Stearic Acid Grafted Carboxymethyl Chitosan and Its Nanoencapsulation of Macadamia Oil

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Abstract. This work is aims to synthesize a novel stearic acid (SA) grafted N,O-carboxymethyl chitosan (NOCC), and then use it as a wall material to nanoencapsulation macadamia oil. The grafted copolymer is a amphiphilicity sample. By the catalysis of 1–(3-dimethyl amino propyl)-3-ethyl carbodiimide hydrochloride (EDC HCl) and N-hydroxy succinimide(NHS), we got hydrophilic and hydrophobic NOCC-SA polymers via the condensation reaction between the carboxyl of arboxymethyl chitosan and the carboxyl of stearic acid in a water bath. Macadamia oil has significant effect on whitening and spotting, also as a bioactive compound with health beneficial potential, which are used as safe additives in food , medicine, cosmetics. However Macadamia oil is sensitive to light, thermal condition and oxidation. Nanoencapsulation could be an adequate technique to overcome these challenge. Here, we obtained the analysis by scanning electron microscope and grainsize analyzer that most nanocapsules sizes ranged from 130.2 to 200.8 nm. To sum up, this study showed that amphiphilic chitosan were a kind of potential carrier. It could increase the solubility of hydrophobic substances and make it sustained release by nanoencapsulation.

1. Introduction

Macadamia integrifolia, also known as Australian walnuts, Queensland fruits and macadamia nuts, belong to evergreen trees and dicots. Among many dried fruits in the world, macadamia integrifolia have high nutritional and medicinal value, and therefore it have the highest economic value, and always been regarded as the “king of dried fruit” [1]. The main fatty acid content of macadamia oil is mainly composed of unsaturated fatty acids such as oleic acid, palmitic acid and stearic acid, and a small amount of linoleic acid. Among them, macadamia integrifolia contain more than 80% of unsaturated fatty acids, making macadamia oil with lower blood pressure, blood lipid regulation, and can be used as an effective additive in food and drugs. However, it can also be used as an effective

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additive for moisturizing, nourishing and whitening products [2]. It can be applied directly to the basal layer of the skin and very widely used in cosmetics, skin care products. Because of the high ratio of unsaturated fatty acids, Macadamia oil is extremely susceptible to oxidation, which is affecting the storage quality and transport of the oil. Therefore, nanoencapsulation technique might be a suitable solution to solve these problems. In order to protect sensitive ingredients, nanoencapsulation technology allows “wall material” enveloped these ingredients or “core” materials from adverse reactions, volatile loss, or nutritional deterioration [3]. In this research, stearic acid grafted N,O-carboxymethyl chitosan as a amphiphilicity polymer because of its ability to control the release of sensitive ingredient, and cross-linking to form nanocapsulates. Nanocapsules based on chitosan and modified starch as a wall material to enveloped Macadamia oil as an active ingredient by freeze-drying. In their study, the sizes of most nanocapsules ranged from 339.3 to 553.3 nm and chitosan: Hicap is 1.5: 8.5%, which showed the lowest oil release. In another study, Abreu [4] use chitosan and cashew gum nanogel for L.sidodies oil encapsulation systems. Few studies have used amphipathic modified chitosan as a wall material to deliver hydrophobic substances (such as plant essential oils)[5]. The amphiphilic NOCC-SA polymers were prepared by stearic acid grafted N,O-carboxymethyl chitosan, which nanocapsulation macadamia oil can improve the biological activity and utilization of macadamia oil, making it more versatile and greatly increase its economic value. What’s more amphiphilic NOCC-SA polymers can be a meaningful hydrophobic substances model, provide new ideas for following related research.

2. Materials and methods

2.1. Materials and reagents

chitosan was purchased from Aladdin Industrial Co. Ltd. (Shanghai,China). The degree of deacetylation and viscosity of chitosan were determined as 95% and 100-200 mpa.s, respectively. stearic acid (SA), 1－(3-dimethyl amino propyl)-3-ethyl carbodiimide hydrochloride (EDC·HCl), N-hydroxy succinimide(NHS) were all purchased from J&K Scientific LTD. (Beijing, China). All other reagents were of analytical grade.

