



# Mechanical and barrier properties of starch-based films plasticized with two- or three component deep eutectic solvents



Magdalena Zdanowicz<sup>a,b,\*</sup>, Caisa Johansson<sup>b</sup>

<sup>a</sup> West Pomeranian University of Technology, Polymer Institute, ul. Pulaskiego 10, 70-322 Szczecin, Poland

<sup>b</sup> Department of Chemical Engineering and Chemical Sciences, Karlstad University, SE-651 88, Sweden

## ARTICLE INFO

### Article history:

Received 11 March 2016

Received in revised form 15 May 2016

Accepted 17 May 2016

Available online 19 May 2016

### Keywords:

Starch

Deep eutectic solvent

Plasticizer

Mechanical properties

Barrier properties

Crosslinking

## ABSTRACT

The aim of this work was to prepare two- and three-components deep eutectic solvents (DES) and investigate their potential as starch plasticizers. Starch/DES films were prepared via casting method. Mechanical properties, water vapor- and oxygen transmission rates were measured; additionally contact angle and moisture sorption were determined and FTIR analysis was applied on the films. Native potato starch and hydroxypropylated and oxidized starch (HOPS) with common plasticizers (e.g. polyols, urea) and DES were studied. Moreover, influence of three methods of DES introduction and concentration of plasticizer on the films properties were compared. HOPS films were prepared by two methods: as non-cured and cured samples. Some of DESs containing citrate anion exhibited crosslinking ability of polysaccharide matrix. Non-cured HOPS/DES films exhibited more favourable mechanical and barrier properties than cured analogue films. Samples prepared with unmodified potato starch had higher mechanical and barrier properties than films made with HOPS. Starch-based films plasticized with novel DESs with parallel crosslinking activity exhibited satisfactory mechanical and barrier properties.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Introduction of plasticizers into polymer materials like starch lead to more flexible films with lower glass transition temperature,  $T_g$ , of the polymer. Plasticizing additives can also facilitate starch processability e.g. during extrusion or hot pressing. Plasticizers are low molecular weight molecules with polar groups (like hydroxyls or amine groups) which are capable to form hydrogen bonds with –OH groups on the glucosidic units (AGU) of polysaccharide chains, and to disrupt intermolecular bonds between chains, thus leading to increased chain movements with a more flexible material as a result. The most used starch plasticizers are water and glycerol, but other compounds like polyols, e.g. sorbitol, mannitol, xylitol (Mathew & Dufresne, 2002; Talja, Helén, Roos, & Joupilla, 2007), amines: urea (Lourdin, Coignard, Bizot, & Colonna, 1997; Wang, Cheng, & Zhu, 2014; Wang et al., 2016), ethanolamine (Schmitt et al., 2015) triethanolamine (Jost and Stramm, 2016), carboxylic acids or their salts (Lourdin et al., 1997; Niazi, Zijlstra, & Broekhuis, 2015; Seligra, Jaramillo, Famá & Goyanes, 2016), sugars or their mixtures with other plasticizers (Teixeira, Da Róz, Carvahlo, & Curvelo, 2007) and its derivatives like isosorbide (Battagazzore, Bocchini,

Nicola, Martini, & Frache, 2015) glycol/alginate mixtures (López et al., 2015) and ionic liquids (Wilpiszewska & Szychaj, 2011) can be applied as plasticizers. Glycerol diacetate/triacetate compositions were shown to be inefficient as plasticizers (Lourdin et al., 1997) whereas phase separation has been observed for starch and starch blends plasticized with polyethylene glycols (Lourdin et al., 1997; Laohakunjit & Noomhorm, 2004). Glycerol tends to migrate in starch materials, leading to starch retrogradation after longer time of storage. Other plasticizers, like some amines, are toxic; isosorbide is expensive and carboxylic acids lead to changes in molecular weight of polysaccharide chains (Menzel et al., 2013; Olsson et al., 2013).

