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CRYSTALLINE STARCH CITRATE BIOPOLYMER NANORODS AS POTENTIAL STABILIZERS IN NANO AND MICRO EMULSIONS

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Abstract: The area of green chemistry which involves the synthesis of biodegradable polymers with better stabilizing properties is fast-developing. Starch biopolymer was citrate modified and converted to crystalline nanorods through green methods and was fully characterized using the fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The crystalline starch citrate showed better morphological and thermal stability properties than the ordinary and modified normal starch which has not been converted to nano form. The TGA result revealed a single step thermal degradation at 240 to 410 °C and percentage weight loss of about 89%. The SEM and TEM also confirmed the synthesis of rod-like or cylindrical nanoparticles with little or no aggregation. This property coupled with the thermal stability makes starch citrate nanoparticles a good stabilizer for nano and micro emulsions.

Keywords: Starch citrate, nanoparticles, stabilizer, biopolymers.

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INTRODUCTION

The most abundant forms of biodegradable polymer which include cellulose, starch, and chitin have become the major point of interest of researchers in the field of material chemistry (1). These biodegradable biopolymers which find diverse applications in medicine, pharmacy, chemistry and other major field of science are chosen because of their biocompatibility, biodegradability, and availability (2, 3). Polysaccharides are known to occupy a larger space in the world of biodegradable polymers and are well known for their versatility in sensing, drug delivery, tissue engineering applications (4) because of the recognition, stabilization and catalytic properties that they possess due to the presence of available hydroxyl groups that can interact with other organic and inorganic hydrophilic or hydrophobic groups in reaction media (5, 6).

Starch occurs as a biodegradable, non-toxic, biocompatible semi-crystalline granule which is made up of about 70% branched amylopectin and about 30% linear amylase and it is one of the most available biopolymers in the universe with its application extent depending on the degree of modification and processing it has passed through (7). Processing operations like gelatinization, retro-gradation, gel formation and crystallization which modifies the internal bonding system and degree of substitution of starch tend to affect the quality and performance of starch for application in industrial sectors (8). Although, these hydrophilic properties inherent in starch biopolymers makes it difficult for the synthesis or growth of starch nanoparticles and there is therefore a need to either increase the hydrophobic content of starch by grafting it with hydrophobic addenda or by developing nano-precipitation techniques for synthesizing of hydrophilic starch nanoparticles in less toxic organic reagents (9).

There are earlier reports on the synthesis of starch nanoparticles by a complex formation between starch and butanol but the significant loss in yield which plagues this method due to the hydrolytic process involved creates a major setback on the use of the technique (10, 11). Although a better method with almost 100 percent yield which involved a high pressure homogenization has been reported for corn starches but this method lacks reproducibility (12). The method which gave both high yield and reproducibility is the nano-precipitation technique which has already been successful for the synthesis of nano forms of poly (lactic acid) and poly (lactic-co-glycolic acid) and is also been recently used for the synthesis of starch nanoparticles (4). This nano-precipitation technique involves a simultaneous emulsification and diffusion technique is easy to scale up for industrial purposes and it gives avenue for starch nanoparticle size and shape control, stability and modification (13, 14).

Nanoemulsions are unstable colloidal dispersions in which at least one of the two immiscible liquids which form the dispersion has its diameter in the range of twenty to two hundred nanometers (15, 16). These nanoemulsions with their oil phase homogenized into aqueous phase have a thermodynamic stability which depends on the nature and concentration of stabilizers and emulsifiers used. They are used to encapsulate poorly soluble drugs and food bioactives for safe delivery to the site of interests (17, 18). The citric acid treatment of ordinary starch or starch nanoparticles expands the application of starch biopolymers in the area of stabilization of nano or micro emulsions (19). Starch citrate which is generally regarded as a form of resistant starch, it does not swell and gelatinize in hot water conditions, hence it can be conveniently used as stabilizers and reinforcements in both cold and hot conditions (7, 20).