2.2. Synthesis of N,O-carboxymethyl chitosan (NOCC)

NOCC was prepared according to the previous report by Chen [6] with some modifications. Briefly, 5 g chitosan dispersed and mixed thoroughly in 500 mL of isopropyl alcohol flask at room temperature. Then, the solution comprising 35 g monochloroacetic acid and 10 mL of 10 M NaOH was dropwise added to the stirred slurry over a period of 30 min. The alkaline slurry was stirred for additional 20 min. The resulting mixture was heated at 60 ^{o}C for 3 h. And then, dialyzed against distilled water with 7000 Da molecular weight cut-off membrane for 48 h. Finally, the dialyzate was freeze-dried to afford NOCC [7].

2.3. Preparation of stearic acids grafted NOCC

The preparation of NOCC grafted coplymers were preformed by using stearic acid (SA). Briefly, 500 mg NOCC was dissolved in 50 mL of distilled water to make solution I. And then, 500 mg stearic acids was dissolved in 40 mL of hot ethyl alcohol absolute, and add 1.5 times the molar amount of EDC·HCl and NHS were stirred at 65°C until completely dissolved to prepare solution II. Subsequently, Solution II was added to solution I under vigorous stirring conditions. The reaction was carried out at 60°C for 5 h, dialyzed against distilled water for 48 h, and freeze-dried for 2 d.

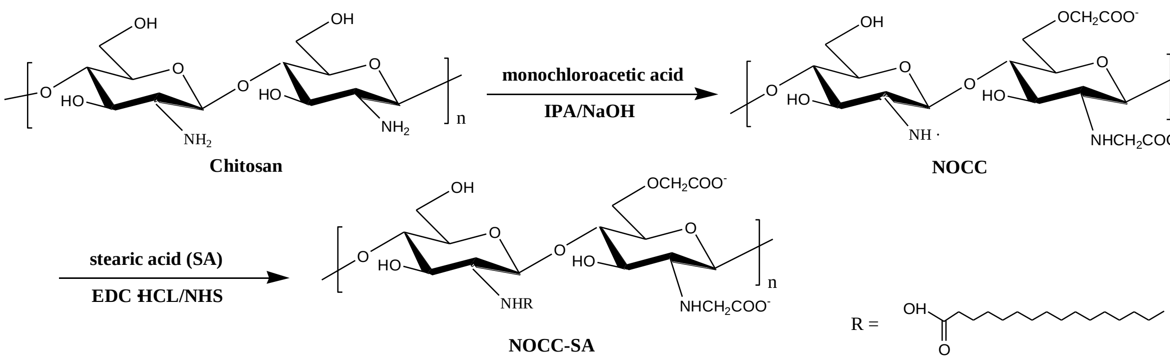

Figure 1. The proposed mechanisms for the synthesis of stearic acids grafted NOCC.

2.4. Preparation of NOCC-SA nanocapsulation Macadamia oil

NOCC-SA nanocapsulation macadamia oil were prepared with slight modification of previous studies [8-9]. Briefly, 500 mg NOCC-SA was dissolved in 50 mL of distilleded water, after it was completely dissolved. The macadamia oils was added in a 1:4 ratio (w/w, macadamia oils/ NOCC-SA solution) to the solution. The resulting mixture flask at room temperature for 1d, and dialyzed against distilled water with 7000 Da molecular weight cut-off membrane for 48 h. Then, dialysate was treated three times with probe-type ultrasonic cell crusher: Power 80 W; Pulse on 2.0 s; Pluse off 3.0 s; Time 2 min, over 0.8 µm filter. Finally, the dialyzate was freeze-dried into nanocapsule powder.

2.5. Characterization of the products

Morphology of the freeze-dried nanocapsules was examined to study the surface structures of powders by scanning electron microscopy (SEM; S-4800, HITACHI, Tokyo, Japan). The samples were glued onto an adhesive tape mounted on the specimen stub, and particles were covered with gold-palladium prior to analysis. Preparation a suitable concentration of NOCC-SA macadamia oil nanocapsules solution, add 2 mL of nanocapsules solution to the cuvette, and measure the nanocapsules size with a laser particle size analyzer.

