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Original Research Paper

Fast and scalable preparation of starch nanoparticles by stirred media milling

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ABSTRACT

A study on the preparation of starch nanoparticles (SNPs) by stirred media milling was conducted in the present work. The effects of milling time and solids concentration on the particle size were investigated. It was found that the particle size of native starch was reduced from 3–20 μm to around 245 nm in 90 min by stirred media milling. The stability analysis of SNPs carried out by dynamic light scattering (DLS) technique revealed good stability over a period of one week. The morphology of prepared starch nanoparticles was characterized by scanning electron microscopy (SEM), Transmission electron microscopy (TEM). The structural changes on SNPs were investigated by wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectroscopy (FTIR). The stirred media milling was found to produce SNPs effectively without the use of any surfactants or additives. The effective, low cost, and easily scalable physical method for the production of starch nanoparticles was presented.

1. Introduction

Starch is a major source of carbohydrates and the great reserves of polysaccharide occur in the different plants. It is considered a polymeric carbohydrate consisting of anhydrous glucose units linked primarily through α-D-(1-4) glycosidic bonds. A starch basically consists of two molecules – the linear and helical amylose (20–30%) with molecular weight of 10^6, and the branched amylopectin (70–80%) with a molecular weight of about 10^{10} [1,2]. The starch occurs as a semi-crystalline microparticles and has a semi-crystalline structure with crystallinity in the range of 15–45% [3]. It is abundantly available low cost natural biopolymer, which has been widely employed as the most important ingredients in many industries such as food, medicine, textile, and chemical industries [4]. Starch and its products are non-toxic, biocompatible, biodegradable, renewable, inexpensive, and widely available; makes them promising alternative in many applications [5,6].

Newer and advanced applications of starch have been continually explored in the last decade [6–9]. The starch has been widely used polysaccharides for synthesis and stabilizing agent for nanoparticles of different types [10–14]. Recently bio-based nanomaterials such as nanocellulose, nanochitin and nanostarch have received greater interest due to their environmentally friendly nature [15]. Starch nanoparticles are expected to play a major role because of their significantly different and unique properties than their bulk counterpart. A comprehensive review of starch nanoparticles preparation, characterization, and applications was reported by Le Corre et al. [16]. The authors reported three widely used methods for preparation of starch nanoparticles, viz., acid hydrolysis, regeneration, and mechanical method. The preparation of starch nanoparticles was reported by different mechanical methods such as an environmentally friendly, high pressure homogenization [17], high-pressure homogenization and miniemulsion cross-linking technique [18], and by high-intensity ultrasonication method [19].

Nanomilling in the stirred media mills is an efficient process for the preparation of ultrafine materials owing to its advantageous features, viz., ease of operation, simple construction, high size reduction rate, and low wear contamination [20]. Stirred media mills have been successfully employed for the preparation of different types of nanoparticles [21–25]. This technique has huge potential, which is evident from the commercialization of several poor water soluble nanodrugs by the nanomilling method [26]. The grinding technique is important in the processing of biomaterials, for example, particle size reduction is a first step in the biomass conversion [27]. Fewer research reports were available in the area of preparation of bio-based nanomaterials by stirred

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media milling. Several relevant reports on the preparation of submicron and nanosize biomaterials by stirred media mills were found in the literature such as preparation of nanoparticles of starch [28], cellulose [29], chitosan [30]. The objective of the present work is to explore the feasibility of the production of starch nanoparticles on the large-scale by wet stirred media milling method. The effects of milling time and solids concentration on the quality of prepared starch nanoparticles were investigated. Stability of prepared SNPs was also evaluated. In addition, changes in the structural properties of starch nanoparticles were investigated by SEM, TEM, XRD, and FTIR analysis.

2. Materials and methods

2.1. Materials

The maize starch was purchased from M/s. National chemical laboratory, Vadodara, India. The particle size of the native starch sample range was between 3 μm and 20 μm (see Section 3.5). All the suspensions were prepared in the Millipore water (Millipore, Elix, Bangalore, India). High density (6000 kg/m^3) yttria stabilized zirconia (ZrO_2) grinding media (chemical composition: 93% ZrO_2, 5% Y_2O_3 and 2% others); purchased from M/s. Saint Gobain ZirPro, France, was used for the nanogrinding experiments.

