



## Review

## Carbohydrate functionalized hybrid latex particles

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## ABSTRACT

In this review we highlight the progress in the synthesis of carbohydrate functionalized hybrid latex particles, focusing on different synthetic approaches which use carbohydrates as a surfactant/stabilizer, initiator, grafting site and/or as a macromonomer. These nanocomposites are receiving increasing attention in academia as well as in industry, due to increasingly stringent societal demands for biobased, biodegradable, and biocompatible materials. Furthermore, we will report on the use of nanostructured carbohydrate materials, such as cellulose nanocrystals, starch nanocrystals, and starch nanoparticles. These novel materials represent an interesting emerging field, and examples of latex nanocomposites have only recently been reported. It is the authors' opinion that using carbohydrate materials for the synthesis and production of latex polymers will become of increasing importance as we move towards a more sustainable future.

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## 1. Introduction

Amongst the biopolymers available to polymer chemists, carbohydrates in particular stand out as they are biodegradable, encompass a broad diversity in structure and functionality, are abundant, and are produced at sufficient scale to be of industrial importance (Poli et al., 2011). Cellulose and starch (*i.e.* amylose and amylopectin), are two prime examples of carbohydrates that meet these criteria, and have consequently found widespread use in academia as well as in the chemical industry (Heinze & Koschella, 2005; Whistler, BeMiller, & Paschall, 1984).

Cellulose, amylose, and amylopectin are high molecular weight polymers, all consisting of glucose monosaccharide units linked through  $\alpha(1 \rightarrow 4)$ ,  $\alpha(1 \rightarrow 6)$  or  $\beta(1 \rightarrow 4)$  glycosidic bonds. Despite this structural similarity, these carbohydrates possess remarkably different physiochemical properties. The  $\beta(1 \rightarrow 4)$  glycosidic linkages in cellulose provide a highly regular helical structure responsible for introducing a high degree of crystallinity and strong inter- and intramolecular hydrogen bonds. This makes cellulose a stiff, water-insoluble polymer and consequently an important skeletal component in plants. Conversely, amylopectin is a branched polymer and an important part of the metabolism cycle of plants (Zeeman, Kossmann, & Smith, 2010) due to the presence of  $\alpha(1 \rightarrow 6)$  glycosidic bonds present in addition to the  $\alpha(1 \rightarrow 4)$  glycosidic bonds. Once isolated, amylopectin is a predominantly amorphous polymer and can be readily digested by enzymes to release the stored energy. However, in plants amylopectin is deposited in semi-crystalline, water-insoluble granules, interspersed with amorphous amylose, offering the possibility of prolonged energy storage (Zeeman et al., 2010). This diversity in physiochemical properties of cellulose and starch, which originates from minor structural differences, is one of the main reasons why carbohydrates are used in a broad range of (industrial) applications, and why much research is currently dedicated to exploring novel uses for these biopolymers and their chemically modified analogs. For industrial applications (Santana, Angela, & Meireles, 2014) such as paper manufacturing (Cimpeanu & Kern, 2014), corrugating (Vishnuvarthanan and Rajeswari, 2013), gypsum fibre board (Qiang et al., 2002), and textiles (Meshram, Patil, Mhaske, & Thorat, 2009), starch is the carbohydrate of choice as the starch granules can be readily dispersed or solubilized in water, partially or fully depolymerized through the use of acids and enzymes, and modified through functional hydroxyls that are more reactive than those in cellulose (Maurer, Kearney, & Rapids, 1998). In paper coating, for example, starch adds binding power, flexibility, thickening, higher stiffness, and film formation properties to the coating (Maurer et al., 1998). However, the use of starch also increases water sensitivity, which impairs wet strength, wet rub resistance, and can cause rheological problems due to retrogradation. Consequently, over the past decades starch faces increasing competition from synthetic binders, which have become the dominant binder technology because they outperform starch in some (or multiple) aspects (Maurer et al., 1998). With increasing environmental constraints and societal pressures, alternatives to synthetic binders are becoming increasingly relevant. Two recent developments that meet this sustainable requirement are the use of starch nanoparticles and the use of starch containing synthetic latexes.