3. Results and discussion

3.1. Preparation of phenolic acids grafted NOCC

In this study, stearic acid (SA) grafted NOCC were synthesized by using EDC HCl and NHS as catalyst. The possible mechanism for the stearic acid grafted NOCC was proposed in Figure 1. Firstly, NOCC was synthesized in isopropyl alcohol/NaOH/ monochloroacetic acid system. And then, The use the EDC HCl and NHS as catalyst, which can catalyzes the reaction of the carboxyl group on SA with the amino group on NOCC. During the reaction, EDC HCl is used to activate the carboxyl group and NHS is used to assist the reaction. NOCC and SA are linked together by amide bonds. The obtained NOCC-SA grafted coplymers were amphiphilic samples.

3.2. Morphology

Scanning electron microscope (SEM) is based on the interaction between electrons and substances to obtain the physical properties and chemical properties of the tested sample. SEM images of the NOOC-SA macadamia oil nanocapsules are shown in follow Figure 2.By the analysis of represented by Scanning electron microscope images, we know that the obtained nanocapsules showed a spherical shape surface without rough.

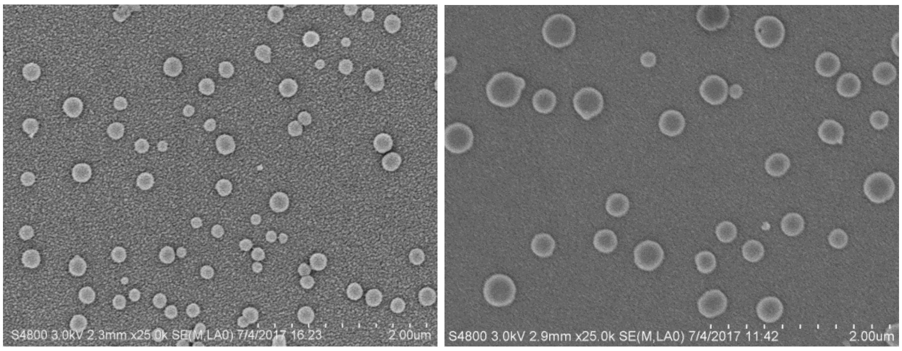

Figure 2. The SEM images of NOCC-SA macadamia oil nanocapsules.

3.3. Particle size

The hydrodynamic size of nanocapsules were determined by Malvern 3000HS (Malvern Instruments Ltd., UK). In order to quantitatively determine the nanoparticle size of NOOC-SA macadamia oil nanocapsules, set the detection angle to 90°, 25°C, and λ=532 nm. Most nanocapsules sizes ranged from 130.2 to 200.8 nm. Particle size analysis chart of NOOC-SA macadamia oil nanocapsules as shown Figure 3:

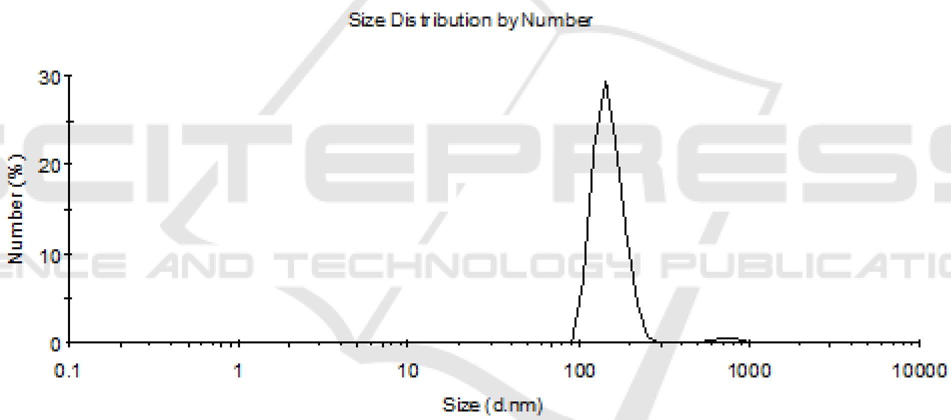

Figure 3. The size distribution of NOOC-SA macadamia oil nanocapsules.

4. Conclusions

The preparation, characterization of stearic acids grafted NOCC were investigated in the study. Results suggested that the stearic acids could be easily grafted into NOCC by using EDC·HCl and NHS as catalyst. In addition, the nanocapsules showed a Spherical and smooth surface by SEM images. In conclusion, NOCC-SA is the promising coat material for developing delivery systems for the hydrophobic substances. The findings obtained from the study suggest that NOCC-SA is amphiphilicity which had a great potential to improve the stability of macadamia oil for its utilization in perfumery, food industries, antimicrobial and antiseptic products.

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