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The study of size and stability of n-butylcyanoacrylate nanocapsule suspensions encapsulating green grass fragrance

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Abstract. Green grass fragrance has been widely used in many fields. However, fragrances are volatile compounds that do not last long. In order to prolong its odor, nanocapsules encapsulated green grass fragrance were prepared. The paper deals with the preparation of green grass fragrance nanocapsules by emulsion polymerization. N-butylcyanoacrylate (BCA) with excellent biocompatibility and biodegradability was used as encapsulant. The nanocapsule suspension systems were characterized and its stability was investigated. The physicochemical properties of polymeric nanocapsules (average diameter and polydispersity) were evaluated as a function of time to assess the system stability. The result showed that the system (containing 0.8% of green grass fragrance, with a polydispersity index (PDI) near 0.1 and an average diameter in the range of 20-30 nm) was an ideal state and relatively stable. Besides, the distinction of stability of three nanocapsule suspensions with different green grass fragrance content was also obvious from scanning electron microscopy (SEM).

1. Introduction

Fragrance is a mixture of fragrant essential oils, aroma compounds, fixatives and solvents. It is used to give the human body, objects, and living-spaces a pleasant scent. Green grass fragrance has an intense, fresh grassy-green, leafy odor. It has been widespread used in perfuming, daily chemical and other industries as a pleasant fragrance of covering up the bad odor and purifying the air [1]. However, applications of green grass fragrance have turned out to be particularly complicated due to its chemical and physical properties, such as low stability, high volatilization and release in the presence of light, heat and oxygen [2]. Hence, finding technologies to solve these problems is much desired. Among the existing approaches (e.g., nanoparticles, liposomes, cyclodextrin inclusions) [3], it is obvious that nanoencapsulation has attracted increasing attention.

In general, nanoencapsulation is one of nanotechnology, which can improve the stability, solubility and bioavailability of encapsulated species, increase their protection, reduce evaporation, promote easier handling and control the release during prolonged storage and applications [4-7]. It is already today an important processing method in industry and bears great potential for a wide range of applications in numerous fields [8], including foods, pharmaceutical, chemical, cosmetics, perfumes, textiles, agriculture, etc.[9] And it is a processing by which one material or a mixture of materials, such as volatile and flavor being coated with or entrapped within another material or system, producing particulate dispersions or solid particles, with sizes ranging from 10 nm to 1 μm [4]. The

coated material is called the core, active material or nucleus, and the coating material is called the wall material, shell, carrier or encapsulant [10, 11].

An important step in developing microcapsules is the selection of a wall material that meets the required criteria [12]. N-butylcyanoacrylate (BCA), which has been widely used in the medical field, is the most attractive for emulsion polymerization system owing to its biodegradability, availability, biocompatibility and low toxicity. And it has several biomedical applications, such as tissue adhesives [13-17] that were based on the fact that the anionic polymerization could be easily initiated by traces of nucleophiles like water, amines, alcohols, or phosphines [18]. Polybutylcyanoacrylate (PBCA) nanoparticles have been extensively investigated for 30 years to be used as drug carrier for their excellent properties [19-24]. So BCA was chosen as the coating material to build the shell on the green grass fragrance.

Additionally, an important issue to be considered for nanocapsules encapsulated perfume materials is their mechanical properties. For example, the use of suspension systems of polymeric nanocapsules is often limited due to problem of stability over prolonged storage. A colloidal suspension does not normally show phase separation, since both sedimentation and aggregate formation are slow. However, storage for many months can sometimes result in aggregation and consequently phase separation [25, 26].

Hence, this work was aimed to prepare a series of PBCA nanocapsule suspensions encapsulated green grass fragrance and the emphasis was on the relationship between the stability and the particle size and polydispersity of them.

2. Materials and methods

2.1. Materials

Butylcyanoacrylate (BCA) was purchased from Zhejing Jinpeng Chemical Company. Castor oil polyoxyethylene ether 40 (EL-40) was provided by Shanghai Haojiong Reagent Co. Ltd. Hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. Green grass fragrance was blended by Guangzhou Levon Flavor & Fragrance Technology Co., Ltd. Deionized water was produced in laboratory.