The major improvement which citric acid modifications gives starch nanoparticles is that it improves their thermal stability and interfacial tension properties (1) for enhanced performance as good stabilizers or emulsifiers in any nano and micro emulsions produced either in cold or hot reaction conditions (21, 22). The citrate derivatives of starch can be used as structure-directing agents in synthesis of transition metal nanoparticles, directly compressible recipients in tablet formulations and heavy metal adsorbents in polluted or contaminated effluents (7). Hence, the purpose of this research is to synthesize starch nanoparticles with stable shapes and to modify with citric acid so as to improve their thermal, stabilization and emulsification properties in nano and micro emulsions.

MATERIALS AND METHOD

Water-soluble maize starch and citric acid were obtained from Sigma Aldrich, USA. All reagents used were of analytical grade and further purifications were not carried out.

Synthesis of starch nanoparticles

The method of Chin *et al*. was adopted and slightly modified. Starch nanoparticles were dissolved in NaOH/urea (NU) (0.8:1 wt %) solution mixture and introduced into excess absolute ethanol under controlled conditions. In general, 1 wt % native starch solution was prepared by dissolving native starch powder in the NaOH/urea solvent and adding 1 mL aliquot starch solution drop-wisely into 10 mL absolute ethanol which was continuously stirred. The resulting mixture was then centrifuged and the supernatant was removed to obtain the regenerated starch nanoparticles, which were rinsed with absolute ethanol to remove NaOH and urea [15].

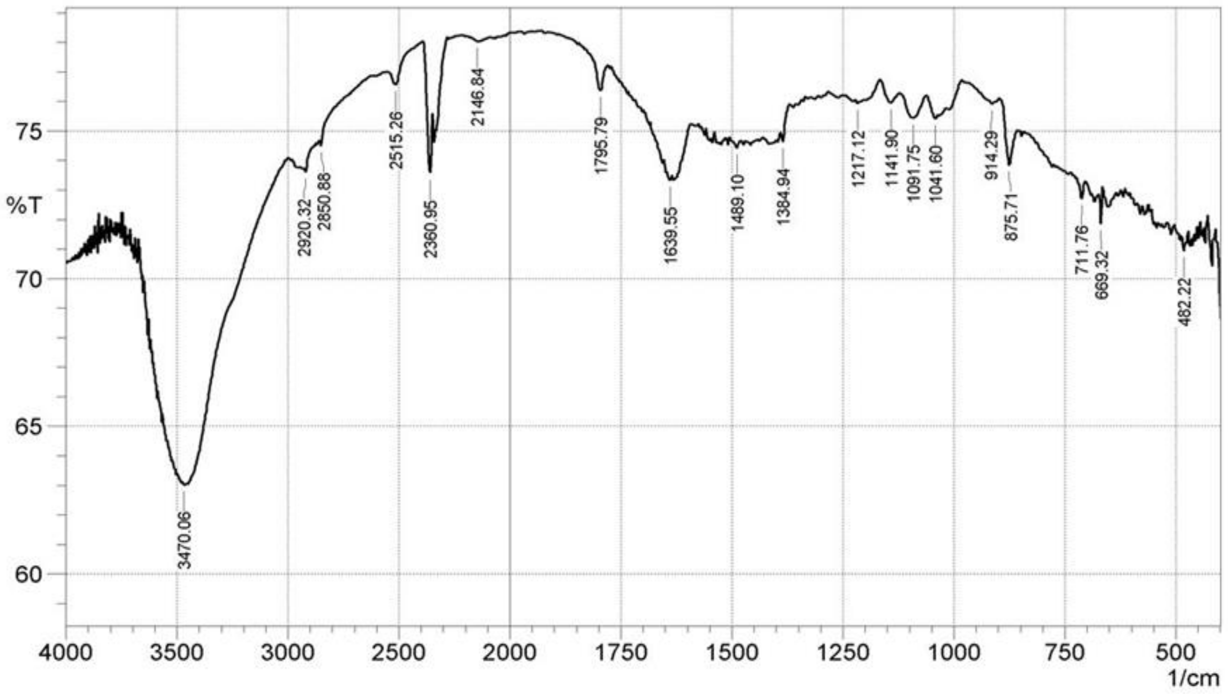
Citric acid treatment of starch nanoparticles