Carbohydrate (modified) nanoparticles have also generated a significant amount of interest for biomedical applications (Caro & Pozo, 2015; Liu, Jiao, Wang, Zhou, & Zhang, 2008; Oh, Lee, & Park, 2009). The hydrophilic nature of many carbohydrates provides “stealth” properties allowing the nanoparticle to effectively evade the host’s immune system and deliver a payload to a target tissue (Lemarchand et al., 2006; Lemarchand et al., 2004). Furthermore, certain carbohydrates can promote selective cell uptake due to specific receptor interactions. But perhaps the most

important properties that carbohydrates provide is that they are non-cytotoxic and biodegradable (Oh et al., 2009).

The above examples demonstrate the potential of carbohydrate functionalized nanoparticles, especially in industrial applications such as paper manufacturing, where the blending of starches with synthetic latexes is often still the state-of-the-art technology (Maurer et al., 1998; Bloembergen, McLennan, Lee, & van Leeuwen, 2008). The objective of this review paper is to present an overview of the various academic and industrial routes towards carbohydrate functionalized hybrid latex particles. First, a brief summary of general carbohydrate chemistry will be provided and, subsequently, used to describe how modification of soluble carbohydrates results in functional building blocks that can be used in a range of polymerization processes. Furthermore, we will discuss the emerging field of carbohydrate nanostructures and how these colloids can be used to synthesize carbohydrate functionalized hybrid latex particles. Last, the review will be concluded with a perspective by the authors on the future directions in this field.

## 2. Brief overview of carbohydrate chemistry

Carbohydrates have been intensely studied since the early 19th century, but it took until the beginning of the 20th century before their molecular structure was determined, and until the end of that century before these polymers were chemically synthesized (Kobayashi, Kashiwa, Shimada, Kawasaki, & Shoda, 1992). Many excellent and comprehensive books, book chapters and review papers have been written on the topics of carbohydrate structure, chemistry and properties and the interested reader is referred to these works for a more in-depth review (Cumpstey, 2013; Kaur, Ariffin, Bhat, & Karim, 2012; Robyt, 1998; Zaikov, 2005). Here, we will limit ourselves to a brief overview of carbohydrate chemistry, for the benefit of the reader, to support the following sections of this review.

### 2.1. Carbohydrate modification using small molecule chemistry

Although some carbohydrates contain reactive carboxylic acid or amine functionalities, the predominant accessible functionality on carbohydrates are the less reactive hydroxyl groups. Consequently, much attention has been dedicated to the selective modification of carbohydrates to introduce chemical functionalities other than hydroxyl to expand their use into various industrial applications, see Scheme 1. The extent of derivatization of a carbohydrate is given by the degree of substitution (DS) and defined as the number of hydroxyl substitutions made per monosaccharide repeat unit. Carbohydrates based on glucose, such as cellulose, dextran, amylose and amylopectin, have 3 available hydroxyls per repeat unit and therefore the maximum DS equals 3.

Modifications of carbohydrates are commonly performed through the formation of esters and ethers with the available hydroxyls (Cumpstey, 2013). Etherification is an important industrial process that yields carboxymethylated (1) and hydrophobically modified (2) carbohydrates. In general the etherification involves the reaction of any hydroxyl on the carbohydrate with an alkylation agent in the presence of a base. The industrially important anionic carboxymethyl cellulose, for example, is prepared by treating cellulose with mono chloroacetic acid in the presence of sodium hydroxide to form a carboxymethyl ether (Heinze & Koschella, 2005). Hydrophobically modified hydroxyethyl cellulose and hydroxypropyl cellulose, which are commonly used as viscosity modifiers or colloidal stabilizers, are synthesized through etherification of cellulose with the corresponding epoxy alkanes in the presence of base (Fox, Li, Xu, & Edgar, 2011). Esterification of carbohydrates involves the reaction of a carbohydrate with an acy-

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