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PhD topic

Biocatalysed synthesis and structural studies of hydrophobic starch derivatives aimed at obtaining polymer materials for the production of biodegradable packaging

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Description of the PhD work

The main objective of the study is to obtain new functional materials based on starch, with improved mechanical properties, increased hydrophobicity and therefore more favorable for use in the production of biodegradable packaging. For this purpose biochemical modifications of the polymer, searching for new pro-ecological and unconventional ways of syntheses are conducted.

Presentation of the PhD work

Development of biobased polymers to replace the traditional petrochemical polymers and the use of clean, environmentally friendly technologies has attracted much attention in the last decades. There is a search for cheap, natural and biodegradable materials. Starch is one of the most interesting biopolymer because of its low cost, availability, biocompatibility and biodegradability. However, the hydrophilic nature, low moisture resistance, high fragility, incompatibility with hydrophobic, non-polar polymers significantly limit the application of native starch for industrial uses. Food, pulp, paper, cosmetics and packaging industries mainly need modified starch with improved processing properties compared to native starch. The plasticization of starch is hampered by its polarity and intermolecular and intramolecular hydrogen bonds responsible for the semi-crystalline nature of this polysaccharide. Disadvantages of starch processing result in addition to the fact that both the glass transition temperature and the melting point is higher than its decomposition temperature. The partial or complete immiscibility in nonpolar and hydrophobic synthetic polymers, friability, and low resistance to moisture, is another limitation of application. Therefore, different types of modifications have been implemented to improve the mechanical properties of starch and its hydrophobisation. One of the most commonly used modification of this biopolymer is esterification using acid anhydrides and fatty acids. However, solvents used for decades in the processing of starch, like DMSO, DMF or pyridine, have a negative impact on the environment, thus reducing further the commercialization process of starch esterification for obtaining biodegradable materials useful in the packaging industry. The use of such organic solvents on an industrial scale is also expensive because it requires high temperatures and long reaction time. Elimination or reduction in the use of toxic solvents from the process of starch modification became possible due to an application of solvent free synthesis in microwave field, enzymes, as well as the new type of less harmful solvents – ionic liquids. The main objective of PhD work is to search for new proecological methods for the synthesis of hydrophobic starch derivatives. Biochemical modifications of starch, mainly enzyme-catalysed esterification based on fungal lipases, are conducted. As acyl donors unsaturated higher fatty acid like oleic acid or rich in these acid, pure and waste oils like rapeseed and sunflower oils are used. Reactions are carried out in two steps. Firstly, the oil is hydrolysed with a *T. lanuginosus* lipase in a buffer solution form. Then the glycerol is removed from the obtained hydrolysate and the remaining fatty acid mixture is used for the esterification of formerly pregelatinised in ionic liquid potato starch. Esterification is also catalysed by fungal lipase from *T. lanuginosus* but immobilized on a polymer carrier and the reaction is carried out in the anhydrous conditions. In the next step to confirm the polysaccharide modification and determine the physicochemical properties of the obtained esters, the following methods are used: determination of the degree of substitution; elemental analysis; ^{1}H NMR and FTIR spectroscopy; X-ray powder diffraction; thermal analysis (DSC/TG) and scanning electron microscopy (SEM). Then the hydrophobic starch derivatives obtained in the above way are tested in order to determine the possibility of their use in the production of biodegradable packaging by determination of MFR and bulk density; plasticization of modified starch on a blender ; testing of the extrusion process on a single-screw laboratory extruder (determination of basic processing parameters); testing of

the film in terms of mechanical strength at static tension, Elmendorf tear strength, moisture absorption and impact resistance hydrophobicity by measuring the surface wettability angle. The last step are studies on the biodegradability of the films obtained in the soil and phytotoxicity tests on monocotyledonous and dicotyledonous plants in a specially prepared vegetation hall.