Citric acid (5 g) and sodium hypophosphite (1 g) were dissolved in 6 mL of water and the starch nanoparticle was added to the citric acid solution and mixed vigorously with a glass rod. The mixture was placed in an oven to dehydrate at 100 °C for 30 minutes to eradicate the surface moisture and form a stable citric acid coat on the starch nanoparticles. The oven temperature was increased to 120 °C and the material was allowed to react further for 4 hours. The nano-starch citrate was slurried in water for 30 minutes and adjusted to pH 2 using acetic acid, then later filtered, washed with water and air-dried (7).

RESULTS AND DISCUSSION

This method uses the solubility difference and precipitation equilibria of starch-urea and starch-ethanol complex to synthesize starch nanoparticles. The starch dissolves to produce a temporary starch-urea complex in the alkaline urea solution and is immediately precipitated in absolute ethanol as nanoparticles.

FTIR Analyses



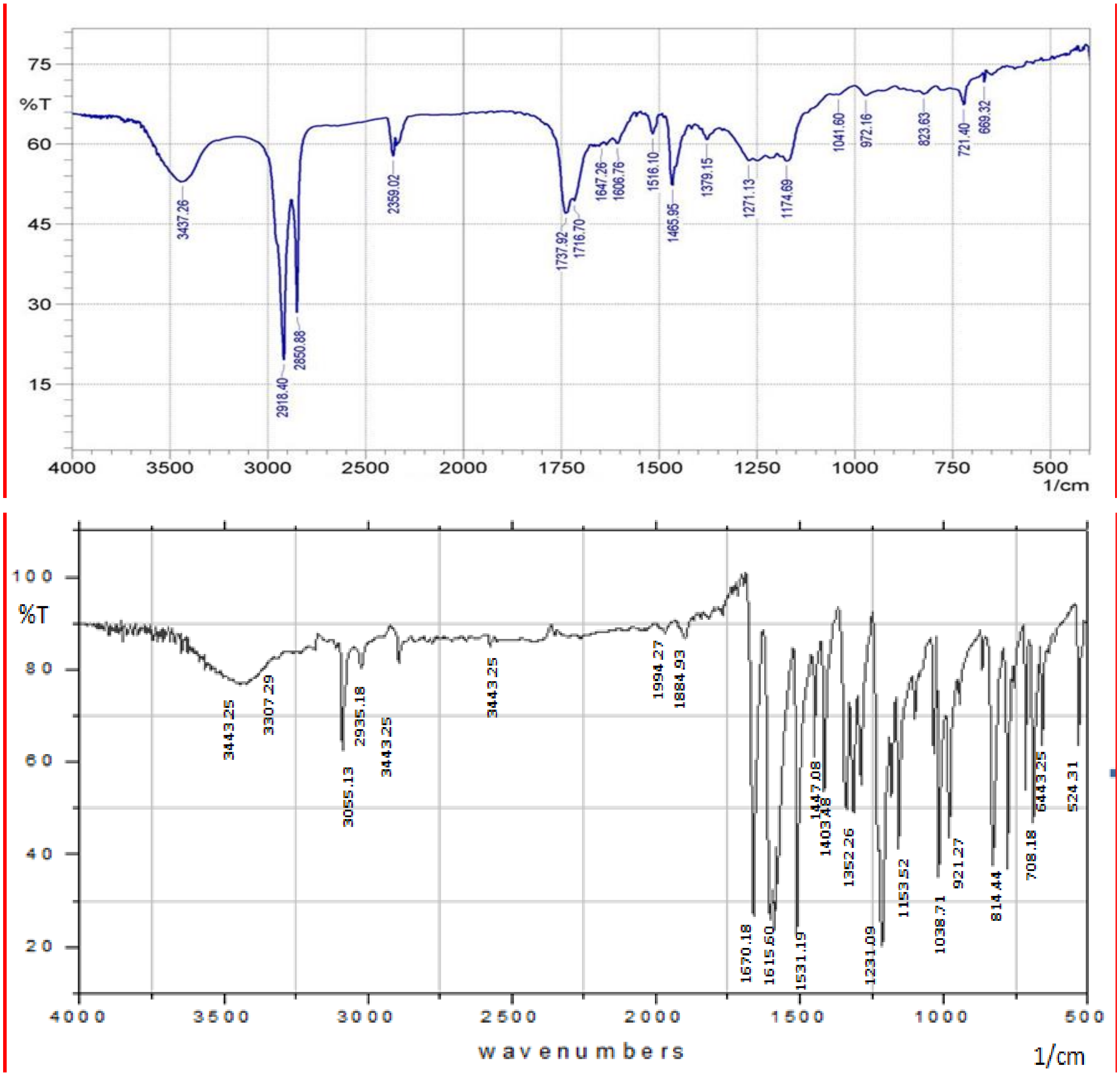


Figure 1: FTIR of starch, nano starch and starch citrate nanoparticles (from top to down)

