



Enzymatic acylation of starch

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ABSTRACT

Starch a cheap, abundant and renewable natural material has been chemically modified for many years. The popular modification acylation has been used to adjust rheological properties as well as deliver polymers with internal plasticizers and other potential uses. However the harsh reaction conditions required to produce these esters may limit their use, especially in sensitive applications (foods, pharmaceuticals, etc.). The use of enzymes to catalyse acylation may provide a suitable alternative due to high selectivities and mild reaction conditions. Traditional hydrolase-catalysed synthesis in non-aqueous apolar media is hard due to lack of polysaccharide solubility. However, acylated starch derivatives have recently been successfully produced in other non-conventional systems: (a) surfactant-solubilised subtilisin and suspended amylose in organic media; (b) starch nanoparticles dispersed in organic medium with immobilised lipase; (c) aqueous starch gels with lipase and dispersed fatty acids. We attempt a systematic review that draws parallels between the seemingly unrelated approaches described.

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1. Introduction

Polysaccharides constitute an extremely interesting group of biogenic polymers, used by organisms in crucial functions such as energy storage as well as diverse structural and defence orientated workings. Much is said by the fact that evolution has endowed plant attacking microorganisms with vast collections of enzymatic tools that degrade the polysaccharidic materials that constitute the bulk of plant defence. Also polysaccharidic building blocks are the main products of photosynthetic pathways that harness solar energy in order to sustain life as we know it. As a result polysaccharides are to be found in great abundance in biomass. Starch in particular is the second most abundant polysaccharide and acts as energy storage in plants.

Starch's use in applications outside its natural role, however, has been rather limited. It follows that any process that would enhance the properties of this cheap material for other applications is of great interest from a biotechnologist's or a materials scientist's point of view. Different modifications (chemical or otherwise) of these polymers have been investigated for many years in order to produce useful derivatives, with hydroxyl related chemistry claiming a large share due to the abundance of such groups on the polysaccharidic backbone. One such type of reaction is acylation of the polymer's hydroxyls to produce different types of

polysaccharide esters. Many types of starch esters have been prepared and have found uses in a wide range of applications. The hydroxyl groups of the anhydroglucose unit (AGU) monomers, offer a site suitable for esterification with acyl group containing substrates. Acetylated starches have been around for many years and low DS (degree of substitution: mol acyl per mol anhydroglucose) derivatives are used in the food industry in order to control and adjust the rheological behaviour of pastes (Liu et al., 1997; Raina et al., 2006). Succinate starches are another popular group of esterified starches with great commercial importance. Starch succinates reinforce swelling capability at lower temperatures (Rudnik et al., 2005), while alkenyl succinate starch derivatives introduce hydrophobic groups to the hydrophilic chain giving the starch emulsifying capabilities. Medium and long chain fatty acid starch esters are used in starch copolymerisation, as it has been noted that fatty acid ester acts as an internal plasticizer (Thiebaud et al., 1997), while their potential use in drug delivery systems and other biomedical applications is also being investigated (Malafaya et al., 2001). In order to obtain the starch esters with carboxylic acids, the most popular approach involves use of the acid anhydride or acid chloride (more effective for higher esters), in the presence of pyridine which acts both as catalyst and solvent (Sagar and Merrill, 1995). These reactions can proceed with the starch in suspension or gelatinised, but generally show low selectivity. This can sometimes be controlled with use of different reagents or conditions (Tomasik and Schilling, 2004). It is evident that use of harsh reaction conditions, alkaline or acid catalysis and toxic chemicals is in many cases required for the production of starch acylates. This may limit their suitability for use in

Abbreviations: DS, degree of substitution; AGU, anhydroglucose unit; FAME, fatty acid methyl ester; AKD, alkyl ketene dimer.

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