

Effect of surfactants on the size-distribution of starch nanoparticles during wet grinding

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ABSTRACT

Conventional and non-conventional surfactants were utilized to fabricate corn-starch nanoparticles. The surfactants used were pluronic F-68, span 20, Aerosol TR and Aerosol OT. Starch, in premix with either of the surfactants with concentration 0.5% to 2% were grinded in Netsch MiniCer® laboratory circulation machine (Netsch, Germany) at 25 Hz. Zirconium beads of 1mm diameter were used as the grinding media. At 0.5 hr grinding time, 0.5% pluronic reduced corn starch to the lowest size of 335 ± 5.57 nm. The other surfactants yielded particle size equal to or above 382 ± 9.5 nm. However, with 1 hr grinding, 1% pluronic F-68 reduced the particle size of corn starch to the minimum level of 353 ± 14.50 nm. At 1 hr grinding, the other surfactants reduced the size equal to or above 399 ± 9.50 nm. The lowest PDI was 0.393 ± 0.06 and 0.417 ± 0.02 , respectively with 1% TR-OT at 0.5 hr and 2% TR-OT at 1 hr grinding. Pluronic demonstrated the highest efficiency in size reduction followed by ATR-AOT (1:4).

Keywords: starch, nanoparticles, surfactants

1 INTRODUCTION

Starch has unique molecular properties, which are the causes of its enhanced and limited applications, simultaneously. Starch itself as well as its end products are biocompatible, non-toxic and non-immunogenic. Thus, starch has been reported to be well tolerated in animals and human [1-3]. On the other side, the processing of starch is not straightforward due to the involvement of several parameters in its properties [4-5], therefore, the above factors make development of starch nanoparticles intricate too.

With the increasing demand of nano scale materials, the fine grinding has found wide applications in pharmaceutical and nonpharmaceutical industries [6 -9]. Grinding is achieved by high-speed stirred mills, also called nano or media mill. In the present study, wet grinding using Netsch MiniCer® laboratory circulation machine (Netsch, Germany) (Figure 1) along with the processing aid was used to prepare starch nanoparticles of desired size and the poly dispersity index (PDI).

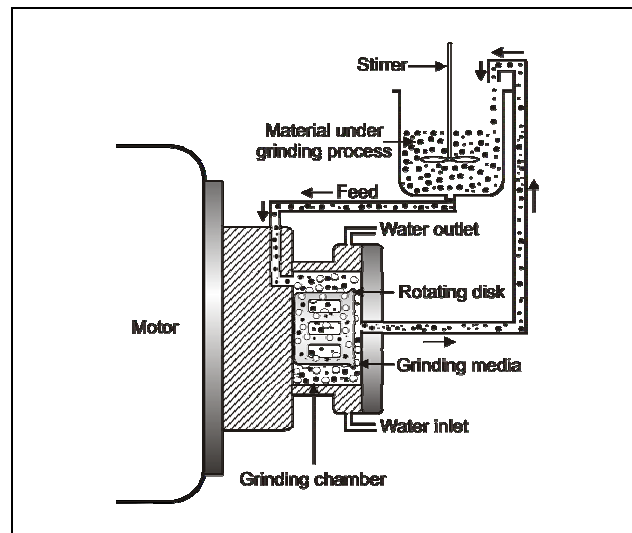


Figure 1: Schematic of Netsch MiniCer® laboratory circulation machine

2 EXPERIMENTAL

2.1 Materials

Corn starch pluronic F-68 (Sigma), span 20 (R&M Chemicals), Aerosol TR (ATR) (Cytec) and Aerosol (AOT) (Cytec) were used as such without any processing or modifications. Zirconium oxide beads of 1 mm diameter were used as the grinding media for a metal-free fine grinding.

