

Starch fatty acid esters – versatile bio-based thermoplastics

The biopolymer starch is well-known in the kitchen for baking, cooking, and as a component of flour and is available in large quantities. This makes starch interesting as sustainable resource to convert it into biodegradable products to replace non-biodegradable synthetic polymers. The esterification of polysaccharides is a convenient and efficient method to modify the properties of starch and to open up new important applications like biobased thermoplastics. The reaction products natural and harmless fatty acids such as lauric acid with starch under certain conditions yields starch-based thermoplastic.

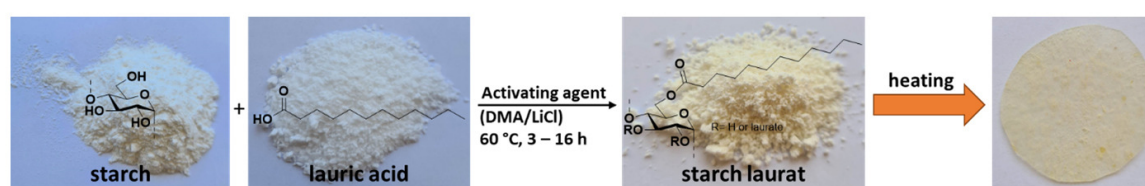


Fig. 1. Graphical abstract: Conversion of starch with lauric acid in presence of an activating agent to the melttable starch laurat.

The less reactive carboxylic acid is activated by activating by simple agents like 4-toluenesulfonyl chloride (Tos-Cl), *N,N'*-dicyclohexylcarbodiimide/4-(1-pyrrolidinyl)pyridine (DCC/PP), 1,1'-carbonyldiimidazole (CDI), and iminium chloride (ImCl) formed from *N,N*-dimethylformamide and oxalyl chloride. The reactive intermediates formed possess different reactivity towards the hydroxy groups of starch and thus, the conversion can be easily controlled. In this way, the different amount of hydroxy groups starch can be esterified and the so-called degree of substitution (DS) can be varied that controls the melting temperature of the product. The maximal DS is 3, i.e. all hydroxy groups are converted.

The reactions discussed here were carried out in medium *N,N*-dimethylacetamide and LiCl under homogeneous conditions. The studies of reaction efficiency include reaction time and activating agent applying three moles lauric acid and activating agent per repeating glucose unit carried out at 60 °C for 3, 6, and 16 h. The products possess DS values of laurate ranging from 0.68 to 2.18. The DS of the starch laurates obtained under comparable conditions applying different activating agents increased in the order DCC/PP < CDI < Tos-Cl < ImCl. The DS values affect melting; for example, starch laurate with a DS of 0.68 melts at about 190 °C, whereas a product with a DS of 1.31 has a significant lower melting temperature with about 110 °C, and with a higher DS of 1.59, it already melts at about 100 °C. This tendency was observed for all samples prepared. Comparing starch esters obtained with different activation agents, however, with comparable DS values, display different melting temperatures. The reason may be side reactions like chain degradation that is pronounced with Tos-Cl while DCC does not yield reduction of the molar mass. The measurement exhibits an increasing reduced viscosity by increasing DS values.

The structure of the starch ester could be well characterized by means of NMR spectroscopy. The substitution pattern depends on the activating agent. For instance, Tos-Cl, DCC/PP and oxalyl chloride/DMF promote a reaction at the primary OH, while CDI leads to starch esters that are predominantly substituted at position 2.

Products with predominant substitution at position 2 decompose upon melting while 6-O-substituted products show excellent thermoplastic behavior.

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[Synthesis and properties of thermoplastic starch laurates](#)

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