Deep Eutectic Solvents in the Production of Biopolymer-Based Materials

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Abstract: Deep eutectic solvents (DESs) are multipurpose media for polysaccharide treatment. Thus, the DESs are also used as a plasticizers in preparation of thermoplastic films from natural polymers. Since attempts are being made to reduce the production of petroleum-based polymer materials, DESs are a good alternative in the production of biopolymers. DESs have desirable properties such as low costs, biodegradability and non- or low toxicity. This review summarizes research that are dealing with preparation of biopolymer-based materials with DESs in the role of plasticizer.

Keywords: deep eutectic solvents, biopolymers, plasticizer, chitosan, starch, cellulose.

INTRODUCTION

Currently, a great importance is attached to green technology and chemistry, which has the task of protecting the environment from the negative impact of human participation. A large amount of waste is generated and the problem is that a large part of that waste is not biodegradable. Packaging waste occupies a significant share of the total amount of waste generated in the world. Among packaging materials, polyethylene, as a petroleum-based polymer is one of the concerns for the environment.1,2 According to the statistical data, the formation of petroleum-based packaging materials has increased 8% annually and only around 5% are recycled.3 Petroleum-based polymers can cause different levels of contamination after disposal in the land or coast, due of extremely difficult biodegradation. To prevent such pollution, much attention is paid to the production of biodegradable polymers.4 Disposed polymers could be broken down by chemical hydrolyse or enzymatic catalysis process. The degradation process of polymer chains usually includes end products like CH₄, CO₂, biomass, water and other compounds which can significantly affect the environment. Natural polymers (chitosan, starch, cellulose, proteins from animal and plant origin) are emerging as an alternative for synthetic plastic packaging materials.5,6

The use of deep eutectic solvents (DESs) has contributed to the development of numerous green environmentally friendly methods. These green solvents found application in many fields like biochemistry (cosolvent media of transformations, catalysts), nanotechnology, electrochemistry, analysis, pharmacy, biomedicine, biotechnology and chemistry (reaction media, catalysts, solvents, extraction media, substrates).7-13 Most of the DESs are based on renewable components, such as sugars, carboxylic acids, polyols, amines and others. Components used for eutectic mixture preparation are cheap and most importantly biodegradable and non-toxic or low toxic. DESs’ physical and chemical properties (biodegradability, viscosity, thermal stability, polarity, electrical conductivity) could be tailored by changing hydrogen bond donor or acceptor compound and the molar ratio of used compounds.12-14

In the production of biopolymer-based materials, DESs could be applied as plasticizers.15 Most common used DESs as plasticizers are ChCl : urea, ChCl : citric acid, ChCl : malonic acid and ChCl : glycerol. The plasticizers used in production of thermoplastic films are non-toxic, non-volatile and biodegradable molecules. They reduce cohesion forces between polymer chains and diminish glass transition temperature and brittleness of the film. They could improve film extendibility, flexibility and processability.16,17
In this review plasticization of natural polymers such as starch, chitosan, cellulose and agar with DESs are reviewed. The paper gives an overview of the DESs used as well as the characterization of the produced thermoplastic films.

**CHITOSAN-BASED FILMS**

Chitin is a biopolymer found in biological materials such as fungal cell walls and the exoskeleton of crustaceans. In alkaline media, chitosan is derived from chitin by deacetylation. It is biodegradable material with antibacterial and antifungal properties. Chitosan can be degraded by several enzymes in vivo in mammalian tissues. Degradation leads to formation of non-toxic oligosaccharides forms.[18] Chitosan is an excellent material for film forming because of its good mechanical properties and selective permeability to gases (O_2 and CO_2).[19] Table 1. summarizes the reported investigations that deal with chitosan-based films plasticized with DES.

Galvis-Sánchez et al.[20] used four different DESs in order to investigate their potential as plasticizers on thermoplastic chitosan. In this study, two types of chitosan (deacetylation degrees 76 and 81) were used. Final films are hot-pressed. For the preparation of ChCl based DESs, malic acid, lactic acid, citric acid and glycerol were used as hydrogen bond donors. Mechanical properties, as well as water vapor permeability, were tested on chitosan films. The obtained films differed in morphology, thickness, elasticity, tensile strength and water resistance. The film with the most homogenous surface was Chit76-ChCl/citric acid. Films contained Chit76 were less permeable to water vapor and showed lower thickness than films containing Chit81. Chit76-ChCl/malic acid film showed the highest elasticity and the best tensile strength is attributed to film Chit76-ChCl/citic acid.

