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Plasticizing of chitosan films with deep eutectic mixture of malonic acid and choline chloride

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ABSTRACT

Chitosan (CS) films containing deep eutectic solvent (DES) based on malonic acid (MA) and choline chloride (ChCl) were successfully prepared by solution casting method by using DES content ranging from 0 to 82 wt%. A strong interaction of CS with the components of DES was demonstrated by analyses of water sorption isotherms, atomic force microscopy and FTIR results. The plasticizing effect of the MA and ChCl mixture on the CS matrix was shown by static bulk mechanical measurements, thermal analysis and quantitative nanomechanical mapping (QNM). Elongation at break increased from 3 to 62% at increase of DES content from 0 to 67 wt%, while further increase of DES content led to the decreasing of maximal elongation. Introduction of DES into CS films led to the appearance of glass transition temperature in the region +2 - -2.3 °C. QNM results indicated homogeneity of the films containing up to 75 wt% of DES.

1. Introduction

The negative environmental impact of the production and recycling of non-biodegradable plastics has led to intensive search of new eco-friendly and biodegradable materials based on renewable bioresources. Polysaccharides such as starch, cellulose and chitin are the most abundant natural polymers and they are considered as prospective starting resources for the production of green materials. Chitin can be found in fungal cell membranes and in the exoskeleton of invertebrate species (crustaceans). The main drawback of chitin is its low processability in comparison with synthetic polymers. Deacetylation of chitin is used to produce chitosan (CS), which is a linear polymer of 2-amino-2-deoxy-D-glucopyranose and can be processed by using acidic water solutions.

CS is a non-toxic and biocompatible polymer with high sorption capacity and bactericide properties (Kumar, 2000), which makes it promising for the preparation of wound dressing films (Rafique, Mahmood Zia, Zuber, Tabasum, & Rehman, 2016), drug delivery hydrogel (Bugnicourt & Ladavière, 2016) as well as sorbents for water purification (Thakur & Voicu, 2016) and membranes for separation of liquid mixtures (Choudhari, Premakshi, & Kariduraganavar, 2016; Yang, Li, Jiang, Lu, & Chen, 2009). However, films prepared from pure CS demonstrate poor mechanical properties, which limits their application. This has led to intensive elaboration of materials based on the CS modified either chemically or by the addition of reinforcing fillers and plasticizers. Reinforcing with inorganic nanoparticles (Bari & Mishra, 2017; Cano, Pollet, Avérous, & Tercjak, 2017; De Silva, Mantilaka, Ratnayake, Amaratunga, & de Silva, 2017), chitin nanowhiskers (Ma, Qin, Li, Zhao, & He, 2014; Rubentheren, Ward, Chee, & Tang, 2015), cellulose (Abdul Khalil et al., 2016; Rahmi, Lelifajri, Julinawati, & Shabrina, 2017; Tian, Yan, Lu, & Jiang, 2017), and carbon based nanomaterials (Azarniya, Eslahi, Mahmoudi, & Simchi, 2016; Cobos, González, Fernández, & Fernández, 2017; Delavar & Shojaei, 2017; Liu et al., 2017) has been recently reported to increase the tensile strength and tensile modulus of the CS-based films. The reasons for this effect are the high strength and tensile modulus of modifiers and strong interaction between them and the CS matrix, which efficiently transfer the load between the filler and the matrix.

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Interaction between –NH_2 groups of CS and surface functional groups of graphene oxide has been demonstrated by FTIR (Cobos et al., 2017). However, this modification leads to an increase in the brittleness of the material (decreasing of elongation at break). Glycerol (Cobos et al., 2017; Epure, Griffon, Pollet, & Avérous, 2011; Ziani, Oses, Coma, & Mate, 2008), xylitol and sorbitol (Matet, Heuzey, Pollet, Ajji, & Avérous, 2013) has been used to increase the elasticity of polysaccharide-based films. It has been shown that lactic acid, which was used as plasticizer together with glycerol, interacts with CS and decreasing the strong intramolecular hydrogen bonding between polymer chains and hampers the crystallization of polymer (Meng, Heuzey, & Carreau, 2014). Plasticized thermoplastic starch was prepared by using 30% addition of 1-butyl-3-methylimidazolium chloride (Sankri et al., 2010). It was found that plasticizing of starch with ionic liquid (IL) lead to an increasing of elongation at break from 100% till 400% in comparison with glycerol plasticized starch, while Young's modulus decreased by one order of magnitude, which demonstrates the feasibility of using of IL for polysaccharide plasticizing. Zhang et al. (2017) prepared starch-based films plasticized by 1-ethyl-3-methylimidazolium acetate, which lead to enhanced mechanical properties and increased electrical conductivity of films. The same IL was used for plasticizing of CS (Shamsudin, Ahmad, Hassan, & Kaddami, 2015). Based on FTIR data interaction between −OH groups of CS, imidazolium cation and acetate anion, which decreases the interaction between CS macromolecules was proposed. Additionally, it has been demonstrated that the specific sorption properties of methylimidazolium-based IL toward CO_2 make it possible to produce the gas-selective membranes based on CS and polystyrene (Otvagina et al., 2016), which shows the way for the application of specific physico-chemical properties of ILs for the preparation of films with desired characteristics. These results demonstrate that ILs are interesting candidates for the plasticizing of polysaccharides. At the same time, the main disadvantages of ILs are their high cost and toxicity.

