Effect of surfactant concentration on the synthesis of hydrogel microbeads using the emulsion polymerization process for acrylamide/acrylic acid copolymers

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Abstract. Personal care and cosmetic goods frequently contain microplastic particles, specifically microbeads with an average diameter of 250 mm, which make up about 5% of the product weight. Pollution may result from these microbeads' persistence in the environment. The goal of this study is to use emulsion polymerization to synthesize hydrogel microbeads from copolymers based on acrylamide. The study focuses into the surfactant concentrations affects swelling behavior and particle size. Scanning electron microscopy (SEM) is used to assess particle size and determine the swelling ratio, and Fourier transform infrared spectroscopy (FTIR) is used for chemical analysis. The results show that while swelling capacity decreases with increasing surfactant concentration, smaller and more homogeneous particles are produced. The result provides a systematic method to creating microbeads with adjustable characteristics. Additionally, the chosen synthesis materials have the potential to sustainably minimize water contamination and lessen the accumulation of hazardous residues.

1 Introduction

Microbeads are frequently found in a variety of personal care and cosmetic products (PCCPs), including toothpaste, soap, face cleansers, and sunscreen. Synthetic polymers, such as high-density polyethylene (HDPE), polyester (PES), polyvinyl chloride (PVC), and polyethylene (PE), are frequently used to create the main ingredients [1]. It has been reported that synthetic polymers can accumulate in living organisms, potentially causing long-term adverse effects, and negatively impacting overall environmental quality. The synthesis of microbeads with a three-dimensional covalently crosslinked network allows for excellent water absorption, effective encapsulation of active substances, and contributes to exfoliation, stain removal, and improved cleansing efficiency. These typically particles have an average size ranging from 10 to 250 μm, and variations in particle size influence their suitability for different types of applications. The appropriate selection of polymeric materials is a key factor in enhancing the performance of microbeads. Therefore, the development of alternative materials such as acrylamide-based polymers, which possess biocompatible properties, can be applied in the development of medical materials, including hydrogels for wound dressings, drug delivery systems, or tissue scaffolds. These materials can be designed with structures that allow for controlled release of active substances and efficient fluid absorption, while also not causing irritation to cells or tissues in the body [2]. Additionally, acrylamide-based polymers tend to be more environmentally friendly compared to other synthetic polymers.

However, there are still certain limitations that need to be addressed, including mechanical weakness that can lead to structural degradation prior to use, and irregular control over the encapsulation and release rates of active substances. These factors could affect the stability of formulations and the overall efficacy of the products. Emulsion polymerization provides benefits in regulating particle size, maintaining system stability, and adapting to different types of materials. It also enables adjustment of system composition to fine-tune polymer characteristics like water uptake, mechanical durability, and controlled release of active agents [3]. According to a study by Sarva Mangala Praveena, Siti Norashikin, and Akizuki (2018) [4], the population group of students to working adults aged between 21 and 29 years uses PCCPs on average three times per day. The two most used products are toothpaste and facial foam/scrubs, which often contain synthetic microbeads. Each use can release between 4,000 and 94, 500 microbead particles into wastewater [5]. Although some microbeads are removed in wastewater treatment plants, many still escape directly into the environment. This has made PCCPs a significant source of microplastic pollution in natural water bodies,

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particularly in marine ecosystems. Currently, there are no effective and sustainable methods for the long-term removal of microplastics. For the reasons mentioned above, this research aims to develop hydrogel microbeads from synthetic acrylamide polymers using the emulsion polymerization technique. The goal is enhancing the properties of the microbeads to make them suitable for use in PCCPs, focusing especially on particle size and swelling behavior by examining the influence of varying surfactant concentrations. Ultimately, this research aims to provide guidelines for designing microbeads that balance both effective performance and reduced environmental impact by utilizing materials with potential biodegradability or long-term ecological compatibility.

