LWT - Food Science and Technology 97 (2018) 76–82

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Production of recrystallized starch microspheres using water-in-water emulsion and multiple recycling of polyethylene glycol solution

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ARTICLE INFO

Keywords:
Starch microspheres
Delivery system
Polyethylene glycol
Recovery
Cost-effectiveness

ABSTRACT

Recrystallized starch microspheres (RSMs) were prepared by using water-in-water emulsion method. Polyethylene glycol (PEG) solution was used as the continuous phase. To enhance the cost-effectiveness of this method, PEG was recovered and reused. The recovered PEG was used without (DR-PEG) and with supplementing with fresh PEG (RS-PEG). An exponential concentration-apparent viscosity relationship (R^2 = 0.99) of PEG solution was used to calculate the concentration of recovered PEG solution. When the DR-PEG solution was used, the yield of RSMs decreased 0.7%–11.9% as the recycle number increased. The clumping of microspheres was observed in the first and second recycles. When the RS-PEG solution was used, the yield of RSMs continuously increased from 78.2% to above 83.0% and the desirable features of the RSMs including spherical shape, well-dispersed nature and well-organized crystalline structure remained unchanged up to 5 recycles. These findings will enable production of RSMs in more cost-effective way and help minimize the waste of PEG.

1. Introduction

Starch microspheres are micron-sized particles with spherical or nearly spherical geometry. These microspheres have attracted increased research interest due to their broad application in pharmaceutical, food, cosmetics and other industries (Glenn et al., 2010; Wang et al., 2015; Zheng et al., 2015). Starch microspheres are biocompatible, biodegradable, non-toxic, possess excellent storage stability, and they can be produced at relatively low cost. Starch microspheres have found niche application in pharmaceutical area, for example, as drug delivery vehicle (Pereira et al., 2013), haemostatic agent (Bjorses et al., 2011) and embolization agent (Pieper et al., 2015). Starch microsphere-based products such as Spherex™, Arista™ and EmboCept™ are developed and commercialized for the above mentioned purpose. Recently, the application of microspheres is increasing in food formulations (Diarrassouba et al., 2015; Gómez-Estaca, Gavara, & Hernández-Muñoz, 2015). The successful application of starch microspheres in pharmaceutical area also makes them a very promising candidate in functional food, for example, for development of control and targeted delivery systems for bioactive food components.

Emulsion method is the most commonly and broadly used method to produce starch microspheres, especially those which are targeted for controlled release application. In this method, the dispersed droplets of emulsion are used as "spherical template", and starch molecules inside the droplets are recrystallized (García-González, Uy, Alnaief, & Smirnova, 2012) or crosslinked (Malafaya, Stappers, & Rui, 2006) to convert the spherical droplets into solid microspheres. The microspheres obtained by recrystallization and crosslinking are known as recrystallized starch microspheres (RSMs) and crosslinked starch microspheres (CSMs), respectively. The emulsion method can be classified into water-in-oil (W/O) (Baimark & Srisuwan, 2014) and water-in-water (W/W) emulsion, depending on the composition of the continuous phase. Currently, W/O emulsion method is most frequently and widely used to produce starch microspheres. However, large quantity of organic solvent is required as continuous phase and/or washing agent for preparing microspheres through W/O emulsion method. For this reason, specialized equipment is required for handling organic solvents used in this method. In addition, there is higher and real risk of health, safety and environmental pollution when W/O method is used for industrial production starch microspheres. Moreover, residues of toxic organic solvents and emulsifiers may remain in the microspheres, which can pose additional safety risks.

To avoid the aforementioned disadvantages, W/W emulsion method was developed. It is a unique form of aqueous two-phase system (ATPS)

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https://doi.org/10.1016/j.lwt.2018.06.034
Received 22 February 2018; Received in revised form 12 June 2018; Accepted 17 June 2018
Available online 18 June 2018
0023-6438/

Abbreviation

RSMs	Recrystallized starch microspheres
CSMs	Crosslinked starch microspheres
ACS	Acid-modified cassava starch
PEG	Polyethylene glycol
ATPS	Aqueous two phase system
W/W emulsion	Water-in-water emulsion
W/O emulsion	Water-in-oil emulsion
DR-PEG solution	Recovered and directly reused PEG solution (without PEG supplement)
RS-PEG solution	Recovered and supplemented PEG solution (with fresh PEG supplement)

wherein two aqueous solutions are separated into dispersed and continuous phases after mixing. ATPS have received considerable research interest, however, they are primarily used for the extraction and purification of sensitive substances such as proteins and peptides (Silva, Coimbra, Rojas, & Teixeira, 2009). In W/W emulsion method, aqueous solutions of non-toxic polymer (usually polyethylene glycol, PEG) are used as continuous phase instead of organic solvents, which avoids the use of toxic organic solvents and emulsifiers. This method is especially suitable for the microencapsulation of sensitive substances such as proteins and peptides. This is because the interfacial tension of W/W emulsion is very low which helps preserve the functional properties of proteins and peptides.