The transmittance peaks at 3470 cm^{-1}, 2920 cm^{-1}, and 2850 cm^{-1} represents the O-H, symmetric and asymmetric C-H groups respectively while the carbonyl functional group in the starch is shown at 1639 cm^{-1}. The presence of the anhydroglucose glycosidic bond (C-O-C) is revealed at 914 cm^{-1} while the peak at 1091 cm^{-1} confirms the C-O functional group. Several bending vibrations of the C-H group are seen at 1041, 875 and 711 cm^{-1}. The presence of transmittance peaks of typical functional groups at reduced wavenumbers and the disappearance of some bands at the fingerprint region confirms the formation of starch nanoparticles (23). The reductions include 3470 to 3437 cm^{-1} for hydroxyl functional group, 2920 to 2850 for C-H stretching vibrations, 2515 to 2359 cm^{-1} for internal hydroxyl group vibrations, 1795 to 1737 for carbonyl group in starch to the synthesized nanostarch (15). Although some bending vibrations like 1384 to 1465 for C-H and 1217 to 1271 cm^{-1} for OH revealed a minimal increase in wavenumbers. The nanostarch citrate spectrum contain additional transmittance peaks at 1670 cm^{-1} for the C=O of polysaccharide esters, 3307 cm^{-1} for OH of citric acid and several bands for C-H wagging and scissoring which are as result of the citric acid treatment [20].