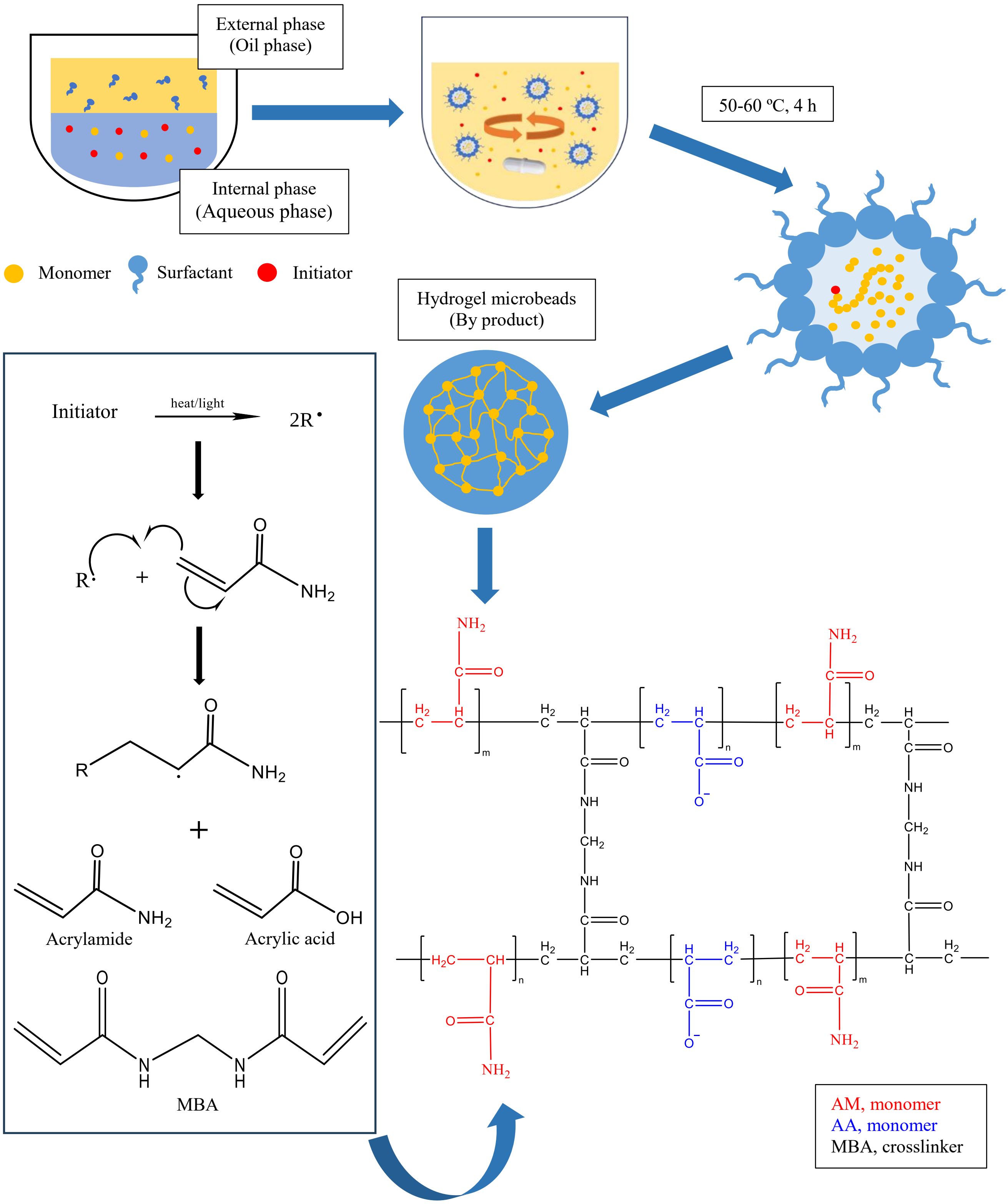

Fig. 1. Overview of the synthetic route employed in the preparation of hydrogel microbeads.

2 Materials and Methods

2.1 Materials

Acrylamide (AM) and acrylic acid (AA) (Acros Organics, 99 %) were used as monomers. N, N-methylenebisacrylamide (MBA) served as the crosslinker. Ammonium persulfate (APS) was used as the initiator. Cyclohexane was employed as the continuous oil phase in the emulsion system, while sorbitan monooleate (Span 80) acted as the surfactant. All chemicals were used as received without further purification.

