



# Thermoplastic starch with deep eutectic solvents and montmorillonite as a base for composite materials

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## ABSTRACT

Thermoplastic starch (TPS) materials were prepared from potato starch, deep eutectic solvents (DES) as plasticizers [choline chloride (ChCl) with urea (U) or imidazole (IM) at molar ratio 1:2 and 3:7, respectively] and urea intercalated montmorillonite (UM). Extrusion and thermocompression were used as processing methods. It was found that UM resulted in decreasing melt viscosities of TPS composite materials at processing temperature range (120–140 °C), especially pronounced when ChCl/IM was applied. XRD revealed differences between values  $d_{001}$  parameter for UM and TPS/DES-UM materials, as well as amorphization of the starch-based films. Thermomechanical, mechanical properties and contact angle values were dependent on the type of applied plasticizer and UM content. Moreover, it was found that increasing clay content resulted in decrease of TPS/UM composites thermal conductivity.

## 1. Introduction

A search for biodegradable polymeric materials from sustainable source causes growing interest on using thermoplastic starch (TPS) as an alternative to other more expensive biopolymers, e.g. polylactide (PLA) (Barczewski et al., 2018) or – as a component of PLA/TPS blends (Shirai et al., 2013; Teixeira et al., 2012). TPS is formed through plasticization of native starch using polar organic compounds able to form internal hydrogen bonding with the polysaccharide glycosidic units. Water and glycerol (Gl) are the most often used starch plasticizers but other polyalcohols (e.g. sorbitol), alkanolamines (e.g. ethanalamine, diethanolamine), amides (e.g. urea, formamide) or carboxylic acids (e.g. citric and malic acid) have been also applied (Jannsen and Moscicki, 2009; Ma and Yu, 2004; Shi et al., 2007; Mekonnen et al., 2013; Nafchi et al., 2013; Niazi et al., 2015).

TPS-based composites are manufactured in order to improve material properties. For such composites starch plasticization with Gl and reinforced with natural fillers, i.e. plant fibers or montmorillonite (M) is the most common. Lot of works describe an influence of the pristine or modified clay on mechanical and/or barrier properties of TPS films (Huang et al., 2006; Wang et al., 2009; Tang et al., 2008; Wang et al., 2010; Aouada et al., 2011). One of the methods for clay modification

with environmentally acceptable compound is intercalation with urea (Kottegoda et al., 2014; Pereira et al., 2012; Wanyika, 2014). However, TPS materials with conventional plasticizers, including Gl, suffer some drawbacks such as recrystallization which lead to material stiffness and brittleness.

The mentioned drawbacks of TPS can be minimized by an application of ionic liquids (ILs) as starch plasticizers (Wang et al., 2010; Wilpiszewska and Spychaj, 2011), and especially more convenient, cheap and ecofriendly media known as deep eutectic solvents (DES). These liquid solvents are mixtures of two or more compounds containing hydrogen acceptor (often choline chloride, ChCl) and the hydrogen donor (e.g. urea, U or Gl) (Abbott et al., 2003; Francisco et al., 2012; Francisco et al., 2013). There have been known some reports on using DES for starch plasticization by melt processing techniques (Abbott and Ballantyne, 2011; Zdanowicz and Spychaj, 2011; Abbott et al., 2012; Leroy et al., 2012; Abbott et al., 2014; Zdanowicz et al., 2016). TPS films plasticized with such DES as ChCl/U or ChCl/Gl were obtained via extrusion followed by subsequent thermocompression and exhibited improved mechanical properties, e.g. Young's modulus was similar to low density polyethylene (Abbott et al., 2012; Abbott et al., 2014), whereas tendency to starch recrystallization decreased.

**Abbreviations:** TPS, thermoplastic starch; ChCl, choline chloride; U, urea; UM, urea intercalated montmorillonite; IM, imidazole; M, montmorillonite; Gl, glycerol

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TPS materials plasticized with DES and simultaneously filled with M and then processed via extrusion/compression molding have not been studied so far. There is only one report related to starch/DES systems with clay introduction, but starch-based films were prepared via casting method (Zdanowicz and Johansson, 2017). TPS/M materials plasticized with DES can be considered as suitable for film forming processes (thermoextrusion or extrusion with blow molding) or film processing (thermoforming) as well as for melt foaming, melt impregnation of natural fibers or subsequent modification with (nano)fillers to obtain biocomposite materials. Examples of melt formed films from TPS/M materials via blow molding (Mc Glashan and Halley, 2003) or thermoforming (Mohan and Kannay, 2015) have been described. Melt foaming process of TPS/organofilled M was also presented (Chen et al., 2005). Moreover, interest on investigation of TPS/M-based multicomponent composite materials formed and/or processed via melt applicable techniques is noteworthy; for instance: (i) TPS/clay/polyurethane foamed microfiller composites (Spychaj et al., 2010), (ii) TPS/M/alumina trihydrate antinflaming materials (Ahamed et al., 2016), (iii) biocomposites based on TPS/M/wood flour (Sarsani et al., 2016).

Summarizing, the aim of this study was manufacturing and characterizing TPS/UM composite films with two types of plasticizers, i.e. ChCl/U, and ChCl/imidazole, and U intercalated M.

## 2. Experimental

### 2.1. Materials

Potato starch with equilibrium moisture content about 12 wt% was obtained from Nowamyl SA, Nowogard (Poland). Cloisite-Na<sup>+</sup> montmorillonite was received from Southern Clay, choline chloride ( $\geq 98\%$ ) and imidazole ( $\geq 99\%$ ) were obtained from Sigma-Aldrich. Urea ( $\geq 98\%$ ) was purchased from Chempur (Poland). All the components were used as received with no additional pre-treatment.

