Colloids and Surfaces A 542 (2018) 15–20

Contents lists available at ScienceDirect

Colloids and Surfaces A

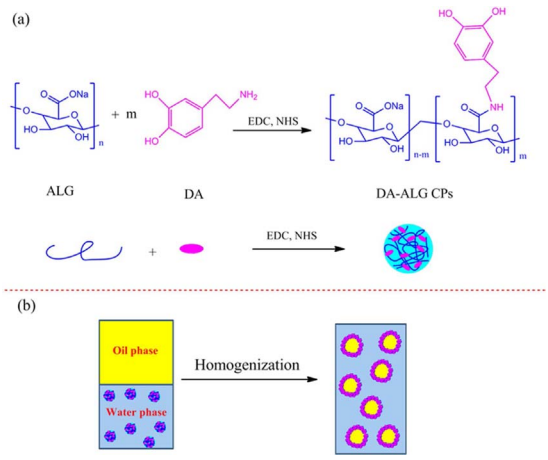
journal homepage: www.elsevier.com/locate/colsurfa

Alginate-based colloid particles from direct chemical self-assembly using as particulate emulsifiers

Rongli Zhang[a,b,*], Jingjing Lv[a], Cuige Zhang[a], Renchun Yang[a], Xingchen Sun[a], Bo Song[b], Ching-Ping Wong[b]

[a] School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu, 241000, China
[b] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, United States

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Dopamine
Alginate
Self-assembly
Colloid particles
Pickering emulsion

ABSTRACT

A new kind of dopamine modified alginate colloid particles (DA-ALG CPs) was prepared via the direct chemical self-assembly triggered by the amidation reaction between dopamine and alginate in aqueous solution. The structure and morphology of the DA-ALG CPs were characterized by infrared spectroscopy, Zeta PALS and scanning electron microscope. The prepared DA-ALG CPs were then used as particulate emulsifier to prepare Pickering emulsions. The properties of the emulsion were characterized by optical microscope. The results revealed that the prepared DA-ALG CPs exhibited good emulsifying property at a wide pH value range, which will endow the potential application of the Pickering emulsions stabilized by DA-ALG CPs in food and biological medicine fields.

1. Introduction

Alginate (ALG) is a linear anionic polysaccharide consisting of blocks of α-L-guluronic acid and β-D-mannuronic acid residues, covalently linked together in different blocks [1,2]. It is generally regarded as safe by the U.S. Food and Drug Administration in view of its

* Corresponding author at: School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu 241000, China; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States.
E-mail address: zrl326@163.com (R. Zhang).

https://doi.org/10.1016/j.colsurfa.2018.01.037
Received 7 December 2017; Received in revised form 17 January 2018; Accepted 18 January 2018
Available online 31 January 2018
0927-7757/

biodegradability, biocompatibility, non-immunogenicity and non-toxicity [3]. As a natural biopolymer, alginate and its derivative have got increasing attractions in the cosmetics, food and pharmaceutical industries as a drug carrier because of their high viscosity stabilizing properties and gelling ability in aqueous solutions [4].

In recent years, the application of nanomaterials prepared from biopolymer has got many attentions in biotechnological and biomedical fields due the nano-size effect and their intrinsic properties. The alginate based colloid particles (CPs) with good biodegradability and biocompatibility should have potential application in biotechnological and biomedical fields. Many literatures reported the preparation and the application of alginate based CPs, the application of which is mainly focused on drug delivery system for various agents [2,5–7]. The mostly common methods used to prepare alginate based CPs are external gelation and internal gelation. The external gelation (or ionotrophic gelation) method is accomplished by dropwise adding alginate aqueous solution to a calcium ion solution under constantly stirring. A cross-linking cationic polymer (such as poly-L-lysine, chitosan and some others [1,8–11]) is then added in. Through the electrostatic interactions between polymers, a polyelectrolyte complex CPs formed. This external gelation method allows for the creation of a large amount of beads. However, the size distribution of CPs prepared from this method is multi-dispersed. The internal gelation (or emulsification) is another method to prepare alginate based CPs [1,12–14]. Firstly, an insoluble calcium salt is mixed with alginate in an aqueous phase. After emulsifying the mixture into an oil phase using some emulsifier, a water-in-oil emulsion is formed. Adding an organic acid and lowering the pH release Ca^{2+} ions from the insoluble salt, which triggers gelation and leads to the formation of CPs. The size distribution of CPs prepared from this method is mono-dispersed. However, the purity of CPs and the removal of emulsifier in this method are complicated. So, it is necessary to develop simple method to prepare alginate based CPs and explore new application fields for them.