2.2 Preparation of hydrogel microbeads

The hydrogel microbeads were prepared via an emulsion polymerization. Briefly, 30 mL of cyclohexane was mixed with Span 80 as the surfactant in a 250 mL reaction flask and stirred at room temperature for 15 min to form the external (oil) phase. For the internal (aqueous) phase, AM, AA monomers, and MBA were dissolved in 30 mL of deionized water in a 50 mL beaker and stirred at room temperature for 15 min. Afterwards, the aqueous phase was gradually added into the oil phase under continuous stirring to form the emulsion. The reaction flask was then purged with nitrogen gas for 10 min to remove oxygen. Next, APS (initiator) was added to initiate the polymerization. The reaction was carried out at 50–60 °C for 4 h under nitrogen atmosphere, allowing free radical polymerization to proceed (Figure 1). After completion, the reaction mixture was cooled to room temperature. The product was separated by centrifugation to remove cyclohexane, and the resulting white solid microbeads were washed twice with cyclohexane to remove residual surfactant. Finally, the microbeads were dried in a vacuum oven and stored in a desiccator [6]. The yield was approximately 95% (Figure 2). The formulation ratios are presented in Table 1.

Table 1. Mole ratio of prepare hydrogel microbeads for synthesis.

%Surfactant (%v/v)	AM (mmol)	AA (mmol)	MBA (mmol)	Particle size
2.0	35.20	34.70	0.65	25.29±6.07
4.0	35.20	34.70	0.65	11.07±2.78
6.0	35.20	34.70	0.65	9.67±2.61
8.0	35.20	34.70	0.65	7.73±2.77
10.0	35.20	34.70	0.65	6.66±1.66

A free radical polymerization is a polymerizing approach by which successive addition of free radicals takes place to form a polymer unit. It is a type of chain-growth polymerization, with a cationic, anionic and coordination polymerization. It is an essential technique for obtaining different polymers and material composites. Free radical polymerization via the emulsion technique was effectively employed to synthesize polymer microbeads. In this process, monomer droplets were dispersed in an aqueous phase stabilized by surfactants, forming a stable emulsion system. polymerization was initiated by free radicals generated from an initiator dissolved in the continuous aqueous phase. During polymerization, free radicals diffused from the aqueous phase into the monomer droplets, triggering chain reactions that resulted in polymer growth within the droplets. The surfactants played a critical role in stabilizing the monomer droplets, preventing coalescence and ensuring uniform polymerization. Consequently, polymer particles with controlled size and morphology were obtained.

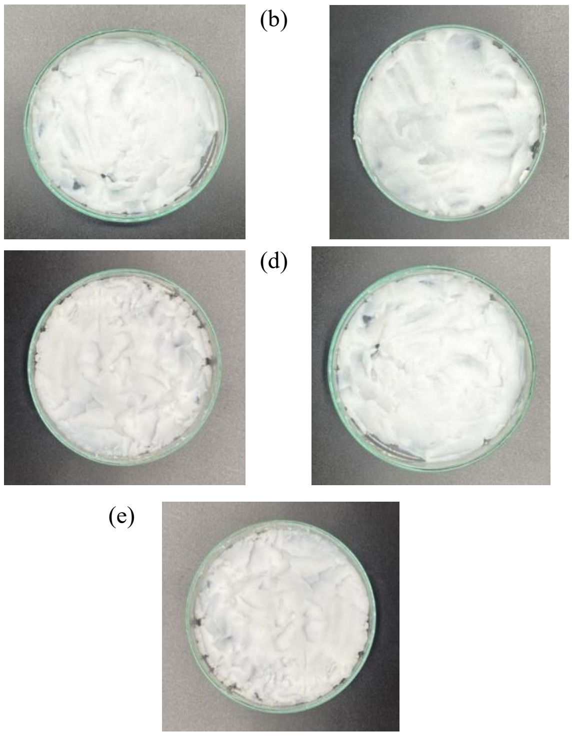

Fig. 2. Hydrogel microbead products synthesized via polymerization at varying concentrations of surfactant. (a-e). 2%, 4%, 6%, 8%, and 10%, respectively.

2.3 Fourier Transforms Infrared (FTIR) Spectroscopy

The prepared samples were finely ground and mixed with anhydrous potassium bromide (KBr) in a 1:100 (w/w) ratio. The mixture was then pressed into pellets (approximately 1 cm in diameter) using a hydraulic press at 1 ton of pressure for 30 sec. Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out over the wavenumber range of 4000–400 cm⁻¹.