Preparation of chitosan films in a combination with DES (ChCl:malic acid) as a plasticizer was reported by Jakubowska and coworkers.[21] The prepared films contained DES in various ratios (0 – 80 wt %). Mechanical, barrier, structural and thermal properties of DES-modified materials were investigated and compared to the unmodified films. Chitosan-DES films showed better characteristics than native chitosan films in terms of elasticity and roughness. As the DES content in films was increased, so did the water vapor transmission rate.

Sokolova et al.[22] also reported an eutectic mixture of ChCl and malonic acid as a plasticizer in preparation of chitosan-based films by casting solutions on Petri dishes. DES content range in chitosan films was 0 – 82 wt %. Thermal analysis, quantitative nanomechanical mapping and mechanical measurement on chitosan-based films were conducted. Results for Young’s modulus showed a decrease from 2400 MPa (pure chitosan) to 60 MPa (Chit68/ChCl-malonic acid-82 wt %), while Jakubowska et al.[21] reported Young’s modulus decrease from 2418 MPa and 1717 MPa for pure chitosan to 2.4 MPa (Chit72/ChCl-malonic acid-80 wt %) and 1.3 MPa (Chit83/ChCl-malonic acid-80 wt %), respectively. The elongation at break was ranged 16 – 63 %,[22] 3.3 – 150 % and 14.7 – 189 %,[22] when content of DES increased 0 – 67 %, 0 – 70 % and 0 – 70 %, respectively. It can be concluded that as the degree of deacetylation increases the value of elongation at break also increases.

**Table 1.** Composition of chitosan-based films plasticized with DES.

| Deacetylation degrees of chitosan (DD) | DES | DES amount | Other components in film | Reference |
|--------------------------------------|-----|------------|--------------------------|----------|
| 76                                   | ChCl : malic acid (1 : 1) | 30 % | – | [19] |
|                                       | ChCl : citric acid (1 : 1) | | | |
|                                       | ChCl : lactic acid (1 : 1) | | | |
|                                       | ChCl : glycerol (1 : 2) | | | |
| 81                                   | ChCl : malic acid (1 : 1) | 30 % | – | [19] |
|                                       | ChCl : citric acid (1 : 1) | | | |
|                                       | ChCl : lactic acid (1 : 1) | | | |
|                                       | ChCl : glycerol (1 : 2) | | | |
| 72                                   | ChCl : malonic acid (1 : 1) | 30; 40; 50; 60; 70; 80 wt % | – | [20] |
| 83                                   | ChCl : malonic acid (1 : 1) | 20; 30; 40; 50; 60; 70; 80 wt % | – | [20] |
| 68                                   | ChCl : malonic acid (1 : 1) | 10; 20; 33; 50; 67; 75; 85 wt % | – | [21] |
| 76                                   | ChCl : lactic acid (1 : 1) | 10; 20; 30 % | Curcumin | [22] |
| n.d.                                 | ChCl : glycerol (1 : 2) | 8 pph | Microcrystalline cellulose and curcumin | [23] |
| n.d.                                 | ChCl : urea (1 : 2) | 1; 3; 5 wt % | – | [24] |
| n.d.                                 | ChCl : urea (1 : 2) | – | Carboxymethyl cellulose | [25] |
Almeida et al.\[23\] reported research where chitosan films were prepared in combination with DES and curcumin by knife coating technique. Chitosan-based films with different ratios of ChCl-lactic acid and curcumin were prepared and barrier, mechanical and optical properties were investigated. No significant changes were observed in Young’s modulus with the addition of curcumin. However, tensile strength and elongation at break values are dependent on curcumin content. Water vapor permeability was not significantly affected by DES content, but the addition of curcumin led to a reduction of water vapor permeability. As the content of DES was increased from 0 to 30 wt %, tensile strength values were decreased 34 – 13 MPa. The same trend was noticed in Young’s modulus results where increasing of DES content led to a reduction from 43 to 15 MPa. Further, Pereira and Andrade\[24\] published research on the preparation of chitosan films in combination with DES (ChCl-glycerol), curcumin and microcrystalline cellulose. All results of obtained films were compared with glycerol-plasticized and unplasticized chitosan film. The work aimed to obtain the pH-responsive film. Water vapor permeability and water-solubility properties of DES-plasticized films were improved in comparison with unplasticized chitosan films, meaning that films with DES had higher water solubility, water sorption capability and water vapor permeability.