2.2. Preparation of nanocapsules

Polybutylcyanoacrylate (PBCA) nanocapsules were prepared by emulsion polymerization as described in literatures [27, 28]. A glass beaker was equipped with a magnetic stirrer (Shanghai Mei Yingpu instrument and Meter Manufacturing Co., Ltd.). Deionized water, emulsifying agent and core material were added in the beaker, and emulsified at 1100 rpm for 10 min. Then the pH of the system was adjusted to 2.0 with an aqueous solution of HCl (1M). BCA was added to the beaker at the speed of 3d/min. After that, the reaction was carried out for 1 h in room temperature, using a stirring rate of 1100 rpm, too. At last, the pH of this system was adjusted to 7.0 using an aqueous solution of NaOH (1M), and the reaction would go on for another 0.5 h.

2.3. Particle size and polydispersity measurements

The mean size and the size distribution of the BCA encapsulated green grass fragrance nanocapsule suspensions were measured using a dynamic light scattering instrument (Zetasizer Nano ZS, Malvern Instruments Ltd, UK) in three replicates. The size distribution was evaluated for all samples according to the polydispersity index (PDI). PDI is an indicator of the nanocapsule size distribution in the range 0-1 and the values of it < 0.2 indicate a monodisperse emulsion, whereas values > 0.5 show larger distributions [27].

2.4. Nanocapsule suspensions stability measurements

The stability of the PBCA nanocapsule suspensions encapsulated green grass fragrance was evaluated by the size and PDI of the suspensions stored at room temperature for a period of time (24 h, 15 d and

30 d). The morphology and structure of nanocapsules were examined using a scanning electron microscopy (Hitachi S-3400 N, Hitachi High-Technologies, Japan) at an accelerated voltage of 15.0 kV and at 90 d after the samples preparation. The nanocapsule samples were fixed on metal stubs with double sided tape and coated with gold by a gold sputter coater in a high-vacuum evaporator.

3. Results and discussion

3.1. Effects of green grass fragrance concentration on size and PDI of nanocapsules

The particle size and the size distribution of the green grass fragrance nanocapsule suspensions were measured by Zetasizer Nano ZS (Malvern Instruments Ltd, UK). The average diameter and the PDI were recorded. All measurements were performed in triplicate and the average values were obtained. Figure 1 shows the particle size and distribution of nanocapsules changing with core material concentration. Data are expressed as mean ± standard deviation with error bars as shown in figure 1.

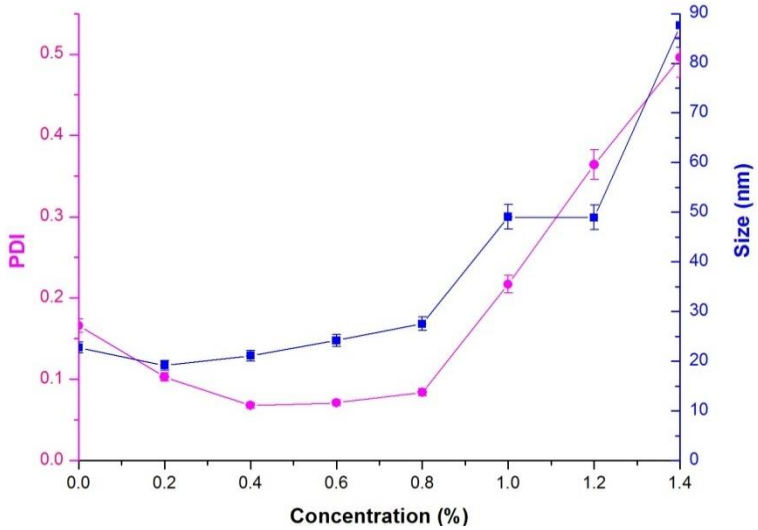

Figure 1. The average size and PDI of PBCA nanocapsule suspensions as a function of green grass fragrance concentration for storage time 24 ± 0.1 h.

Fixing emulsifier concentration at 1.6% and changing the core content, nanocapsule systems of various particle size and PDI were gained. Making the adjustment is to improve the proportion of core material in the system, hoping to get higher stability and loading capacity. As showed in figure 1, it also ensured that the particle size and distribution of nanocapsule were relatively ideal when the ratio of emulsifiers to core material decreased compared with the previous work [27]. The average diameter of PBCA nanocapsules encapsulated green grass fragrance enhanced with green grass fragrance increased, whereas PDI just increased sharply when green grass fragrance concentration more than 0.8%. An excess of core material would be attached on the outside of the capsule resulting in particle size increased and distribution unevenly. From results of Zetasizer Nano ZS, it can be concluded that the size distribution of the nanocapsules (containing 0.8% of green grass fragrance) was monodisperse, and had a narrow peak.

