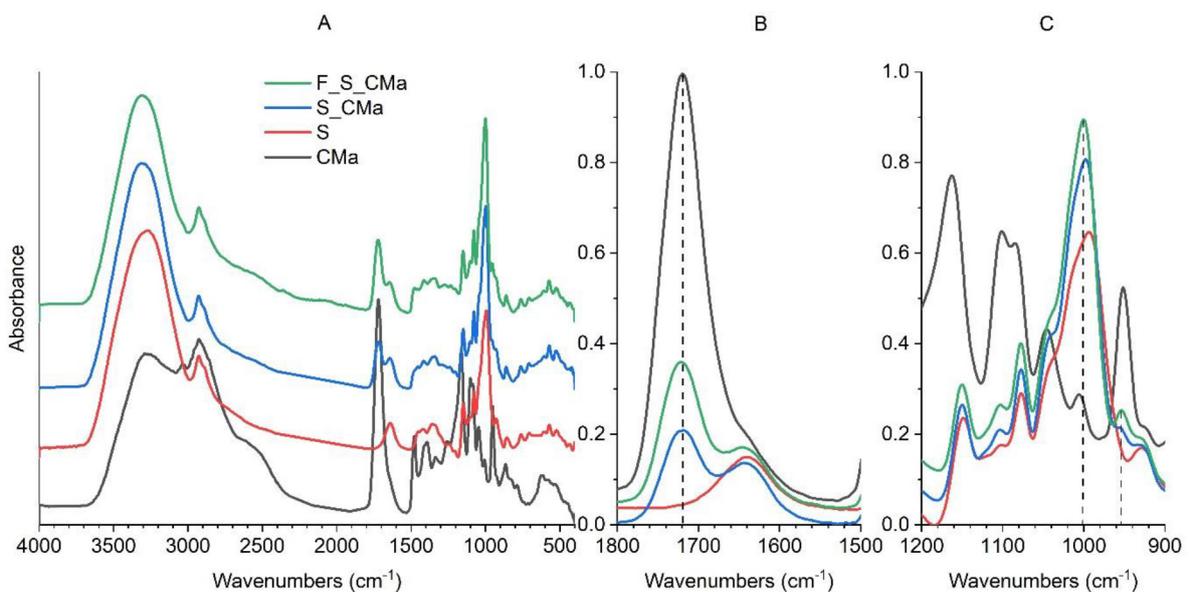


Figure 9. The FTIR-ATR spectra of DES (choline chloride : malic acid 1:1 – CMa), potato starch (S), starch/DES mixture (30 wt.% of DES – S_CMa) and starch film plasticized with DES (F_S_CMa)

FTIR spectra of the starch/DES (choline chloride : malic acid 1:1) system were shown. For starch-based mixtures and films, the characteristic bands of starch ($\sim 3000\text{ cm}^{-1}$ – associated to OH, $\sim 2900\text{ cm}^{-1}$ – CH_2 , $\sim 1620\text{ cm}^{-1}$ – water, $\sim 1000\text{ cm}^{-1}$ – C-O-C) and a new band, corresponding to carbonyl groups, from the plasticizer were observed. There was no significant shift of the carbonyl band, thus the esterification/cross-linking of starch could not be confirmed (probably because of the low degree of conversion). However, an increase in the intensity of this band was noticed.

XRD

To study the effect of DES on the crystallinity of starch materials, XRD diffraction measurements were performed (Figure 10). The native potato starch exhibits B-type crystallinity, typical for the tuber, with characteristic signals at ca. 6° ,

15° , 17° , 20° , 22° , 24° and 26° . For DES plasticized films with lactic acid, malonic acid, and tartaric acid, a peak residue of about 5° was still observed. Many sharp signals could be noticed for the films with DES containing itaconic acid, which directly indicated partial crystallization of the plasticizer. The highest content of the amorphous phase exhibited films F_S_CLe and F_S_CMa. The results of XRD measurements correlate to the mechanical test results.