2.4 Scanning Electron Microscopy

The morphology and particle size distribution of the microbeads were analyzed by preparing dried samples, which were ground using a mortar. Approximately 0.05 g of the sample was spread onto carbon tape mounted on a stub. The surface morphology was imaged, and preliminary particle sizes were determined using a Scanning Electron Microscope (SEM; Thermo Fisher Quanta 450) operated in low-vacuum mode. Particle sizes were measured from SEM images using ImageJ software.

2.5 Swelling test

The swelling test of the microbeads was conducted by weighing approximately 1.00 g of the dried sample and placing it in a nylon fiber bag. The sample was then immersed in deionized water at room temperature for specific time intervals. At each time point, the sample was removed, weighed, and the weight was recorded. The swelling ratio (%SR) was calculated using the following formula.

$$\textit{Swelling Ratio (\%SR)} = \frac{W_S - W_0}{W_0} \times 100 \qquad (1)$$

Where W_s is the weight of the microbeads in the swollen state and W_0 is the initial dry weight of the microbeads before swelling.

3 Results and Discussion

3.1 FTIR characterization

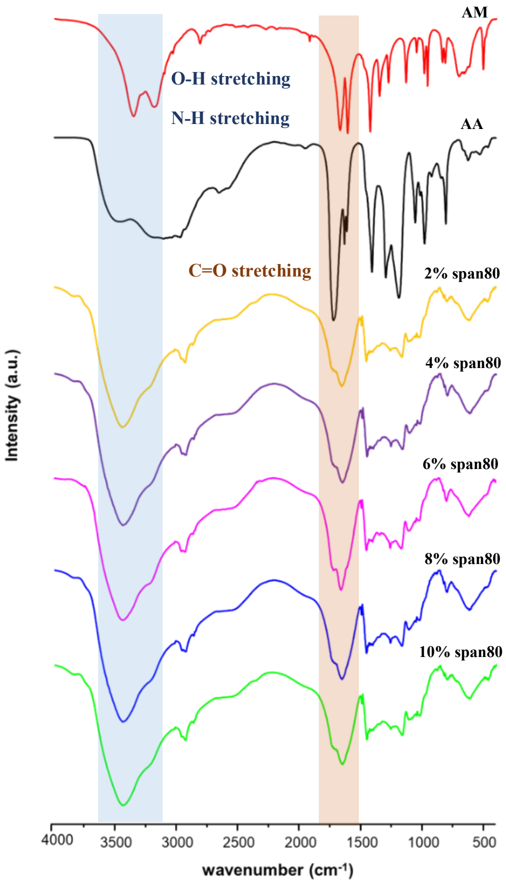

Fig. 3. FT-IR spectra of hydrogel microbeads with different surfactant concentrations compared to acrylamide monomer (AM) and acrylic acid monomer (AA).

The chemical structure of these 5 hydrogel microbeads with difference surfactant concentration is compared to AA and AM monomer were investigated by FTIR spectroscopy shows in the Figure 3 AM and AA monomer, characteristic absorption bands were observed at 3600-3400 cm^{-1} broad peaks attributed to -OH or -NH stretching vibrations, indicating the presence of hydroxy and amide groups. The peaks around 2950-2900 cm^{-1} are assigned to -CH_2 stretching vibrations from the polymer backbone. The absorption band at 1750-1700 cm^{-1} is attributed to the C=O stretching of the carboxylic groups (-COOH, from AA), while a second carbonyl peaks observed around 1650-1600 cm^{-1} corresponding to the amide group (C=O, from AM). These two peaks confirm the successful incorporation of both monomers into the hydrogel matrix. In the copolymer, key peaks from both AM and AA are observed, confirming successful polymerization.

The broad band at ~3400 cm^{-1} is due to overlapping –OH and –NH stretching vibrations, indicating the coexistence of hydroxyl and amide groups in the network. The C=O stretching vibrations from both the carboxylic acid and amide groups are seen at ~1715 cm^{-1} (AA) and ~1650 cm^{-1} (AM) respectively. Importantly, the disappearance of the vinyl groups C=C stretching peak (normally observed in the monomer form around 800–900 cm^{-1} in the copolymer spectrum indicates the completion of polymerization. FTIR analysis verifies that both AM and AA monomers have been efficiently polymerized into the copolymer chain using free radical polymerization. The detection of signature chemical groups and the absence of vinyl group peaks validate the formation of the poly (AM-*co*-AA) hydrogel network.