Over the last two decades novel plasticizers from a group of materials named deep eutectic solvents, or low temperature transition mixtures, have been tested as polysaccharide plasticizing agents (Abbott, Ballantyne, Conde, Ryder, & Wise, 2012; Leroy et al., 2012; Ramesh, Shanti, & Morris, 2012; Zdanowicz & Szychaj, 2011). Deep eutectic solvents (DES) are mixtures of two or more components where the melting temperature of the mixture is much lower than the melting temperature ( $T_m$ ) of the individual components. For example, a mixture of choline chloride (CC) and urea (U) is liquid at room temperature, despite the fact that  $T_m$  of CC is 302 °C and  $T_m$  of U is 132–135 °C (Abbott, Capper, Davies, Rasheed, & Tambyrayah, 2003). So far, only few reports about DESs as starch plasticizers have appeared. Mainly CC:U (Abbott et al., 2012; Leroy et al., 2012; Ramesh, Shanti, & Morris, 2012; Zdanowicz & Szychaj,

\* Corresponding author. Permanent address: West Pomeranian University of Technology, Polymer Institute, ul. Pulaskiego 10, 70-322 Szczecin, Poland.

E-mail address: [mzdanowicz@zut.edu.pl](mailto:mzdanowicz@zut.edu.pl) (M. Zdanowicz).

2011); CC:glycerol (Leroy et al., 2012) and CC:carboxylic acids mixtures (Zdanowicz & Szychaj, 2011) have been tested as plasticizers for unmodified starch. Very recently, imidazole-based DESs were studied as starch plasticizers or solvents (Zdanowicz, Szychaj & Mąka, 2016). Most of these reports are related to unmodified corn starch films performed via extrusion (Leroy et al., 2012), melt processing (Abbott et al., 2012) or casting method (Ramesh et al., 2012).

Most of the literature concerns mechanical characteristics of starch/DES films, but there is a lack of information about their barrier properties. DES components are polar and hygroscopic (like choline chloride, urea), and even in case of strong hydrogen bonds between starch and DES components, strongly hydrophilic starch/DES films may be formed.

One way to improve mechanical and barrier properties as well as to increase the hydrophobicity of starch materials is by crosslinking. Crosslinking can occur chemically, using polyfunctional compounds, e.g. epichlorohydrin (Kim & Lee, 2002), polycarboxylic acids (Shen, Xu, Kong & Yang, 2015), ascorbic acid (Yoon, 2014), oxidized sucrose (Xu, Canisag, Mu, & Yang, 2015) or photo-crosslinking (Zhou, Zhang, Ma, & Tong, 2008). Carboxylic acids like citric or malic acid are mainly non-toxic and can be obtained from natural origin. They can act not only as crosslinking agents but also as plasticizers (Niazi et al., 2015). Carboxylic acids act in a dual way, they crosslink starch materials by forming ester bonds between their carboxyl groups and hydroxyl groups onto polymeric chains but may also cause chain scission by acidic hydrolysis. Therefore, the concentration of acid should be selected restrictively, especially when using a casting method where films are prepared in aqueous media which facilitates acidic hydrolysis. For example in the work by Reddy and Yang (2010) the best mechanical properties of films were obtained for 5 wt% of citric acid (CA) added to corn starch.

The aim of this work is preparation of starch-based films plasticized with two or three-component deep eutectic mixtures via casting from aqueous solution. So far deep eutectic solvents have been studied as plasticizers for cast films based on corn starch only. In this work two types of starches have been used: native potato starch and hydroxypropylated and oxidized potato starch (HOPS) and their properties were compared. HOPS was, despite being slightly more hydrophilic than native starch, included in this study because it is a starch grade that has been studied for long time due to its high solution stability and favourable film-forming properties, parameters that are of utmost importance when mixing starch with different functional components, and not least regarding the properties of final cast films. To our knowledge, this is the first report related to modified starch plasticized with DESs. Moreover, choline chloride, the popular component of DESs, was substituted for its derivative choline dihydrogen citrate salt (choline citrate—CCit) in some mixtures. An additional goal is to prepare deep eutectic mixtures which can act both as plasticizer and crosslinking agent. In the case of HOPS-based films two methods of preparation were compared: solvent evaporation at room temperature under constant conditions as well as drying at raised temperature. For all films mechanical tests, barrier- and water sorption properties and analysis of molecular structure by FTIR were performed. Prepared DESs used in this work were characterized by MDSC.