Self-assembly of macromolecue is a common method to prepare polymer-based CPs. It is a kind of micro-phase separation behavior in solvent due to the week interactions (such as hydrophilicity and hydrophobicity, static, hydrogen-bond and some other interactions) between the copolymer chains [15]. The self-assembled CPs from biopolymer have been used in many fields, such as sensors, drug delivery, catalysts, nanoreactors, and others [16]. Fujii et al. [17,18] firstly used triblock copolymer-based shell cross-linked CPs as pH-responsive particulate emulsifiers for the stabilization of L-undecanol-in-water Pickering emulsions. Liu and coworkers systematically reported the self-assembled CPs from amphiphilic random copolymers for the stabilization of Pickering emulsions [19–23]. These prepared self-assembled CPs exhibited good stabilization for oil droplets. However, the fabrication process of self-assembled CPs was complicated and always underwent three steps: the synthesis of amphiphilic copolymers, the self-assembly of amphiphilic copolymers via week interactions and the purification of self-assembled CPs. So, it is necessary to find a simple method to prepare self-assembled CPs for using as particulate emulsifiers. Recently, many literatures have reported the direct chemical preparation of self-assembled CPs, such as in situ aqueous dispersion polymerization, RAFT polymerization of an amphiphilic block polymer, and direct cross-linking in a common solvent [23]. The self-assembled CPs based on a direct chemical method is much more convenient and provides a facile way to prepare versatile particulate emulsifiers.

In this work, we prepared a new kind of dopamine (DA) modified ALG (DA-ALG) CPs via the direct chemical self-assembly triggered by the amidation reaction between dopamine and ALG in aqueous solution. The prepared DA-ALG CPs were then used as particulate emulsifier to prepare Pickering emulsions. It should be noted that dopamine is a biocompatible natural compound in mussel adhesive proteins. Previous research on dopamine has shown that its catechol group can improve the interfacial stabilization performance of polymer at the liquid-liquid interface [22,24–26]. Herein, the preparation and characterization of DA-ALG CPs and its application for stabilizing Pickering emulsion were carefully investigated.

2. Experimental

2.1. Reagents and materials

Alginate (ALG), dopamine (DA), *N*-hydroxysuccinimide (NHS), HCl, NaOH, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), synthetic squalane hydrogenated polyisobutylene (SSHP), isooctyl palmitate, caprylic capric triglyceride (ODO), castor oil, white oil ($26^{\#}$), olive oil and liquid paraffin were supplied by Aladdin Chemistry Co. Ltd. (Shanghai, China).

2.2. Preparation of DA-ALG CPs

DA-ALG was prepared by amidation reaction between the carboxyl group of ALG and amino group of dopamine in the presence of EDC·HCl and NHS. The introduction of hydrophobic DA at the side chain of hydrophilic ALG endowed amphipathicity for DA-ALG, leading to the self-assembly of DA-ALG and the formation of CPs in aqueous solution. Briefly, 1 mmol ALG (repeat unit) was dissolved in 60 mL distilled water under stirring. After 0.5 h in an ice bath, 1 mmol EDC·HCl, 2 mmol NHS and 1 mmol dopamine were successively added in. The reaction was carried out in an ice-bath for another hour and then at room temperature for 24 h. The mixture was placed into dialysis membrane (MC: 14 000) and purified via dialysis in distilled water, obtaining DA-ALG aqueous solution. The synthetic route of DA-ALG is shown in Fig. 1.

2.3. Preparation and the characterization of Pickering emulsions

The aqueous dispersion of DA-ALG CPs (3 mL) was mixed with an equal volume of oil. The oil/water mixture was then homogenized for 3 min by the XHF-D Hspeed homogenizer with a 10 mm dispersing tool operating at 8000 rpm [23]. The optical microscope images and digital microscope images were taken at 24 h after homogenization. The mean diameter of the emulsions droplets was determined by analysis of more than 500 emulsion droplets.

2.4. Characterization and measurement

Infrared (IR) experiment was run by attenuate total reflexion (ATR) mode on a Nicolet FI-IR Spectrometer instrument. The size distributions and the Zeta potentials of DA-ALG were measured using a Zeta PALS (Brookhaven Instruments Corporation, USA). The morphologies of DA-ALG were observed by a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan) operating at 2.0 kV. The Pickering emulsion droplets were observed with an optical microscope (DM-BA450, Motic China Group Co., Ltd.), and the mean diameters of droplets were measured by counting 500 beads using the Motic Images Advanced software.

3. Results and discussion

3.1. Preparation and characterization of DA-ALG CPs

The preparation of DA-ALG is shown in Table S1. The structure of DA-ALG was characterized by FT-IR spectrum analysis after the purified DA-ALG solution was frozen and then lyophilized. As shown in Fig. S1, compared with ALG, the peak at 1720 cm^{-1} became stronger and a new peak at 1240 cm^{-1} corresponding to the C = O stretching mode of amide group appeared in the FT-IR spectra of the DA-ALG, indicating the successful synthesis of DA-ALG. The size distributions of DA-ALG are shown in Fig. 2. As can be seen, the size distribution of $DA\text{-}ALG_{1121}$ was mono-disperse with the mean diameter of 250 nm. However, the size distributions of $DA\text{-}ALG_{1111}$, $DA\text{-}ALG_{1112}$, $DA\text{-}ALG_{1122}$ were poly-