3.2 Morphology and particle size

The morphology of hydrogel microbeads is examined using SEM as shown in Figure 4., the diameters of particles were measured from the ImageJ program to calculate the average particle size. The physical appearance of particles in all conditions is spherical in shape with smooth surfaces. The average value of particle size distribution of microbeads with different surfactant concentrations at magnification 2000x, 2%, 4%, 6%, 8% and 10% were 25.29 ± 6.07, 11.07 ± 2.78, 9.67 ± 2.61, 7.73 ± 2.77 and 6.66 ± 1.66 respectively (Figure 4 (a, d, g, j, m)), the particle size was found to decrease inversely with increasing surfactant concentration. These results are consistent with the study by ISHAK, W.M.W. and M.H. ZULFAKAR [7], The low concentrations, Span 80 does not fully adsorb onto the surface of newly formed droplets, allowing them to coalesce and resulting in larger droplet sizes. This observation aligns with previous reports on the importance of optimal emulsifier concentrations for droplet stabilization. Increasing the concentration of Span 80 provides more surfactant molecules to effectively reduce interfacial tension and cover the droplet surfaces, thereby minimizing coalescence and leading to a reduction in overall droplet size. The distribution graphs (Figure 4 (c, f, i, l, o)) an increase in surfactant concentration resulted. in a relatively uniform reduction in particle size. At the same time, a narrower particle size distribution and a leftward shift were observed, which also increased with higher surfactant concentration.