One of the most important differences of W/W emulsion method with W/O emulsion method is that there is a significant transfer of mass between aqueous continuous and dispersed phases. Some of the limitations encountered while applying W/W emulsion method are that the inter-droplet repulsion is weak and the interfacial membrane is not sufficiently robust. In addition, the amphiphilic molecules do not adsorb well at the water-water interface. The combined effects of these factors means that there is a greater potential for the emulsion droplets to agglomerate and thus the stability of W/W emulsion is generally difficult to control (Esquena, 2016). Interestingly, it has been reported that the W/W emulsion can be stabilized with relative ease using microparticles of readily available biopolymers as emulsifiers (Nguyen, Nicolai, & Benyahia, 2013).

The underpinning science of preparation of polymeric microspheres using many biopolymers such as dextrin (Stenekes, Franssen, Van Bommel, Crommelin, & Hennink, 1999), starch, gelatin (Kong, Li, Wang, & Adhikari, 2011) and agarose (Li & Liu, 2018) has been studied to considerable detail. In the case of starch microspheres, both CSMs

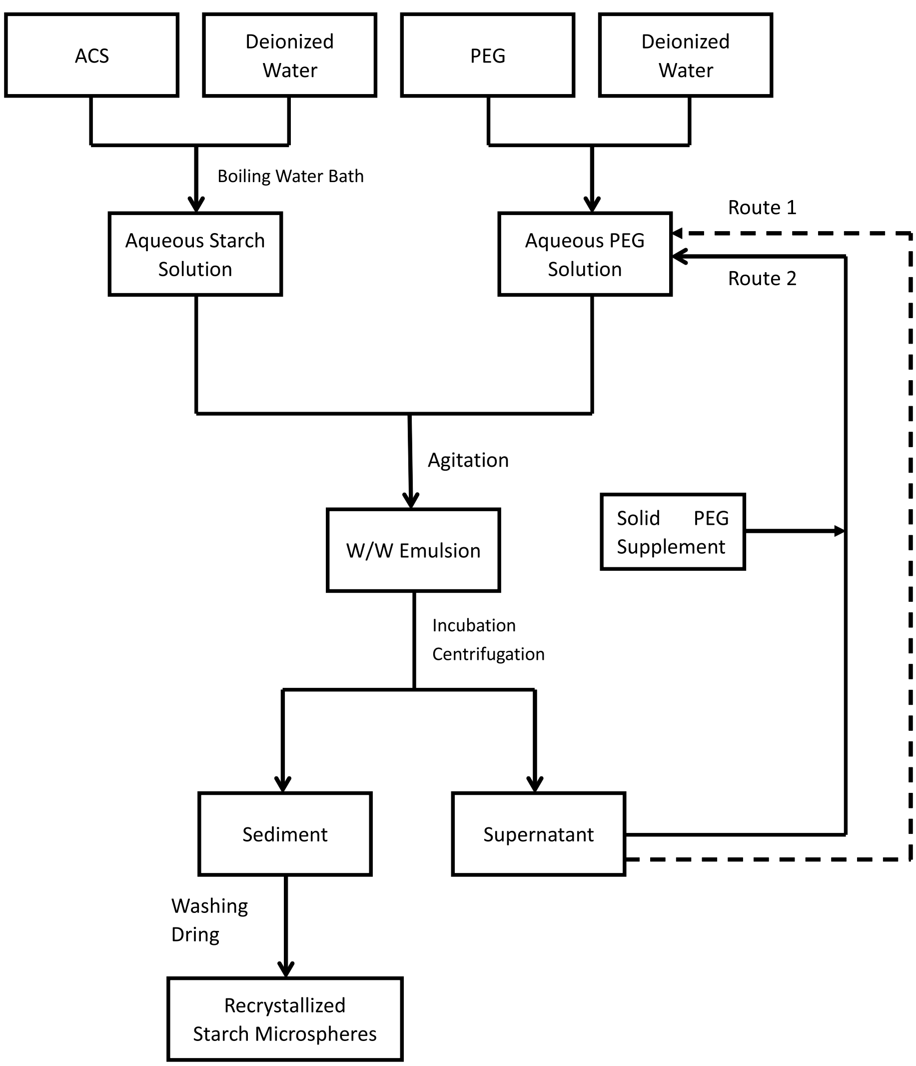

Fig. 1. Schematic flow chart of recycling of polyethylene glycol (PEG) solution for the preparation of recrystallized starch microspheres (Route 1: direct recycling of PEG solution; Route 2: recycling of PEG solution using PEG supplementation).