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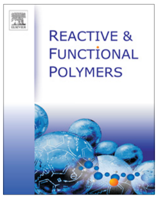

Review

Preparation and application of starch nanoparticles for nanocomposites: A review

Déborah Le Corre [a,*], Hélène Angellier-Coussy [b]

[a] Plant & Food Research Ltd., Private Bag 4704, Christchurch Mail Centre, Christchurch 8140, New Zealand
[b] Unité Mixte de Recherche «Ingénierie des Agropolymères et Technologies Emergentes», INRA/ENSA.M/UMII/CIRAD, Université Montpellier II, CC023, pl. E Bataillon, 34095 Montpellier Cedex, France

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ABSTRACT

The increasing scientific and industrial interest for starch nanoparticles (SNP) has led to the development of numerous methods for preparing sub-micron starch fillers for nanocomposites applications. Starch nanocrystals (SNC), which constitute the focus of this review, are one type of SNP with crystalline property and platelet like morphology. SNC can be extracted from various starch botanical sources, allowing to obtain a large range of amylose content, shape, viscosity in suspension, surface reactivity and thermal resistance. To date, the most common method for extracting SNC remains the mild acid hydrolysis of the amorphous parts of native granular starch. So far, alternative methods render much lower yield. Since first publications on SNC, the principal aim is to use them as reinforcement in polymer matrices. Thanks to the reactive nature of starch, SNC surface can be modified by grafting or cross-linking which renders them more readily dispersible in the polymer matrix. The present review focus on the reinforcing effect and mechanisms of SNC, as well as on their impact of barrier properties of polymers.

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* Corresponding author.
E-mail address: Deborah.lecorre@plantandfood.co.nz (D. Le Corre).

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1. Introduction

Starch is a renewable and biodegradable polymer produced by many plants as a source of storage energy. Humans and their ancestors have always used starchy products. Starch grains have recently (2010) been identified from grinding stones in Europe (Italy, Czech Republic and Russia) dating back to 30,000 years ago [1]. The practical use of starch products (i.e. non-food application) developed when Egyptians cemented strips of papyrus together with starch adhesive made from wheat [2]. Later (from 700 AD) rice starch was used as surface treatment of Chinese papers. Romans also used it in cosmetic creams, to powder the hair and to thicken sauces [3]. Nowadays, main uses of starch have not changed much, with around 60% being used for food and 40% for industrial applications (as described in Fig. 1.16) [4]. Carbohydrate chemists have developed numerous products that have greatly expanded starch use and utility. In 2010, the world starch market was estimated to be 68 million tons [5]. The value of the output is worth □48.8 billion per year, explaining the industrialists and researchers seeking for new properties or high value application.

Most starches in the native form present limitations such as high viscosity, susceptibility to retrogradation, limited digestibility for some, and limited solubility for others. For this reason, most starch used in Food or Industrial applications is first modified [6]. Starches are chemically and/or physically modified to accentuate their positive characteristics, diminish their undesirable qualities (such as high viscosity, susceptibility to retrogradation, and lack of process tolerance), or add new attributes (retention, film formation, digestibility, solubility, etc.). Indeed, mild acid hydrolysis has been used for a long time to modify starch and its properties. In industry, starch slurries are treated with dilute HCl or H_2SO_4 at 25–55 °C for various periods of time, to produce "acid-modified" starch used as sizing agents, in gum candies production, and in paper and paper board production. Recent publications use either of these two acids for preparing starch nanocrystals.

Adding to its renewable nature, relatively low cost and world wide availability, starch is also perceived as an attractive filler to replace fossil-based ones such as carbon black in nanocomposites applications. Carbon black is manufactured by burning oil or natural gas in controlled conditions. It is the most important reinforcing agent used in the rubber industry. In fact, because of its origin from petroleum, carbon black causes pollution and gives to the rubber a black colour. Starch nanoparticles on the contrary are fully renewable and reactive nanoparticles, which have shown good reinforcing and barrier properties associated with white or transparent colours. This explains the increasing number of journal papers recently published on starch nanocrystals as shown in Fig. 1.

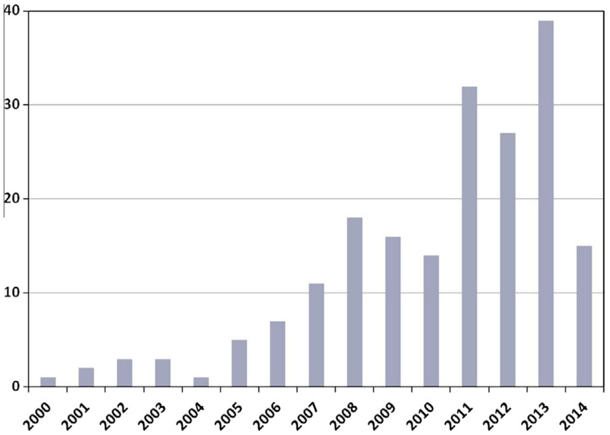

Fig. 1. Evolution of the number of journal articles and patents published with key word "starch nanocrystals". From SciFinder 20/05/2014.

This paper aims at reviewing the different types of starch nano-reinforcements, including starch nanoparticles (SNP) and more particularly starch nanocrystals (SNC), with a focus on their intrinsic properties, possible modification and application to the field of nanocomposites.

2. Starch nano-reinforcements types

2.1. Starch structure

The predominant model for starch structure is multi-scale and consists in the (a) granule (2–100 μm), into which we find (b) growth rings (120–500 nm) composed of (d) blocklets (20–50 nm) made of (c) amorphous and crystalline lamellae (9 nm) [7] containing (g) amylopectin and (h) amylose chains (0.1–1 nm), as presented in Fig. 2.

Starch granules consist mainly of two glucosidic macromolecules named amylose and amylopectin. Amylose is a linear molecule of glucose units linked by (1–4) α-D-glycoside bonds, slightly branched by (1–6) α-linkages. Amylopectin is a highly branched polymer consisting of relatively short branches of α-D-(1–4) glycopyranose that are interlinked by α-D-(1–6)-glycosidic linkages approximately every 22 glucose units [8].

Starch granules consist of concentric alternating amorphous and semi-crystalline growth rings that grow by apposition from the hilum of the granule. Schematically, the semi-crystalline growth rings consist of a stack of repeated crystalline and