SEM and TEM Analyses

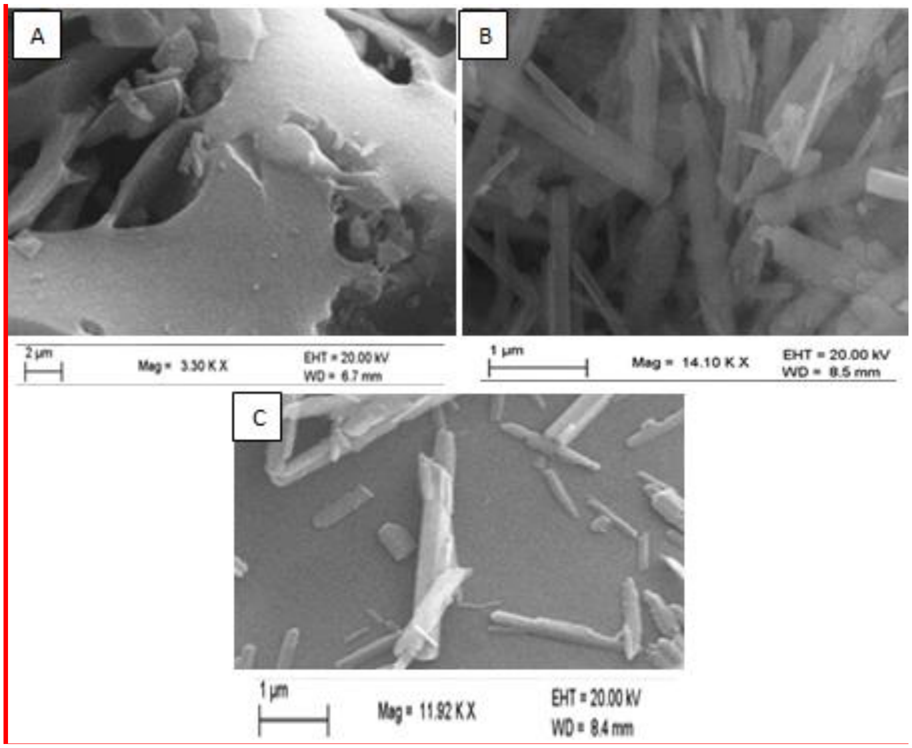


Figure 2: SEM of (a) starch, (b) nano starch and (c) starch citrate nanoparticles.

The scanning electron microscope (SEM) images of the starch shows a non-smooth surface in which a part appears concrete and the other parts appear broken. The surface of the starch appears tightly closed and no pores or gaps could be seen. After the size reduction to the nano level, the SEM shows an aggregate of starch nanoparticles, which looks disorderly arranged. The major difference this picture has with that of the normal starch is the presence of spaces in between these aggregated nanoparticles (13). The nanostarch citrate appears more rod like or cylindrical and shows little or no aggregation, this property coupled with its thermal stability makes it a good stabilizer in nano or micro emulsions of food, detergents and even paint products (21).

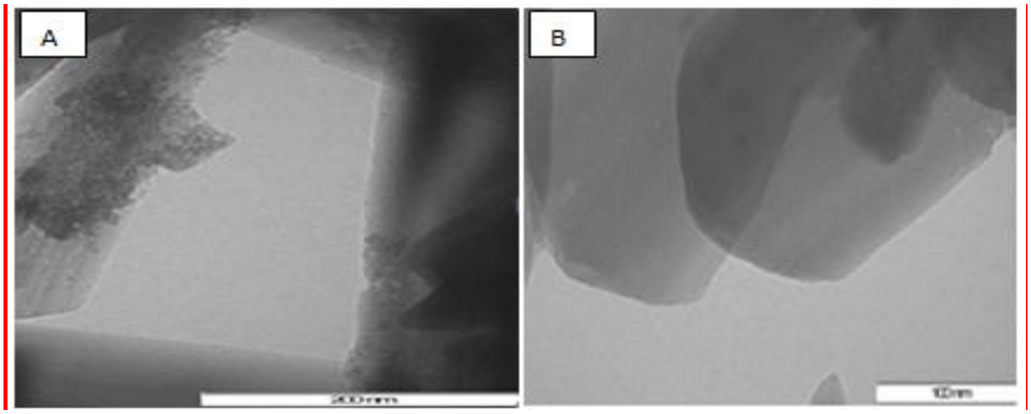


Figure 3: TEM of (a) nano starch and (b) starch citrate nanoparticles.

The transmission electron images (TEM) further confirm the synthesis of starch nanoparticles and its aggregated form while the image for the citric acid treated form appear less conglomerated and rod-like. The reason for this less aggregation might be as a result of the overall negative charge that develops from the surface citrate charges which also tend to stabilize and reduce agglomeration of these nanoparticles by electron-electron repulsion charge effect (21).