### 2.2. Methods

#### 2.2.1. Preparation of deep eutectic solvents

Two DES components (i.e. ChCl and urea or ChCl and imidazole) were placed in a glass jar and heated up to 80 °C for about 2 h to obtain transparent liquids. Acronyms, ratios of ChCl/hydrogen bond donor, melting points found in literature, appearance and small amount of additional water introduced per 100 g DES required to lower the DES viscosity are as follows: ChCl/U (choline chloride/urea), 1:2 mol/mol, 17.0 °C, viscous, colorless, transparent liquid, 7 g water (per 100 g DES) and ChCl/IM (choline chloride/imidazole); 3:7 mol/mol, 55.8 °C (Zdanowicz et al., 2016), viscous odourless, subtly yellow, transparent liquid, 10 g water (per 100 g DES), respectively.

#### 2.2.2. Preparation of urea modified montmorillonite

Urea and montmorillonite (U/M 1:1 weight ratio) were mixed with different amounts of distilled water (0.15; 0.20 or 0.30 g H<sub>2</sub>O/1 g M) using laboratory mixer FML 10 (Reimelt Henschel, MischSysteme GmbH, Kassel, Germany) to obtain a homogenous material. The received composition was subsequently extruded with PRISM Eurolab Digital laboratory extruder (L/D ratio 40:1, screw diameter 16 mm). The temperature profile was 20/60/70/80/80/80/80/70/60/60 °C from the feed throat to the nozzle and screw speed was maintained at 50 rpm. After extrusion, material was dried for 2 h at 105 °C and then turned into a fine powder with mortar and pestle, and kept in sealed polyethylene vials.

#### 2.2.3. Preparation of TPS/UM compositions

Starch, water, UM and DES were mixed together using laboratory mixer FML 10 (25 °C, 350 rpm). In the first step appropriate amount of distilled water was dropwise added to the starch during mixing to increase starch humidity up to 15 wt%. Subsequently, grinded UM (0.5; 1,

2, 4 pph calculated as pristine M on dry starch) was added and the two powder components were mixed for 5 min before adding DES. Then DES containing small amount of water providing decrease of viscosity (7 g or 10 g H<sub>2</sub>O per 100 g DES for ChCl/U and ChCl/IM, respectively) was added dropwise to obtain homogenous starch/UM/DES composition. So, final ratios of components for TPS formulation were the following: (i) 100 g dry starch, 35 g ChCl/U + 5.45 g H<sub>2</sub>O, (ii) 100 g dry starch, 35 g ChCl/IM + 6.5 g H<sub>2</sub>O. In other words percentage ratio of starch to DES was close to 74/26 wt% ignoring water or ca. 71/29 wt% taking into account both plasticizers, i.e. DES and water.

After mixing, the compositions were stored in the hermetically sealed PE bags for 48 h at ambient temperature. Afterwards, they were extruded using PRISM Eurolab Digital twin-screw extruder. The temperature profile was set to 20/80/120/120/120/120/120/120/120/120 °C from the feed throat to the nozzle and screw speed was maintained at 50 rpm. Obtained extrudate was turned into 3 mm diameter pellets using PRISM Varicut 16 pelletizer.

#### 2.2.4. Preparation of TPS/UM films

TPS/UM pellets were pressed between PTFE sheets using hydraulic press (ReMi-Plast s.c. PH10 T, Poland) for 5 min, at 140 °C, under pressure of 6 tons. All obtained samples (thickness ca. 1 mm) were kept in a climatic chamber for 48 h at 25 °C and 50% relative humidity (RH) prior to further investigations.

#### 2.2.5. X-ray diffractometry (XRD)

UM and TPS/UM compositions were analysed in terms of filler intercalation and starch crystallinity, respectively by X-ray diffraction (X'pert Pro, PANalytical, operated at the Cu-K $\alpha$  wavelength 154 Å).

#### 2.2.6. Rheological behaviour

TPS/UM pellets were cooled down to about -50 °C and turned into a powder with Moulinex A505 blender. Rheological behavior of TPS/UM powder was investigated using stress rheometer ARES (Rheometric Scientific) equipped with parallel plate system. A temperature range was 45–250 °C, heating rate 5 °C/min, and at frequency 1 Hz.

#### 2.2.7. Differential scanning calorimetry (DSC)

Phase transitions of starch/DES premixtures (before extrusion) were determined by DSC technique (DSC Q100 TA Instruments) using aluminum hermetic pans with nitrogen as cooling agent. Samples were analysed with standard run at the temperature range from 20 to 200 °C and heating rate 5 °C/min for TPS materials.

#### 2.2.8. DMTA measurement

Dynamic mechanical thermal analyser (DMA Q800 TA Instruments) was used to measure storage modulus (E'), and tan  $\delta$  of the TPS/UM specimens. The measurements were carried out in a dual cantilever mode at frequency of 1 Hz, heating rate 3 °C/min, and temperature range from -90 to 105 °C.

#### 2.2.9. Thermal conductivity measurements

The thermal conductivity measurements were performed using ISOMET 104 (Applied Precision) apparatus equipped with 0.1–2.0 W/mK probe. Selected powdered TPS/UM compositions were placed in PE/aluminium tubes (height: 100.0 mm,  $\phi$ : 16.0 mm, wall thickness: 2.0 mm) with 3D-printed PLA caps at the both ends.

#### 2.2.10. Mechanical tests

Mechanical tests were performed using Instron 5982 (load cell 1 kN). The films were cut into 10 mm wide, 100 mm long stripes. The initial grip separation was 50 mm and the cross head speed was set to 10 mm/min. Samples were maintained at 50% RH, 25 °C for 48 h before measurement. Six replicated samples for each system were tested and the mechanical parameters (tensile strength, elongation at break and Young's modulus) were calculated with Bluehill 3 software.

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