Deep eutectic solvents (DES) have attracted much interest because they demonstrate unique physicochemical properties of ILs in the combination of green nature and low cost (Abo-Hamad, Hayyan, AlSaadi, & Hashim, 2015; Samarov, Smirnov, Sokolova, & Toikka, 2018; Zhang, Vigier, Royer, & Jerome, 2012). DESs are composed of two components, namely a donor and an acceptor of a hydrogen bond, which demonstrate so strong interaction that the crystalline structure of the components is destructed at temperatures much lower than the melting points of the constituents (see the example in Fig. 1a). Choline chloride (ChCl) as a hydrogen acceptor and di- or tricarboxylic acids (for example oxalic, malonic (MA), citric acids) as hydrogen donors are commonly used in the preparation of the most natural DES. The possibility of ChCl and citric acids to plasticize CS was recently shown (Galvis-Sánchez, Sousa, Hilliou, Gonçalves, & Souza, 2016) and the method to prepare CS films by thermo-compression molding was developed. It was shown that the brittle structure of CS/citric acid films was improved by ChCl incorporation in the mixture resulting in less Young's modulus of films but with improved elongation at break. Biofriendly DES based on salts of cholinium cation with citrate, lactat, furoate and salicylate anions were used in the plasticizing of starch (Colomines, Decaen, Lourdin, & Leroy, 2016). Microcrystalline cellulose in combination with ChCl-glycerol DES was used in the preparation of CS films filled with curcumin for pH-testing applications (Pereira & Andrade, 2017).

The benefits of DES-based polysaccharide composites are their natural origin, low cost, easy processing and recycling in combination with unique physicochemical properties of DES. However, there is only little information on the structural characteristics and physicochemical properties of such films in the literature.

In this work, CS/DES films were prepared by casting of a mixed water solution of DES together with CS. The impact of DES content on the structure, morphology, bulk and nanomechanical properties, thermal properties and water vapour sorption ability of the films was studied. A strong interaction between the polymer and the components of DES, which led to a significant decrease of the glass transition temperature of the polymer was shown.

2. Experimental

2.1. Materials

MA (≥98 wt%, Vecton, Saint Petersburg, Russia) was used as received without purification. ChCl - (2-hydroxyethyl) trimethylammonium chloride) was obtained from AppliChem (≥98 wt%, Darmstadt, Germany). The ChCl was dried under vacuum before used. CS (with a M_w = 900 000) was purchased from "Bioprogress CJSC" (Schelkovo, Russia) and used without further purification.

The ^{13}C NMR experiments were conducted in solid state at room temperature with the Avance III 400WB solid state NMR spectrometer

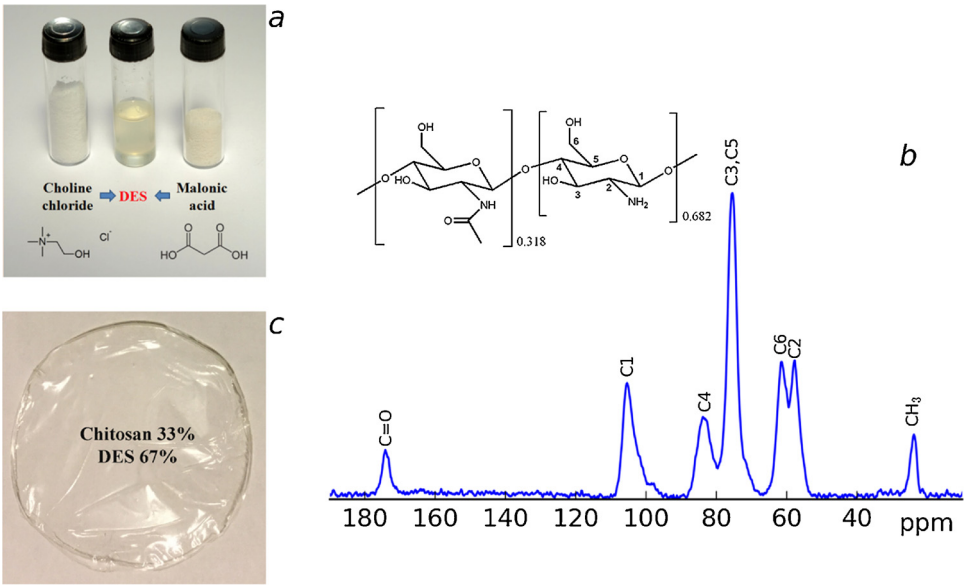

Fig. 1. Schematic illustration of the preparation of DES (a). Solid state ^{13}C NMR spectra of used chitosan and composition of the polymer (b). Typical view of CS/DES films (c).