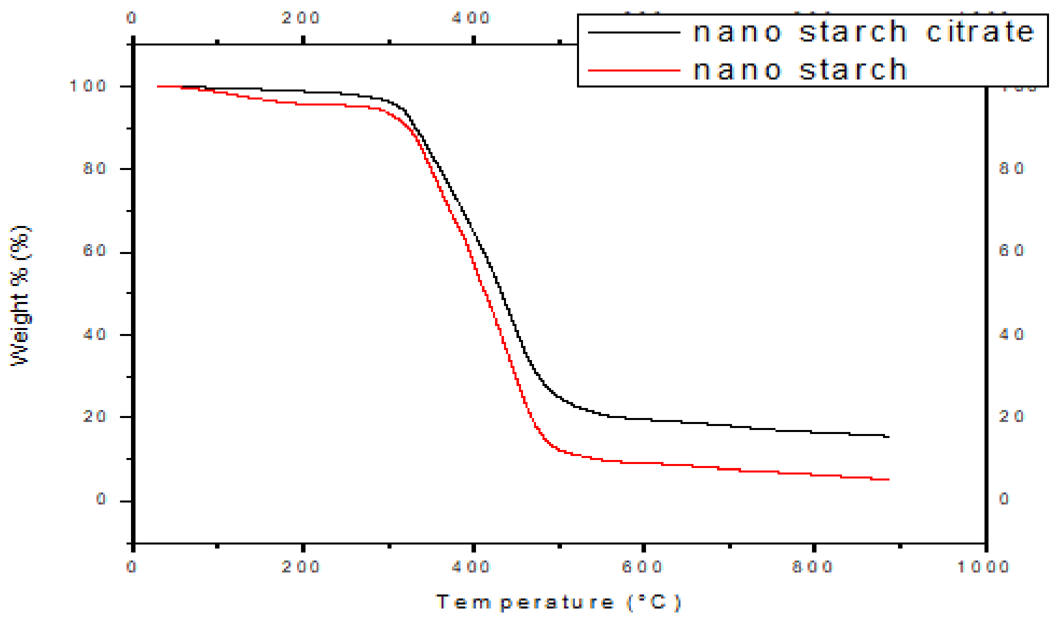


Figure 4: TGA of nano starch and starch citrate nanoparticles.

In Figure 4 above, the effect of citric acid treatment on thermal stability of nanostarch was investigated by thermogravimetric analysis. From the TGA curve, a single-step thermal degradation was observed from 180 to 400 °C for the nano starch with about 93% weight loss. However, the nanostarch citrate showed better thermal stability with its single step thermal degradation observed at 240 to 410 °C and percentage weight loss of about 89% (24). The T_{max} which is the temperature when maximum weight loss occurs in the thermal degradation of these starch biopolymers can also be read from the TGA curves - 280°C for the nanostarch and 310°C for the nanostarch citrate (19). The improvement in the thermal stability can be assigned to the O-H substitution by citrate groups after the citric acid treatment.

CONCLUSION

The derivatization of starch and its applications was well explained in this paper. Although pectins are already been used as stabilizers, starch nanorods are new biopolymers which finds applications in emulsion stabilization. They are thermodynamically stable and have good morphological structure which fits this purpose.

REFERENCES

1. Ma X, Jian R, Chang PR, Yu J. Fabrication and Characterization of Citric Acid-Modified Starch Nanoparticles/Plasticized-Starch Composites. Biomacromolecules. 2008 Nov 10;9(11):3314–20.

2. Yu J, Wang N, Ma X. Fabrication and Characterization of Poly(lactic acid)/Acetyl Tributyl Citrate/Carbon Black as Conductive Polymer Composites. Biomacromolecules. 2008 Mar;9(3):1050–7.

3. Santander-Ortega MJ, Csaba N, Alonso MJ, Ortega-Vinuesa JL, Bastos-González D. Stability and physicochemical characteristics of PLGA, PLGA:poloxamer and PLGA:poloxamine blend nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2007 Mar;296(1–3):132–40.

4. Santander-Ortega MJ, Stauner T, Loretz B, Ortega-Vinuesa JL, Bastos-González D, Wenz G, et al. Nanoparticles made from novel starch derivatives for transdermal drug delivery. Journal of Controlled Release. 2010 Jan 4;141(1):85–92.

5. López-León T, Elaïssari A, Ortega-Vinuesa JL, Bastos-González D. Hofmeister Effects on Poly(NIPAM) Microgel Particles: Macroscopic Evidence of Ion Adsorption and Changes in Water Structure. ChemPhysChem. 2007 Jan 8;8(1):148–56.

6. Chivrac F, Pollet E, Schmutz M, Avérous L. New Approach to Elaborate Exfoliated Starch-Based Nanobiocomposites. Biomacromolecules. 2008 Mar;9(3):896–900.