Investigation of structural and proton conducting properties of the chitosan-based film was conducted by Wong et al.\[25\]. Water uptake, proton exchange, ionic conductivity and morphology of prepared films were investigated. Significant changes were observed in terms of conductivity and water uptake. A major reduction of water uptake from 698 % to 180 % is also noticed. With the addition of DES, better film homogeneity, as well as flexibility, were achieved. Similar research was conducted by Wong et al.\[26\] where the influence of ChCl-urea DES on thermal properties and proton conduction of chitosan-carboxymethylcellulose membrane was investigated. It was proven that proton conductivity was improved in membranes with DES in comparison with those without. In addition, films with DES showed higher thermal degradation stability than conventional membranes such as Nafton-TiO₂.

### STARCH-BASED FILMS

Starch is a naturally abundant polymer consisting of amylose and amylopectin. Amylopectin is a highly branched polymer while amylose has almost completely liner chains. The plasticizers used for the preparation of starch films are polar organic compounds and for that purpose water and glycerol are most often used.\[27\]. Composition of starch-based film plasticized with DES reported by different authors are given in Table 2.

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Abbot et al.\[28\] reported the preparation of recyclable plastics from corn starch in combination with DES (ChCl : urea) using extrusion and compression-molded methods. To determine the role of ChCl in the mixture, starch-urea film is also prepared. The film without ChCl was opaque unlike the film with ChCl which was transparent. The study showed that ChCl incorporation gave more flexible and stronger films. The different mechanical properties of the same film have shown that the choice of film production method has a great influence. Compression molded starch : urea : ChCl (5.05 : 1 : 1.16) film had tensile strength of 5.46 MPa while the extruded film had 12.00 MPa. The differences in elongation at break values were also large, 19.3 % for compression and 41.3 % for extrusion. Most importantly, this research has shown that obtained materials are compostable and recyclable.

Different DESs (ChCl : urea, ChCl : glycerol and ChCl : ethylene glycol) are used as plasticizers in the production of medium density fiberboard by extrusion.\[29\] A blend of corn starch, DES and a mixture of hardwood and softwood sawdust was prepared in order to determine mechanical properties. Manufactured medium density fiberboard with incorporated DES are recyclable and present an environmentally friendly material.

Thermoplastic starch was developed in combination with DESs as functional additives.\[30\] Films are prepared of corn starch, zein protein and DES (ChCl : urea, ChCl : glycerol) on laboratory scale twin screw microcompounder. Results showed that applied DESs acted like efficient plasticizers as well as compatibilizers (in the case of mixtures with a hydrophobic phase) and water uptake inhibitors. Ramesh et al.\[31\] prepared biodegradable polymers composed of corn starch, lithium bis(trifluoromethanesulfonyl) imide and DES (ChCl : urea). In this study ionic conductivity, thermal properties and dissipation factor of cornstarch matrix were scrutinized. The results showed that ion conductivity was the most enhanced in the CS : LiRSFI matrix with 80 wt % of incorporated DES at 50 °C. The increase of DES content led to the decrease of polymer electrolytes melting point. TGA analysis has shown that the incorporation of DES into the polymer electrolytes reduces heat-resistivity while improvement of thermal stability was achieved with minimum addition of DES. Further, the same group of authors reported plasticization efficiency of DES in the crystallinity suppression of polymer electrolytes.\[32\] The examined polymer electrolytes were composed of corn starch, lithium bis(trifluoromethanesulfonyl) imide and DES (ChCl : urea). The results obtained for ionic conductivity are in accordance with previously reported research where the best ionic conductivity was achieved in the case of a polymer composed of 14 wt % corn starch, 6 wt % lithium bis(trifluoromethanesulfonyl) imide and 80 wt % ChCl : urea (1 : 2) at room temperature. It could be concluded that...
mentioned sample composition had high conductivity due to the presence of a larger amorphous elastomeric phase that improves the ionic transport mechanism.