3.2. Storage stability analysis of green grass fragrance nanocapsule suspensions

Figure 2 and figure 3 show the changes of the mean sizes and PDI of PBCA nanocapsule suspensions along with storage time, under the concentration of green grass fragrance in range of 0-1.4%. With the increasing of storage time, there are different changing trends in the size and PDI of sample systems.

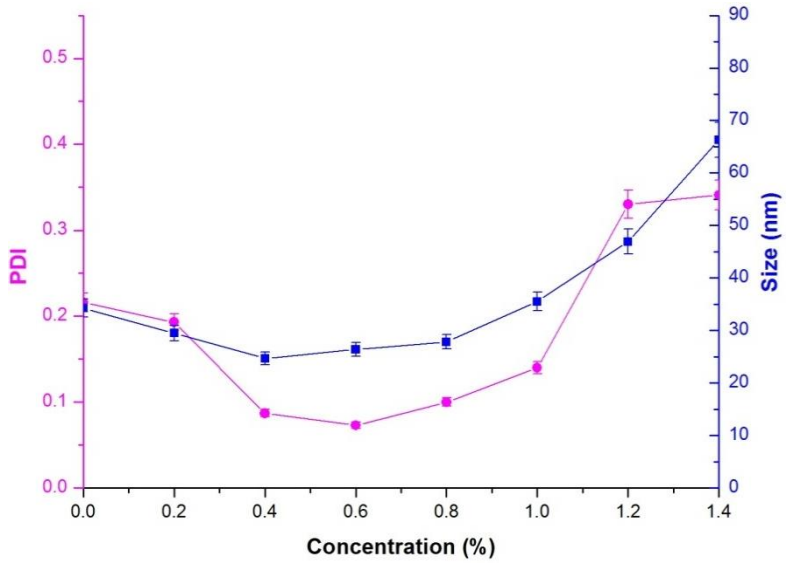

Figure 2. The average size and PDI of PBCA nanocapsule suspensions as a function of green grass fragrance concentration for storage time 15 ±0.01 d.

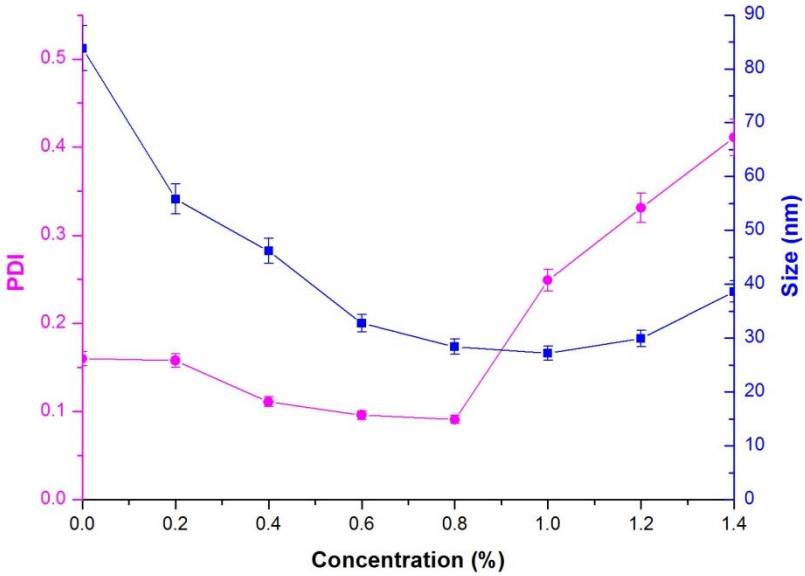

Figure 3. The average size and PDI of PBCA nanocapsule suspensions as a function of green grass fragrance concentration for storage time 30 ±0.01 d.