Visual evaluation and gloss

Appearance and gloss are important performance characteristics of the films. The starch films differed considering transparency and gloss. Figure 11 presents the images of films plasticized with acidic DESs. Two materials were not transparent – the film with DES containing levulinic acid was milky (which could be explained by the

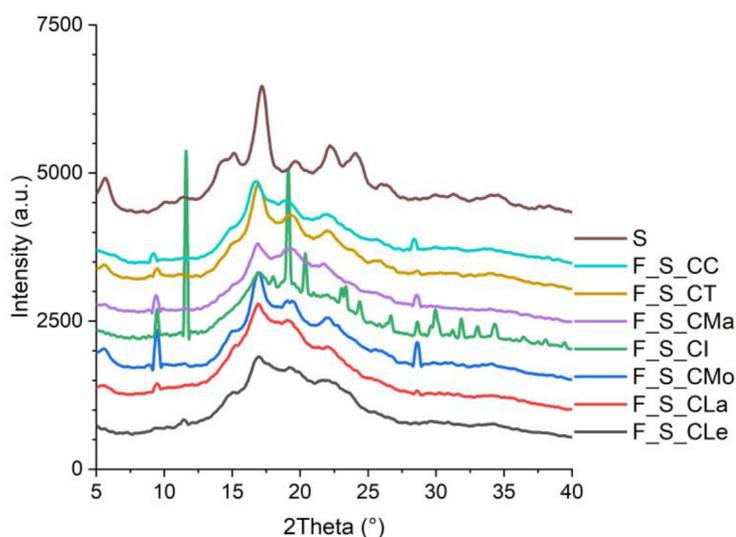


Figure 10. XRD diffractograms of starch/DES films

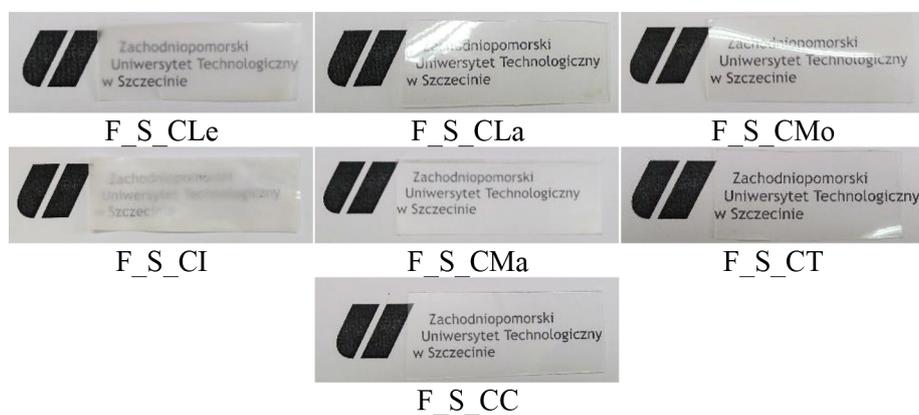


Figure 11. Photographs of starch films obtained by casting and plasticized with various acidic DESs