Abbott and coworkers\(^1\) used DESs in order to modify high density polyethylene with addition of thermoplastic starch. The ultimate tensile strength and elongation at break were determined at high density polyethylene: DES mixtures. Results showed that changes of tensile strength were negligible while elongation at break was significantly increased with DES addition of 1% in comparison with unmodified HDPE. Favero et al.\(^2\) investigated the mechanical behavior and microstructure of immiscible plasticized starch/zein blends combining numerical and experimental approaches. In research, five various plasticizers were used, among them two DESs (ChCl: urea and ChCl: glycerol). It turned out that zein is completely insoluble in used DESs and obtained blends had imperfect interphase. Starch/zein blends with the presence of DESs result in hyperplastic mechanical behavior. The application of DESs as plasticizers and solvents of potato starch was described by Zdanowicz and Spycha.\(^3\) Three different DESs based on ChCl were used. The solubility of starch was shown to be different in each individual DES. Potato starch dissolves at 118 °C, 120 °C and 135 °C in ChCl: urea, ChCl: citric acid and ChCl: succinic acid, respectively. The colorless and transparent film was form by mixing ChCl: urea and starch. The film obtained by dissolving starch in ChCl: succinic acid was colorless and transparent but also porous. The worst film characteristics (yellowish, porous, sticky) were observed in film obtained by mixing ChCl: citric acid.

Zdanowicz and Johansson\(^4\) reported an investigation of two- and three-component DESs in the role of potato starch plasticizers. Prepared DESs were mixed with two types of potato starch (native potato starch and hydroxypropylated and oxidized potato starch) and results are compared. For film preparation, three different methods were used as follows: introduction of individual DES components before gelatinization, liquid DES before and after starch gelatinization. Higher elongation at break and lower tensile strength was noticed in films where DES was introduced after starch gelatinization. Better mechanical and barrier properties were noticed in films with unmodified starch than in films containing hydroxypropylated and oxidized potato starch. Imidazole-based DESs are used as plasticization and dissolution media in combination with potato starch and high-amylose starch in order to obtain thermoplastic starch films.\(^5\) Two-component DESs were used based on imidazole combined with ChCl, glycerol, citric acid and malic acid. The plastification process of prepared films was investigated. DESs containing imidazole with citric and malic acid were not suitable for starch plastification due to the lower dissolving ability of starch. Transparent and highly elastic films are obtained after compression molding using imidazole-based DESs with ChCl and glycerole. Preparation of starch-based films with DESs and different additives (sodium and calcium montmorillonite, tannin and microcrystalline cellulose) was performed by Zdanowicz and Johansson.\(^6\) In film preparation, two different DESs are used (ChCl: glycerol and CCit: urea: glycerol) combined with starch and various mentioned additives. Elongation at break for films containing ChCl: glycerol was in the range from 29.2 to 78.5% while much lower values were noticed in the case of films with CCit: urea: glycerol (5.1 – 29.7%). Maximum tensile strength was 4.7 – 6.1 MPa and 9.9 – 14.5 MPa for ChCl: glycerol and CCit: urea: glycerol films, respectively. In preparation of thermoplastic starch films Adamus et al.\(^7\) used DESs and modified montmorillonite as base. Extrusion and thermocompression are applied as processing methods. In the role of plasticizer two DESs are used, ChCl: urea and ChCl: imidazole. With an increase in the amount of the montmorillonite in the mixture, elongation at break was gradually decreased (245 – 91%) for films with ChCl: urea while for the film with ChCl: imidazole values are slightly changed (131 – 158%). Grylewicz and coworkers\(^8\) reported the preparation of thermoplastic starch films composed of potato starch, DESs and wood fibers. Biocomposites are manufactured by the thermocompression method. The best mechanical properties were obtained for composites containing plasticizer imidazole: glycerol with tensile strength up to 11 MPa and Young’s modulus to 590 MPa.

Sugar based DESs (fructose, glucose and sucrose) in combination with glycerol are also used as plasticizers in preparation of thermoplastic starch.\(^9\) Mentioned DESs have proven to be good plasticizers giving transparent, homogenous and flexible composites. Films with glucose and fructose showed higher tensile strength and lower elongation at break than films containing sucrose. Zdanowicz et al.\(^10\) prepared DESs with glycerol and choline salts with α-hydroxylate anions and used them as starch plasticizers. Thermoplastic starch films are prepared via thermocompression molding and the best process parameters were: 140 °C, 12 tons, 10 min. Based on the obtained results it was concluded that a higher amount of CCit (choline citrate) in the mixture led to the higher viscosity and glass transition temperature of prepared films. Content of CCit also affected tensile strength and elongation at break. Increasing of CCit in DES tensile strength was increased while elongation at break was decreased. At manufactured film with CCit: glycerol: DES retrogradation was not observed even after 12 months. For the purpose of plasticizers, alcohol-based DESs have also been prepared by Zdanowicz et al.\(^11\) Films were obtained by hot melting methods: extrusion and thermocompression. Thermoplastic starch films prepared via extrusion, that contained ChCl: sorbitol (1:2) as plasticizer had better mechanical properties than
films obtained with thermocompression. Maximum values for tensile strength, elongation at break and Young’s modulus obtained for films by extrusion were 10 MPa, 52% and 616 MPa, respectively.