The particle size of PBCA nanocapsule suspensions increased as the storage time increased at the lower green grass fragrance concentration (0, 0.2% and 0.4%); besides, PDI changing along with the storage time. It may occur flocculation firstly, and then coalescence and both of them result in increase of the mean particle size [29]. While the system had a high concentration (1.0%, 1.2% and 1.4%), the change rule of the particle size and PDI was just on the contrary with the law at low core material concentration. There were macroscopic particle in freshly prepared nanocapsule suspensions with higher green grass fragrance concentration, which may be the main reason that the mean particle size was big initially. After the macroscopic particle subsided, the average particle size of the nanocapsules decreased. Another reason that suspension systems were unstable at lower green grass fragrance concentration and mean particle size increased sharply in storage for 30 d. So size change of PBCA nanocapsules had a decrease trend when stored for 30 d, compared to 24 h and 15 d.

In a word, the mean size and size distribution had a larger fluctuation both at lower and higher concentration, leading to uneven distribution of the system. However, the size of nanoparticle suspension not only remained unchanged but also was very small, only 28 nm, when the content of green grass fragrance was 0.8%, compared with 0.2% and 1.4%. Additionally, the polydispersity of the samples that core concentrations were 0.4%, 0.6% and 0.8% did not present statistically significant differences in PDI as a function of time, since they were all below 0.2, but the samples of 0.4% and 0.6% green grass fragrance performed unstable in size.

Hence, according to the changing rules of the particle size and PDI, we supposed that the system which the proportion of green grass fragrance was 0.8% had better stability. It is demonstrated that the content of core material would influence the stability of system. Average particle size and size distribution of stable nanocapsule suspension system was maintained at a stable level within given storage time. Accordingly, stability of nanocapsule suspensions could be estimated by the changing of mean particle size and distribution.

3.3. SEM analysis of green grass fragrance nanocapsules

SEM was used to study the structure and appearance of nanocapsule suspensions. The morphologies of nanocapsules at 90 d are showed in figure 4.

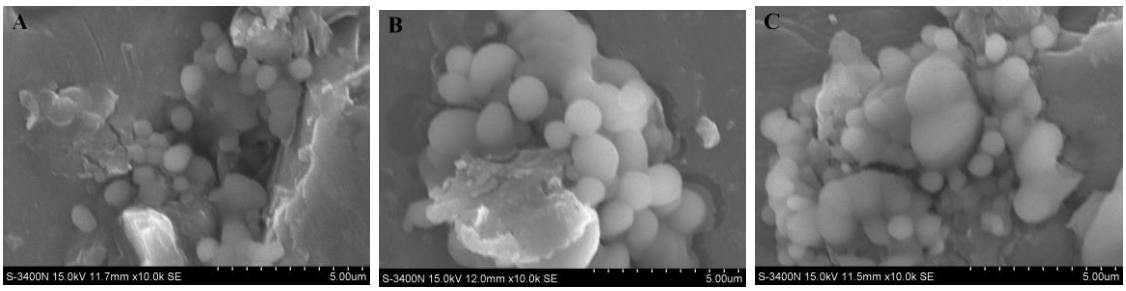

Figure 4. Scanning electron microscopy micrographs of nanocapsules containing green grass fragrance in various concentrations at 90 d after sample preparation, A (0.2%), B (0.8%), C (1.4%).

It confirmed that the nanocapsules had regular globe shape with smooth surface and without holes and cracks, but varying degrees of reunion and adhesion were observed too as shown in figure4. The distinction of the stability of three nanocapsule suspensions was obvious. The average particle size showed a significant change varying in the range 500-900 nm as storage time increased to 90 d, and were larger than the values obtained from Zetasizer Nano ZS. Moreover, combining with distribution morphology of the nanocapsule suspensions loading 0.2% and 1.4% of green grass fragrance, it indicated that flocculation and coalescence existed indeed.

4. Conclusions

This study describes production of PBCA nanocapsules briefly and investigates its storage stability. After 24 h, 15 d and 30 d of storage, even 90 d, no layer separation was observed of all nanocapsule suspensions, but their transparency was different in surface appearance. Unstable system became turbid seriously over time. Besides, the distinction of the stability of three nanocapsule suspensions (with 0.2%, 0.8% and 1.4% of green grass fragrance) was also obvious from SEM.

In respect of mean size and size distribution, relative stable system like containing 0.8% of green grass fragrance nearly did not changed as the storage time increased in a given time range, however, the systems in which percentage composition of green grass fragrance was lower or higher changed greatly, that is, the PBCA nanocapsule system with various physical stability could be achieved by optimizing of process formulation, and stability of it could be estimated by the changing of mean particle size and distribution, and SEM micrographs.

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