2.2 Preparation of Starch Premixes

Added 3.75 gm of starch in about 400 ml of water and heated the mixture at about 76°C until the starch dissolves in water. The mixtures were allowed to cool down naturally to the room temperature and adjusted the pH at 5.5. To the mixtures, added the 4 ml of 0.25% of cross linker, heated to 50°C for 2 hours. The dispersion was allowed to cool down to the room temperature before addition of the required amount of processing aids and stirred well before going to next step. The required amount of surfactants (0.5 to 2%, BOS) was added and stirred well before loading into the nanomill.

2.3 Nanomilling of Starch Premixes

The premixes were treated in Netsch MiniCer® laboratory circulation machine (Netsch, Germany) (Figure 1). The maximum pressure in grinding tank was fixed as 2 bar (200 kPa). To the grinding chamber charged 140 ml of beads, loaded the premix into the collecting vessel and operated the nanomill according to the instructions in the manufacturer's manual [10].

2.4 Determination of Particle Size and PDI

Zetasizer Nano SZ (Malvern Instruments Ltd., UK), integrated with data processing software was used for the measurement of particle size and PDI.

3 RESULTS

The present work is part of an ongoing project on the study of critical factors for the preparation of starch nanoparticles of varying properties by using wet grinding. This paper reports the effect of different surfactants on the particle size and PDI of corn starch.

The effect of different surfactants on the particle size of corn starch is given in Figure 2. The surfactants with different concentrations yielded varied sizes of the corn starch. At grinding time of 0.5 hr, the particles ranged from 335 ± 5.57 nm to 946 ± 105.20 nm. Pluronic at concentration of 0.5% produced the minimum particle size of 335 ± 5.57 nm. At the same grinding time, TR-OT combination (1:4) at concentration of 1% yielded particle size of 382 ± 9.5 nm. At 0.5 hr grinding, the rank of efficiencies of other surfactants in size reduction in the decreasing order was; 1% pluronic (418 ± 3.0 nm) > 2% TR-OT (426.67 ± 16.01 nm) > 0.5% span 20 (478.67 ± 2.31 nm) > 0.5% TR-OT (578.67 ± 18.04 nm) > 1% Span 20 (762.33 ± 24.04 nm) > 2% span 20 (940 ± 105.20 nm). The minimum standard deviation was observed to be 2.31 with 0.5% span 20.

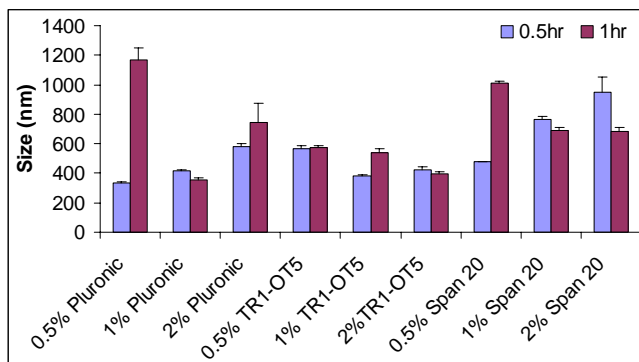


Figure 2: Effect of different surfactants on the particle size of corn starch.

When the material under study was exposed to 1 hr in the grinding zone of nanomill, the particle size range was

observed to be 353.33 ± 14.50 nm to 1166.67 ± 80.83 nm. The minimum particle size of 353 ± 14.50 was noted with 1% pluronic. The second lowest particle size, 399 ± 9.54 was produced with 2% TR-OT. The efficiency of other surfactants with decreasing order was: 1% TR-OT (542.0 ± 27.22 nm) > 0.5% TR-OT (575 ± 15.40 nm) > 2% span 20 (631 ± 27.62 nm) > 1% span 20 (689 ± 19.98 nm) > 2% pluronic (744 ± 130.98 nm) > 5% pluronic (1167.7 ± 80.83 nm). As indicated by the standard deviation, the minimum variation was observed in case of 2% TR-OT blend. In the majority of the cases above, it seemed that the increased grinding time was ineffective in reducing the particle size particularly in the presence of 0.5% and 2% pluronic, 1% TR-OT and 0.5% span 20.

Figure 3 illustrates the effect of surfactants on the PDI of the corn starch.