Table 2. Composition of starch-based films.

| Starch type | DES | DES amount | Other components | Reference |
|-------------|-----|------------|------------------|-----------|
| Corn        | ChCl : urea | 30 wt % | – | [27] |
| Corn        | ChCl : urea ChCl : glycerol ChCl : ethylene glycol | – | Mixture of hardwood and softwood sawdust | [28] |
| Corn        | ChCl : urea (1 : 2) ChCl : glycerol (1 : 2) | 30 pph | Zein protein | [29] |
| Corn        | ChCl : urea 20; 40; 60; 80 wt % | | Lithium bis(trifluoromethanesulfonfyl) imide (LITFSI) | [32] |
| Corn        | ChCl : urea 10; 20; 30; 40; 50; 60; 70; 80; 90 wt % | | Lithium bis(trifluoromethanesulfonfyl) imide | [31] |
| Corn        | ChCl : urea ChCl : glycerol ChCl : ethylene glycol | 1; 3 wt % | High density polyethylene | [32] |
| Corn        | ChCl : urea ChCl : glycerol | 30 pph | Zein protein | [33] |
| Potato      | ChCl : urea ChCl : succinic acid ChCl : citric acid | 30 wt % | – | [34] |
| Potato      | ChCl : urea ChCl : glycerol ChCl : sorbitol | 30 pph | – | [35] |
| Potato      | ChCl : imidazole Glycerol : imidazole Citric acid : imidazole Malic acid : imidazole ChCl : urea | 25 wt % | – | [36] |
| Potato      | ChCl : urea ChCl : glycerol CCit : urea : glycerol | | Microcrystalline cellulose, tannin, sodium and calcium montmorillonite | [37] |
| Potato      | ChCl : urea ChCl : imidazole | 29 wt % | Montmorillonite | [38] |
| Potato      | ChCl : urea ChCl : glycerol Glycerol : imidazole | 30 – 55 pph | Wood fibers | [39] |
| Potato      | Glycerol : fructose Glycerol : glucose Glycerol : sucrose | 35 pph | – | [40] |
| Potato      | Choline lactate : glycerol Choline malate : glycerol Choline citrate : glycerol | 35 pph | – | [41] |
| Potato      | ChCl : xylitol ChCl : sorbitol CHCl : maltitol Betain : sorbitol | 35 pph | – | [26] |
### OTHER POLYMER-BASED FILMS

Cellulose is a biopolymer that has a fibrous form and it is not completely suitable for the production of continuous, film-like materials. Cellulose is insoluble in the most common solvent. Therefore, cellulose derivatives are more appropriate for film preparation.[43]

Wang et al.[44] successfully applied ChCl : urea DES as a plasticizer in the production of regenerated cellulose film. Obtained cellulose films were flexible and transparent. An increase of DES in films led to decreasing in the tensile strength (31.34 – 4.14 MPa) and increasing in the tensile strain at break (25.92 – 34.88 %). The elastic modulus of obtained films was in the range from 14.80 to 185.24 MPa. Sirvio et al. reported preparation of cellulose-based biocomposite films with the addition of DESs in the role of the plasticizers. The thermochemical and mechanical properties of composites were determined. The tensile strength of cellulose-based films followed similar trends to Young’s modulus. Based on the results it could be concluded that DES-based plasticizers had a slightly better effect in comparison with traditional plasticizers. In order to diminish matrix crystallinity formed by lithium bis(trifluoromethanesulfonyl) imide and cellulose acetate, Ramesh et al.[45] incorporate DESs (ChCl : urea) in cellulose-based films. Films were manufactured by the solution casting method. An increase of DES in the film matrix led to the suppression of the crystalline phase. The same group of authors investigated the ionic conductivity of cellulose-based films plasticized with DES.[46] The chemical integrity and ionic conductivity of films were improved with increasing DES content in the matrix. Results showed that films containing DES are more heat-stable than films with pure cellulose acetate.