https://doi.org/10.1051/e3sconf/202567901030

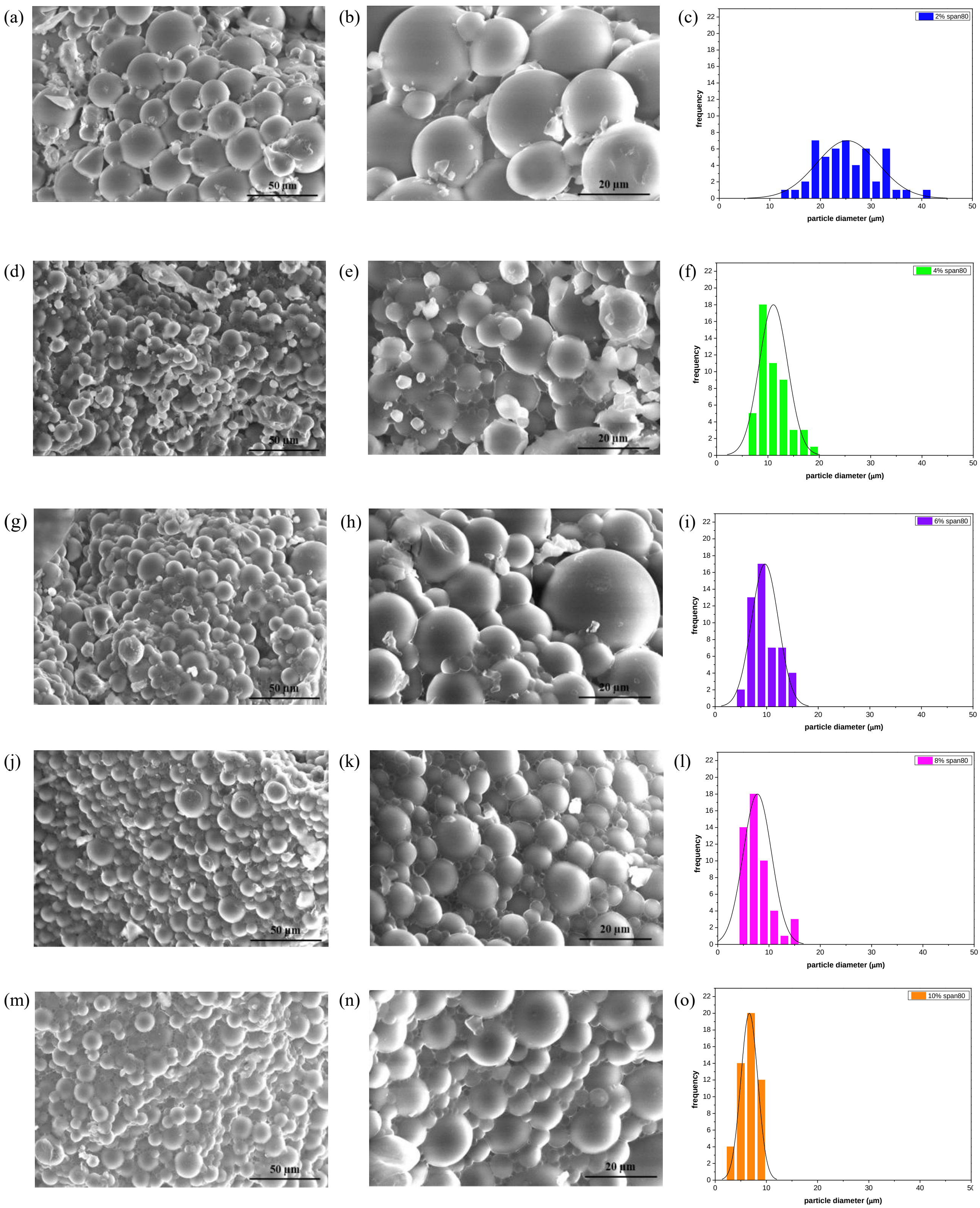

Fig. 4. SEM micrographs of hydrogel microbeads with different surfactant concentrations prepared by emulsion polymerization. (a-c). 2% span80 at magnifications 2000x, 5000x and average value of particle size distribution respectively, (d-f). 4% span80 at magnifications 2000x, 5000x and average value of particle size distribution respectively, (g-i). 6% span80 at magnifications 2000x, 5000x and average value of particle size distribution respectively, (j-l). 8% span80 at magnifications 2000x, 5000x and average value of particle size distribution respectively, (m-o). 10% span80 at magnifications 2000x, 5000x and average value of particle size distribution respectively.

3.3 Swelling behavior

Ability of hydrogel microbeads to absorb and retain an aqueous medium inside the network (Figure 5.), and it is evaluated by immersing the preweighted dried sample in the media. At the beginning solvent molecules attack the surface of the hydrogel and start penetrating the network, causing the expansion of gel meshes that allows other solvent particles to enter the network. Basically, the more hydrophilic the polymer structure, the stronger the polymer-water interaction becomes. Hydrogels with hydrophilic functional groups swell in water exclusively as result of polymer-water interaction forces.

Chemical gels are considered permanent when their polymer networks are stabilized by covalent cross-links, resulting in durable and irreversible structures. Reactive functional groups along the polymer chains enable the formation of these strong and stable covalent bonds, creating a robust gel network. Hydrogel microbeads swell until they reach equilibrium, a state influenced by the strength of polymer–water interactions and the degree of cross-linking. This swelling behavior also depends on the type of polymer and the number of reactive functional groups present along the polymer chain [8].

The swelling ratio of vary surfactant concentrations of hydrogel microbeads were determined based on weight changes in fiber bags as illustrated in Figure 6(a), the study found that the hydrogel microbeads began to reach swelling equilibrium after being immersed in deionized water for 150 min. At surfactant concentrations of 2% and 4%, the resulting emulsions were unstable, indicating that low surfactant levels were insufficient to effectively reduce the interfacial tension between the oil and water phases.

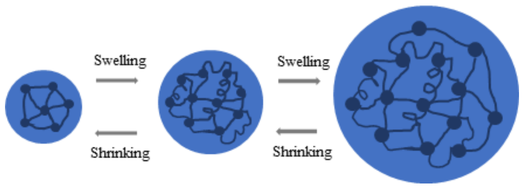

Fig. 5. Swelling property of the polymer matrix, which can uptake and hold significant quantities of water.

Under these conditions, polymerization process was incomplete, resulting in a polymer structure with low mechanical strength due to insufficient crosslinking. Consequently, the swelling ratios at 672.34 ± 7.76% and 673.21 ± 17.56%, respectively. Increasing the surfactant concentration to 6% significantly enhanced the emulsion stability, indicating that a higher amount of surfactant could adsorb at the interface between the oil phase and the internal aqueous phase. This resulted in a stronger adsorption layer and improved emulsion stability, as evidenced by the swelling ratio of 1111.06 ± 12.28%.