2.2. Experimental procedure

The wet nanomilling experiments were conducted in a Dynomill (Research laboratory mill, WAB, Switzerland) operating in a recirculation mode. The mill consists of a silicon carbide chamber (80 mL capacity) and a hardened chrome alloy DYNO®-Accelerator. The grinding media and suspension of initial starch powder prepared in the Millipore® water were charged into the mill. More details of the mill used in the present work are given in our previous work [31]. The pre-suspension of starch was prepared by mixing required amount of maize starch in water. The suspension was sonicated by the ultrasonic probe (Ultrasonic, Germany) for 3 min at 35% amplitude to uniformly disperse the starch particles into water before milling. This pre-suspension was used as feed for the media milling experiment. The milling experiment in Run-5 was started with lower solids loading, and solids concentration was gradually increased thereafter. This was accomplished by dispersing fifteen grams of starch into 100 mL of water. The mill charge was prepared by mixing 60 mL of this starch slurry with 50 mL of water, and the experiment was started. The remaining 40 mL of the original starch slurry was fed to the mill at every 10 min in equal volume of 10 mL. The sample volume of around 0.5 mL was collected after regular time intervals for particle size analysis. Milling experiments were carried out at a stirrer speed of 3500 rpm, a grinding media size of 0.4 mm, and with a grinding media filling ratio of 70% (v/v). The selection of stirrer speed was based on the requirement of maintenance of the minimum flow rate of suspension during milling in a Dynomill. Effects of grinding media size were not investigated in the present work, highest media filling ratio was selected as recommended by the supplier of the mill. The cooling water temperature of 5 °C was maintained to control temperature during milling process for all the Runs, except in the Run-3. The same product temperature of 20 °C was maintained in the beginning of all the experimental Runs. Other conditions employed in the different experimental Runs are shown in Table 1. Higher starch loading was used in milling experiment to explore the effectiveness of stirred media milling technique for large-scale production of starch nanoparticles. The milling experiment was also conducted in a vertical laboratory stirred media mill operating in batch mode. The mill consists of stainless steel vessel of 0.5 L capacity with cooling water jacket and a pin type stirrer with four cylindrical rods placed at right angles. Milling experiment was carried out at a stirrer speed of 1200 rpm, a grinding media size of 0.4 mm, solid mass fraction of 0.1 and total 1 kg of grinding media were used in batch mode operation. More details of this mill system can be found in our previous work [32].

2.3. Characterization

Particle size measurements of the ground sample were carried out with a dynamic light scattering (DLS) technique (Malvern Zetasizer Nano ZS90, UK). All the measurements were performed at 25 °C temperature with a measurement angle of 90°. A disposable polystyrene cuvettes with 4 optical sides were utilized for the size measurements. The sample volume of around 0.5 mL was collected after regular time intervals and diluted with around 40 mL of Millipore water. The samples were then degassed by sonication for 1 min using an ultrasonic probe (Ultrasonic, Germany) prior to particle size analysis. An average value of particle size and the polydispersity index (PdI) was reported from three measurement runs. The starch nanosuspension was taken with mannitol (5%, w/v), which was used as a cryoprotectant in lyophilizer Alpha 1-4 LD plus (Martin Christ, Germany). The suspension is placed in a round bottom flask and freeze dried at −45 °C. The lyophilized powder was dispersed into water using an ultrasonic probe for particle size analysis by DLS technique. The Scanning Electron Microscopy (SEM) images were obtained with a S-3400N (HITACHI, JAPAN). A small amount of milled starch suspension was drop casted on a clean silicon wafer and dried under vacuum. The samples were then coated with a gold layer by Ion sputtering using E-1010 (HITACHI, JAPAN). TEM images were obtained with a Tecnai-20 (Philips, Netherlands), which at accelerating voltage of 200 kV provides 0.27 nm point resolution. The drop of nanosuspension was placed on the carbon coated copper grid and dried at room temperature before analysis. The XRD patterns of the freeze dried powder were recorded using D8 Advanced Diffractometer (Bruker AXS, Germany) with Cu Kα (λ = 1.5406 Å) at scan speed of 0.25°/s with 0.05° step size for 2θ ranging from 5° to 35°. The FTIR spectra (450–4000 cm^{-1}) of the native starch and SNPs powder presented on KBr films were acquired on a Spectrum BX FT spectrophotometer (Perkin Elmer, Germany).

3. Results and discussion

3.1. Preparation of starch nanosuspension by stirred media milling

The size reduction results from the compression and shear stresses induced by high speed moving grinding media with an agitator in the stirred media mill. The quality and product particle sizes obtained from a milling process are determined by the number of stress events undergone by the particles (stress number, SN) and the stress intensity (SI) or stress energy (SE) at each stress event. Thus, optimization of operating parameters to obtain desired particle product quality is carried out by evaluating the specific energy or the stress intensity. Further, the particles to be ground in a grinding process and the resulting smaller particles are not subjected to the same number of stresses and to the same stress intensities. There exist distributions of stress events and stress intensity, governed by the operating parameters. Further, the overall specific energy consumption of the mill is given by the product of stress number and stress intensity (E_m = SE.SN). Therefore, the product fineness can be correlated either with the stress number or the specific energy input at constant stress intensity [33]. More details on the application of the Kwade's stress