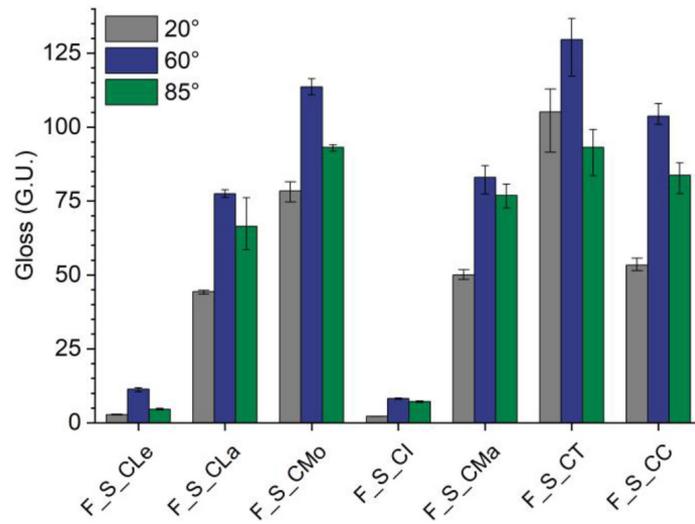


Figure 12. Gloss of starch films plasticized with various acidic DESs

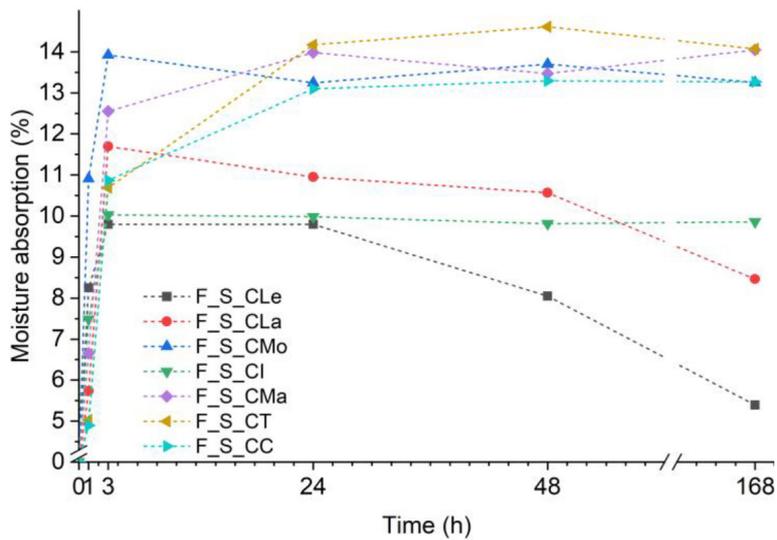


Figure 13. Moisture absorption of starch films plasticized with acidic DESs

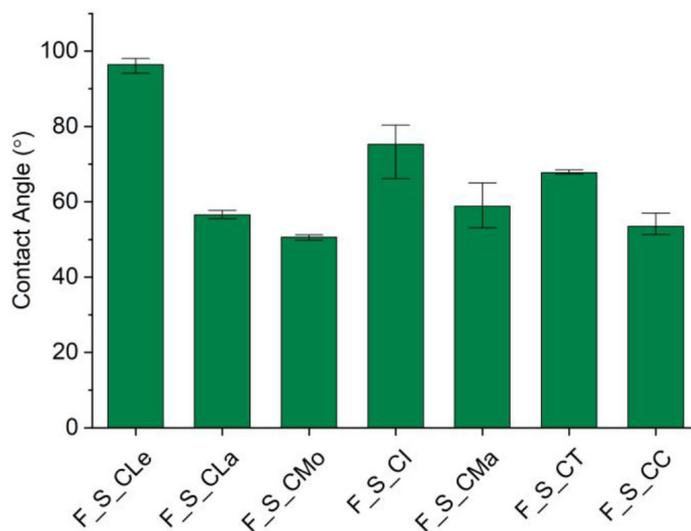


Figure 14. Contact angles of starch/DES films

presence of two phases noticed in Figure 3), and for film plasticized with DES containing itaconic acid the crystallized plasticizer was noticeable.

Additionally, the gloss measurements were performed (Figure 12). The film with DES containing tartaric acid exhibited the highest value of this parameter. Slightly lower values were noted for materials with DES containing citric and malonic acid. As it was expected, for the opaque films (with levulinic and itaconic acids) the lowest gloss values were reported.

Moisture absorption and wettability

Moisture absorption allows to determine the films' susceptibility to environmental conditions. The moisture absorption of materials with DES containing lactic acid and levulinic acid initially increased but after ca. 24 h gradually decreased (Figure 13). This was probably due to the migration of plasticizer (lactic and levulinic acid were the smallest HDB tested), which was not a beneficial phenomenon. The moisture absorption of the system with DES containing itaconic acid stabilized after ca. 3 h - this could be due to the presence of plasticizer crystals. The wettability of the starch films was measured (Figure 14). The sample F_S_CLe exhibited the most hydrophobic character of the surface. The reason could be the presence of the plasticizer on the film surface. Similarly, the plasticizer crystals could be the reason for the relatively high contact angle of F_S_CI.

CONCLUSIONS

The acidic DESs were used as potential potato starch plasticizers. None of the DESs tested exhibited starch-dissolving ability. Similar observations were reported for other DES systems when one of the components was an acid. The presence of acidic DES containing carboxylic acids contributed to the reduction of starch gelatinization temperature and enthalpy. For DESs with dicarboxylic acid, with an increase in the number of hydroxyl groups, the gelation temperature increased. The decrease of aqueous starch/DES solution viscosity was noted, and its value depended on the pH and the structure of the acid molecule. Two systems (F_S_CLe and F_S_CI) did not form transparent films which limits their application. Moreover, for the systems containing DES with the lowest acid molecules, the plasticizer

migration was noted (F_S_CLe and F_S_CIa). In summary, bearing in mind the results of starch/DES systems, the most promising properties exhibited F_S_CMa, (high elongation at break, and reduction of crystalline phase), F_S_CT (the highest gloss) and F_S_CC films (high tensile strength and Young's modulus).

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