The aim of the project is obtaining mainly natural-based deep eutectic mixtures and studying their plasticizing and dissolving properties for starch.

Polymeric materials from oil-based resources (i.e. polyolefins as polyethylene – PE, polypropylene – PP) constitute a serious environmental ballast after usage, because they are resistant to biodegradation. Looking at accumulating landfills, following news from the wildlife which shows medusa-like plastic bags drifting on see depth, we realize that plastics advantage, which is resistance to environmental conditions giving longevity becomes a disadvantage.

One of the solutions of these problems is replacing oil-based plastics with biodegradable polymers, especially for agriculture or food purpose, where the long period of usage is not required. Natural-based polymers, i.e. polysaccharides, polyesters synthesized with natural compounds (like polylactide made with lactic acid) or generated via fermentation polyhydroxyalcanoates (e.g. PHB) are alternative for polyolefins [1].

Starch is one of the polysaccharides, which besides cellulose and chitin is the most abundant biopolymer in nature. Starch and its derivatives are used widely not only for food industry but also for paper, pharmaceutical, textile, metallurgical, foundry and agricultural industries. Starch in its native form can not be directly processed into "plastic" materials. This polysaccharide occurs in granular form, where crystalline structure is formed with hydrogen bonds between amylopectin and amylose chains and hinders its processing. This kind of structure organization obstructs starch flow through forming/processing machine. One of the example of starch modification, facilitating its processing based on starch transformation form crystalline into amorphous from is thermoplasticization (destructurization).

This process requires a plasticizer (modifier), increased temperature and shear stress. Plasticizers are polar compounds, which interact with starch through hydrogen bonds. In contact with plasticizer, there are formed new hydrogen bonds between OH groups of starch units and polar group of modifier, parallely interchain hydrogen bonds are disrupted. Thermoplastic starch-based materials are biodegradable and environment-friendly as well as they are suitable for indirect contact with food. Thermoplastic starch – TPS and its blends are applied to production of disposable cutlery, packaging, bags, raincoats and mulches.

Glycerol (glycerin), ethanolamine, formamide, glycols and ionic liquids are exemplary of TPS plasticizers [2]. Nevertheless, mentioned compounds have some drawbacks. Glycerol is much hygroscopic and lead to starch retrogradation (rebuilt of semi-crystalline structure leading to brittleness of the material, this phenomenon is also responsible for bread staling), formamide is toxic and ionic liquids (IL) are too expensive. Molecular ionic liquids (e.g. imidazolium ILs) can be replaced with deep eutectic solvents (DES) that have similar character to conventional ILs. Eutectics are mixtures or alloys, in which melting temperature of individual component is higher than whole system. Well-known real-life example of such kind of system is eutectic ice – saturated solution of salt (NaCl) with water. Its melting temperature is -21°C. Thanks to eutectics fish can life in cold water under ice floe.

Deep eutectic solvents it is quite new concept. DESs prepared from organic compounds first time appeared in scientific literature at 2003, in Abbott and coworkers work [3] where properties of choline chloride and urea mixture (in 1:2 molar ratio) were described. Mixture of this two compounds is liquid at room temperature, whereas melting temperature of choline chloride is 302°C and urea 133°C. Since that moment, a lot of systems based on choline chloride as proton acceptor (or other ammonium salt) and proton donors as polyols, amines, polycarboxylic acids have been investigated. DESs are cheap, easy to prepare (by mixing of components in appropriate molar ratio and heating) and non- or less toxic. Moreover, they can be obtained whole from natural-based compounds. DESs are also good solvents for metal compounds, polysaccharides and peptides, they can consist enzymatic reaction media without enzymes deactivation. Y. H. Choi with coworkers presented a theory where natural DESs occurred in plants take place in biosynthesis, forming media to dissolution for aqueous insoluble compounds (like some flavonoids) in cells [4].

New issue, proposed in the project is manufacturing and characterization of biocomposites from thermoplastic starch plasticized with DES with natural-based (nano)filler addition, like cellulose or clay (montmorillonite). Even small amount of well dispersed (nano)filler in polymer matrix enhances mechanical and barrier properties of final composite, but influence of new plasticizers on properties of biodegradable starch-based composites have not been so far investigated [5].

Choline chloride : urea and choline chloride : glycerol systems are the most studied DES in the context of polysaccharide processing, but a lot of possible combinations of eutectics have not been studied yet. Some part of compounds applied for starch plasticization are in solid form, that hinders its processing e.g. via extrusion, but introducing the compounds as DES component, in liquid state, can moisture starch granules, facilitate mutual mixing and act as a lubricant during extrusion processing.

Deep eutectic solvents exhibit not only plasticizing ability but also can dissolve polysaccharides. Generally starch is insoluble in aqueous media and most organic solvents. What we can see during potato flavor heating is a gruel, it means gelatinized starch, where granules are swollen even 1000 times more. Differential Scanning Calorimetry (DSC) technique allows to distinguish two kind of transformations: gelatinization and dissolution of starch during heating in certain media.

Obtained starch-based materials modified with new plasticizers will be subjected to mechanical (e.g. tensile strength, elongation at break), barrier (water vapor permeability), optical (transparency) and sorption investigations. Moreover, tendency to retrogradation (rebuilt of crystalline form) after prolonged time of storage will be analyzed. Additionally, electrical resistivity of the final materials will be measured in order to evaluation of antistatic or electroconductivity properties. In Poland, there have not been carried out researches related to application of DES to polysaccharides processing or modification, although the components are cheap and abundant.

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