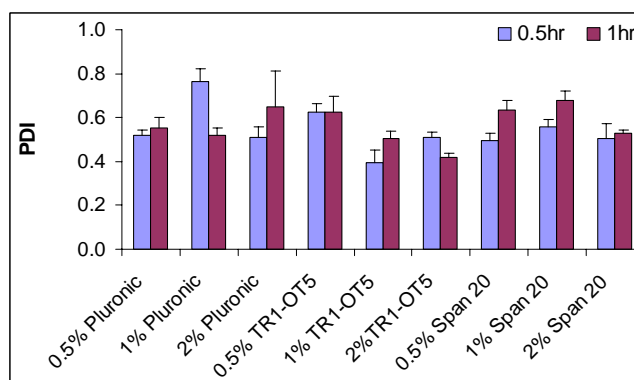


Figure 3: Effect of different surfactants on the PDI of corn starch nanoparticles

After 0.5 hr grinding, at 25 Hz, the PDI ranged from 0.393 ± 0.06 , produced by 1% TR-OT to 0.764 ± 0.06 yielded by 1% pluronic. In case of 1 hr grinding, the PDI range was found to be 0.417 ± 0.02 , resulted from grinding in presence of 2% TR-OT combination to 0.676 ± 0.05 . The time of grinding seemed to have negative effects in presence of 1% TR-OT, 0.5% span 20 and 2% span 20 and otherwise, with rest of the surfactants used in this study.

4 DISCUSSION

A couple of studies using physical treatment of starch have been cited in literature yet, studies on the development of starch particles employing the wet grinding technique are scarce. The use of nanomill offers certain advantages. In the nanomills, the size can be reduced to micron or submicron sizes without use of the organic solvents with manipulation of the operational and formulative variables [11]. In the present study, the particle size and PDI was reduced using different surfactants. The minimum particle size of 382 ± 9.54 nm with the lowest PDI of 0.393 ± 0.06 was achieved with 1% TR-OT blend after 0.5 hr of wet grinding. After 1

hr of grinding, the lowest particle size, 399 ± 9.54 nm with minimum PDI of 0.417 ± 0.020 , was achieved with 2% TR-OT blend. Size reduction in a media mill is predominantly due to shear, compressional and torsional stresses produced by high speed stirring and moving grinding media [12-14]. In a study on starch composite, Yilmaz et al [15] observed reduction of average droplet size of starch composite significantly under the influence of HLB ranging from 0-10. Another study supported the size reduction in presence of the surfactant action [16]. In this study, the surfactants shown to had influenced the reduction in the particle size and PDI of corn starch.

Stenger and coworkers reported that nanomilling, beside size reduction simultaneously causes mechanochemical modification in the materials [16]. Stress-led mechanical activation creates highly energetic particle surface that may induces reactivity potentials with environment, phase transformations and amorphisation. Thus, the resultant particles may have totally different properties such as higher solubility, reactivity or better catalytic performance [18-19]. Keeping the above in view, the nanomill-grinded corn starch in the present study is expected to have varied characteristics. In the present study, the corn starch nanoparticles having size less than 500 nm with low PDI were achieved. The particles of size range 50-3,000 nm are taken up by the Peyer's patches and through the lymphatics, subsequently translocated to blood [20-22]. It has also been reported that the particles of size, 0.5–1.0 μ m are phagocytosed by lymphocytes which, are migrated to the draining lymph nodes [20-21]. Thus, the corn starch nanoparticles may be used, as nano-platform for oral drug delivery, targeting carriers to lymphatics and or for other applications.

The PDI values are bit higher and need to be reduced further. To accomplish this, further study is underway and in upcoming reports elsewhere, the critical factors for particle size of different starches will be presented.

CONCLUSION

Surfactants has shown varying effects on the particle size and PDI of corn starch nanoparticles. Surfactants, particularly the pluronic and TR-OT blend along with other processing and ingredient aids are helpful in developing the corn starch nanoparticles.

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