7. Enturi V, Chowdary BY, Chowdary K. Enhancement of dissolution rate and formulation development of irbesartan tablets by employing starch phosphate: A new modified starch. Asian Journal of Pharmaceutics (AJP): Free full text articles from Asian J Pharm. 2014;8(3).

8. Jivraj M, Martini LG, Thomson CM. An overview of the different excipients useful for the direct compression of tablets. Pharmaceutical Science & Technology Today. 2000 Feb;3(2):58–63.

9. Wepner B, Berghofer E, Miesenberger E, Tiefenbacher K, N. K. Ng P. Citrate Starch — Application as Resistant Starch in Different Food Systems. Starch - Stärke. 1999 Oct;51(10):354–61.

10. Chin SF, Pang SC, Tay SH. Size controlled synthesis of starch nanoparticles by a simple nanoprecipitation method. Carbohydrate Polymers. 2011 Oct;86(4):1817–9.

11. Pang SC, Chin SF, Tay SH, Tchong FM. Starch–maleate–polyvinyl alcohol hydrogels with controllable swelling behaviors. Carbohydrate Polymers. 2011 Feb;84(1):424–9.

12. Kim J-Y, Lim S-T. Preparation of nano-sized starch particles by complex formation with n-butanol. Carbohydrate Polymers. 2009 Mar;76(1):110–6.

13. Loftsson T, Másson M, Brewster ME. Self-Association of Cyclodextrins and Cyclodextrin Complexes. Journal of Pharmaceutical Sciences. 2004 May;93(5):1091–9.

14. Rondeau-Mouro C, Bail PL, Buléon A. Structural investigation of amylose complexes with small ligands: inter- or intra-helical associations? International Journal of Biological Macromolecules. 2004 Oct;34(5):251–7.

15. Shi A, Li D, Wang L, Li B, Adhikari B. Preparation of starch-based nanoparticles through high-pressure homogenization and miniemulsion cross-linking: Influence of various process parameters on particle size and stability. Carbohydrate Polymers. 2011 Feb 1;83(4):1604–10.

16. Veiseh O, Gunn JW, Zhang M. Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging. Advanced Drug Delivery Reviews. 2010 Mar;62(3):284–304.

17. Demitri C, Del Sole R, Scalera F, Sannino A, Vasapollo G, Maffezzoli A, et al. Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. Journal of Applied Polymer Science. 2008 Nov 15;110(4):2453–60.

18. Fujioka R, Tanaka Y, Yoshimura T. Synthesis and properties of superabsorbent hydrogels based on guar gum and succinic anhydride. Journal of Applied Polymer Science. 2009 Oct 5;114(1):612–6.

19. Salam A, Pawlak JJ, Venditti RA, El-tahlawy K. Synthesis and Characterization of Starch Citrate−Chitosan Foam with Superior Water and Saline Absorbance Properties. Biomacromolecules. 2010 Jun 14;11(6):1453–9.

20. Chang PR, Yu J, Ma X. Preparation of porous starch and its use as a structure-directing agent for production of porous zinc oxide. Carbohydrate Polymers. 2011 Jan;83(2):1016–9.

21. Abbas S, Bashari M, Akhtar W, Li WW, Zhang X. Process optimization of ultrasound-assisted curcumin nanoemulsions stabilized by OSA-modified starch. Ultrasonics Sonochemistry. 2014 Jul;21(4):1265–74.

22. Karadag A, Yang X, Ozcelik B, Huang Q. Optimization of Preparation Conditions for Quercetin Nanoemulsions Using Response Surface Methodology. Journal of Agricultural and Food Chemistry. 2013 Mar 6;61(9):2130–9.

23. Manoi K, Rizvi SSH. Physicochemical characteristics of phosphorylated cross-linked starch produced by reactive supercritical fluid extrusion. Carbohydrate Polymers. 2010 Jul;81(3):687–94.

24. Ghosh V, Mukherjee A, Chandrasekaran N. Ultrasonic emulsification of food-grade nanoemulsion formulation and evaluation of its bactericidal activity. Ultrasonics Sonochemistry. 2013 Jan;20(1):338–44.