However, when the surfactant concentration was increased to 8% and 10%, the emulsion began to exhibit greater stability. The particle size of the emulsion increased and became more uniform. This result is consistent with the particle size distribution illustrated in Figure 4. (c, f, i, l, o), Which shows that increasing surfactant concentration results in smaller and more uniformly distributed particles. It is presumed that polymerization is more complete under these conditions, resulting in increased crosslinking within the polymer network.

This structural improvement contributed to a reduction and stabilization in the swelling ratio, at 916.33 ± 8.99% and 820.45 ± 12.24%, respectively. Similarly, the study conducted by Jusoh and Othman (2016) [9], reported an increase in particle formation at higher surfactant concentrations.

The swelling behavior observed in this system can be explained by Figure 6(b), During the initial immersion period, within the first 60 minutes, water penetrated the outer layer of the microbeads but could not evenly distribute into the internal structure. This led to the release or backflow of some of the absorbed water, causing a temporary decrease in the swelling ratio at the early stage. As time progressed, from 80 to 150 minutes, water gradually diffused into the inner polymer network, resulting in an increase in the swelling ratio again. The system eventually reached equilibrium after approximately 160 minutes. Moreover, the incomplete polymerization and the heterogeneity of the polymer network, which arose from the unstable emulsion, are likely key factors contributing to this two-phase swelling behavior. Similar swelling characteristics have been reported in other studies involving hydrogel materials with irregular porous structures [10, 11].

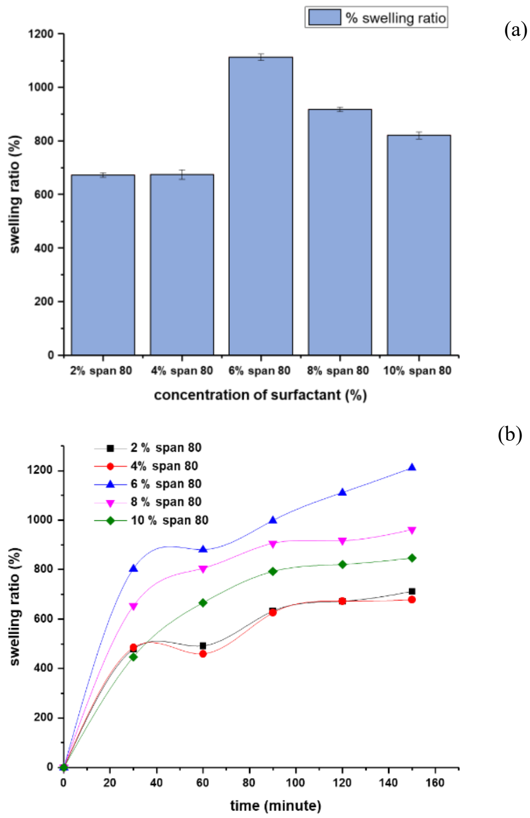

Fig. 6. The effect of different surfactant concentrations on the swelling behavior of hydrogel microbeads. (a). Relationship between surfactant concentration and the swelling ratio (%), (b). Relationship between time and the swelling ratio (%).

4 Conclusions

The results of this study demonstrated that the concentration of surfactant had a significant effect on the stability of the emulsion, which is a key factor influencing the completeness of the polymerization process within the hydrogel microbeads. The experiment revealed that the most stable emulsions were obtained using Span 80 at concentrations of 8% and 10%, which resulted in average particle sizes of 7.73 ± 2.77 µm and 6.66 ± 1.66 µm, respectively.

The swelling ratios of the hydrogel microbeads under these conditions were 916.33% and 820.45%, respectively, indicating a polymer structure with a higher crosslinking density. However, this experiment may have been subject to certain limitations and deviations caused by various factors, such as the accuracy of the equipment or temperature control during the emulsion formation process. Therefore, further studies are recommended to optimize the formulation and synthesis conditions for maximum efficiency. The findings from this study can serve as a guideline for developing high-performance hydrogel microbeads for use in PCCPs, supporting the development of sustainable products that reduce microplastic contamination and encourage ecological responsibility.

The authors would like to extend their appreciations to Department of Industrial Chemistry, Faculty of Applied Science, Graduate College, King Mongkut's University of Technology North Bangkok for their continual supports in providing efficient information and operations.

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