Agar is a polysaccharide extracted from different marine seaweeds. It found application in different areas like biomedical, food, pharmaceutical and biotechnological sciences. It is mainly used as stabilizing, gelling or thickening agent.[47] Sousa et al.[48] reported the preparation of agar films with DESs as plasticizers via compression-molding. In this research, two DESs are used: ChCl : urea and ChCl : glycerol. Microstructure, mechanical properties and water resistance of films are determined. Films agar/ChCl : urea showed very good forming ability while agar/ChCl : glycerol showed poor film forming ability. Agar-based films with ChCl : urea as plasticizer showed tensile strength in the range of 3.83 – 34.3 MPa, elongation at break from 25.3 to 74.1 % and Young’s modulus 13.4 – 754.0 MPa. Further, Sousa et al.[47] investigated the optimization of thermocompression process of agar films with the addition of ChCl and urea. Agar, ChCl and urea are mixed in the ratio of 5 : 1.16 : 1, respectively. The most resistant film was manufactured at 140 °C, 20 min and 176 kN. Pectin is a renewable and natural polysaccharide with poor barrier and mechanical properties so its application in food packaging is limited. In the food industry pectin is usually used as a stabilizer, encapsulating and thickening agent.[49] For the first time, Gouveia et al.[49] reported successful preparation of thermoplastic pectin films with the incorporation of natural DES as a plasticizer. For this research ChCl : glycerol DES was used and films are prepared by thermocompression. Films are manufactured at 120 °C, 196.1 kN, 20 and 25 minutes. The tensile strength of

### Table 3. Composition of various polymer-based films.

| Polymer               | DES                          | DES amount          | Other components in film | Reference |
|-----------------------|------------------------------|---------------------|--------------------------|-----------|
| Cellulose             | ChCl : urea (1 : 2)          | 30.29; 53.25; 58.04; 62.07 % | –                        | [43]      |
| Cellulose             | ChCl : glycerol (1 : 2)      | 12.5; 25.0; 37.5 %  | Hydroxyethyl cellulose   | [42]      |
| Cellulose acetate     | ChCl : urea (1 : 2)          | 10; 20; 30; 40; 50; 60; 70 w % | lithium bis(trifluoromethanesulfonyl) imide| [44]      |
| Cellulose acetate     | ChCl : urea (1 : 2)          | 20; 40; 60 w %      | lithium bis(trifluoromethanesulfonyl) imide| [45]      |
| Agar                  | ChCl : urea (1.16 : 1)       | –                   | –                        | [46]      |
| Agar                  | ChCl : urea (1 : 2)          | –                   | –                        | [47]      |
| Pectin                | ChCl : glycerol (1 : 2)      | 30 %                | –                        | [48]      |
| Pectin                | ChCl : citric acid monohydrate (1 : 1) | 1 %             | –                        | [49]      |
| Agarose               | ChCl : urea (1 : 2)          | 30; 40; 50; 60; 70 wt % | –                        | [50]      |
prepared films with DES was 14.3 and 10.6 MPa after 20 and 25 minutes, respectively. Shafie et al. reported the preparation of pectin-based edible film prepared with DES (ChCl: citric acid monohydrate) as a plasticizer. Preparation of DES was conducted in three different ratios ChCl and citric acid monohydrate (3:1, 1:1 and 1:3). Values of tensile strength, elongation at break and Young’s modulus were in the range of 6.79 – 7.32 MPa, 18.88 – 21.83 % and 23.49 – 33.64 MPa, respectively.

Agarose is a polysaccharide that has desirable properties (nontoxic, renewability, biodegradability, low cost, natural abundance) for the production of eco-friendly material. Agarose films with ChCl were in the range of 6.79 – 7.32 MPa, 18.88 – 21.83 % and 23.49 – 33.64 MPa, respectively.

CONCLUSION

DESs have found a wide range of applications among them a plasticization role in the preparation of thermoplastic films from natural polymers such as chitosan, starch, cellulose, agar, agarose and pectin. This review summarizes researches about the application of DESs in the plasticization process. The most common DESs used as plasticizers are ChCl: urea and ChCl: glycerol. The largest number of published papers relates to the preparation of corn or potato starch-based films. In most cases, DESs act as a good plasticizer, but obtained films had different properties depending on used polymer and plastificator. But there is still room for research, in order to improve the properties of biopolymer-based films and enable their use on a daily basis.

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