## 2. Materials

Native potato starch (TPS) was supplied by Nowamyl S.A. Nowogard (Poland) and hydroxypropylated and oxidized potato starch (HOPS), Solcoat P55, from Solam (Kristianstad, Sweden). The degree of substituted hydroxypropyl groups in HOPS was 0.11 according to the supplier. Choline chloride—CC ( $\geq 98\%$ ), Choline dihydrogen citrate salt—CCit ( $\geq 98\%$ ), Glycerol—G (99%),

Urea—U (pure) from WVR International, and D-Sorbitol—S from Schmulchardt, Germany.

## 3. Methods

### 3.1. Preparation of deep eutectic solvents

Two or three selected components were placed in a glass bottle, sealed and heated up to 95 °C (in case of CCit up to 105 °C) until the mixture was liquid and pellucid (about 1 h was needed to obtain liquid state, except for the mixture with glycerol, which became liquid after about 30 min). The following blends were prepared in molar ratios: CCit:G 1:8, 1:6, 1:4 and 1:2; CC:G, CC:U, CC:S and CCit:U in ratio 1:2; CCit:U:G and CC:U:G in ratio 1:2:2 and finally CC:U:S in ratio 1:1:1 (Table 1).

#### 3.1.1. Preparation of starch-based films: TPS/DES and HOPS/DES

The standard preparation method of starch-based films was as follows: native potato starch (5 wt%) or HOPS (10 wt%), deionized water and DES (before introducing to the system the DES mixture was heated up for a few min in an oven to decrease viscosity) in 30 parts per 100 parts of solid starch material were placed in a 250 mL Erlenmeyer flask. The whole system was mixed with a teflon propeller at 350 rpm at 85 °C for 30 min in water bath. Thereafter the gelatinized potato starch or HOPS solution was poured into polystyrene Petri dishes (diameter about 90 mm). The starting concentrations of the two types of starch materials were different due to differences in viscosity of starch solutions; consequently, the amounts of liquid transferred to the Petri dishes were: 30 g of 5 wt% TPS and 15 g of 10 wt% of HOPS solutions with plasticizer, which should result in approximately the same thickness of the dry films. HOPS solutions were dried at 60 °C for 6 h in a non-ventilated oven (cured samples—c) or left to dry in air in a climate room (non-cured samples—nc). TPS films were found to be more brittle and the TPS compositions were hence dried at lower temperature but for longer time to avoid over-drying and cracking: 40 °C, 50% RH in climate chamber for 24 h. All films were kept in climate room at 23 °C and 50% RH for minimum one week prior testing.

For comparison of influence of film preparation methodology on the resulting properties, the standard method was slightly varied with respect to DES introduction to the system. Standard method: liquid DES before (TPS/CC:U; TPS/CCit:U:G), after starch gelatinization (TPS/CC:U 20/10; TPS/CCit:U:G 20/10), and introduction of individual components of DES separately, before gelatinization (TPS/CC+U; TPS/CCit+U+G); total amount of these components was equal with sum of liquid DES concentration.

#### 3.1.2. Thermal characteristics of DES

Differential Scanning Calorimetry, DSC, was applied for thermal characterisation (transition peaks and initial temperatures of decomposition) of prepared DESs. Measurements were carried out using modulated DSC (MDSC) on the TA system DSC Q2000 (TA Instruments, New Castle, USA) with nitrogen flow. 20 mg of sample was placed in an aluminum pan and sealed. The oscillating heating rate was 1 °C/min overlaid on the linear heating rate of 5 °C/min, and mixtures were heated from –40 to 250 °C.

#### 3.1.3. Mechanical tests

Mechanical tests were performed using a Zwick/Roell Z005 (Ulm, Germany) according to ASTM D 822-02. The films were cut into 5 mm wide stripes, the initial grip separation was 20 mm and the cross-head speed was 10 mm/min. Ten replicated samples were tested. The elongation at break, maximum tensile strength and Young's modulus of the samples were calculated by TestXpert II software.

Download English Version:

<https://daneshyari.com/en/article/1382977>

Download Persian Version:

<https://daneshyari.com/article/1382977>

[Daneshyari.com](https://daneshyari.com)