

Effects of Stabilizing agent on the preparation of Polyurea Microcapsules

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1. INTRODUCTION

Poly(vinyl alcohol) plays an important role as a stabilizing agent in the microcapsule preparation. In general, the stabilizer of capsulation strongly affects not only the colloidal properties but also the membrane properties. In the encapsulation process, an emulsion stabilized with poly(vinyl alcohol) has many advantages over surfactants, including Newtonian fluidity, superior primary wet tackiness, high strength and creep resistant film properties. These phenomena stem from the existence of poly(vinyl alcohol) in emulsion, and therefore the chemical structure of poly(vinyl alcohol) has a strong influence on the emulsion properties in the capsule preparation.

Poly(vinyl alcohol) is a semicrystalline polymer whose hydroxyl groups produce inter- and intra-molecular hydrogen bonding. The hydrogen bonding is greatly affected by stereoregularity of hydroxyl groups. And the aqueous solution of fully hydrolyzed poly(vinyl alcohol) forms high water-resistant due to its high crystallinity and shows a drastic increase in viscosity. On the other hand, the viscosity of an aqueous solution of partially hydrolyzed poly(vinyl alcohol) does not change even at low temperature, but resistant properties of the membrane against water are weak. Therefore in the capsulation system the stabilizing properties are dependent on the concentration, the degree of hydrolysis, and the molecular weight.

In this paper, polyurea microcapsules were prepared by interfacial polycondensation. Physical properties, such as diameter, its distribution, morphology of microcapsule, and emulsion were investigated. The effects of the structure of poly(vinyl alcohol), molecular weight and degree of hydrolysis, on the physical properties had been discussed in detail. Meanwhile, the thermal physical properties were determined by DSC and TGA.

2. EXPERIMENTAL

The preparation of polyurea microcapsule was carried out by a typical interfacial polymerization.

Dispersion phase with H₁₂ MDI as wall-forming material and phytoncide oil as the core substance was prepared. Continuous phase with different molecular weight and degree of hydrolysis of poly(vinyl alcohol) as stabilizing agent and EDA as wall-forming material was prepared. The o/w emulsion was formed by adding the oily solution to aqueous solution of 2.0 wt.% PVA as a protective colloid and by stirring vigorously. The resulting emulsion was stirred under atmospheric pressure at 40°C for 5min. EDA and a catalytic content of DBTDL as a catalyst were added to the solution. After increasing to 70°C, microcapsule was reacted for more 120min. Distilled water was added to the slurry to keep the microparticles monodispersed. The resultant microcapsule slurry was decanted, washed with 10% methanol to remove phytoncide oil and unreacted isocyanates on the surface, and dried in a vacuum oven.

Phase stability of 1st o/w emulsion was evaluated by Turbiscan Lab (Formulation, France). In order to identify the reaction, an FT-IR spectrometer (Impact 400D, Nicolet) was used. For each sample, 32 scans at 2 cm⁻¹ resolution were collected in the adsorption mode. The mean diameter and the diameter distribution were determined by particle size analyser (CIS-100 Image analyser, Galai Production Ltd., Israel). Morphologies of microparticles were observed by Scanning electron microscopy (SEM, Hitachi S-4200, Japan). Differential scanning calorimetry (DSC, 220C, Seiko, Japan) was used to determine the melting point and the melting heat during the heat process, freezing point and freezing heat during the cooling process. The determine temperature varied from -50°C to 400°C with the heating rate 5°C/min.

3. RESULT AND DISCUSSION

Fig. 1 shows FT-IR spectra of polyurea microcapsule. In the Figure, hydrogen bonded N-H stretching vibration at 3300 cm⁻¹, C-H stretching vibration at 2950 and 2850 cm⁻¹ and hydrogen bonded urea carbonyl at 1676 cm⁻¹ are observed and free NCO peak at 2250 cm⁻¹ are disappeared. From these characteristic peaks, it can be concluded that wall membrane of the microcapsule is polyurea.

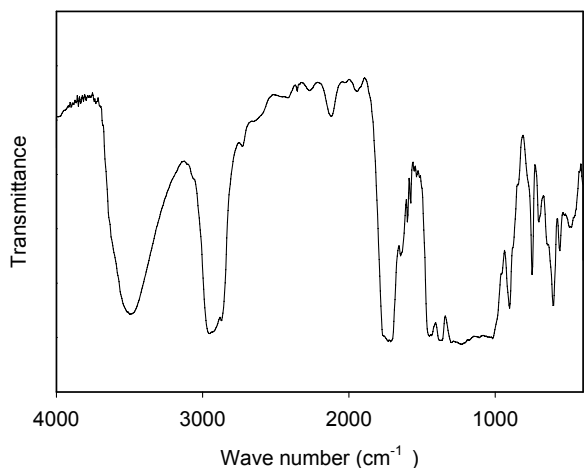


Fig. 1. FT-IR spectra of polyurea microcapsule containing phytoncide oil

Fig. 2 shows viscosity of 2.0 wt% poly(vinyl alcohol) aqueous solutions for different molecular weights with 87% and 98% of hydrolysis (PVA-87 and PVA-98). Poly(vinyl alcohol) aqueous solutions with 98% of hydrolysis has higher viscosity than 87%. And regardless of the degree of hydrolysis, as molecular weights are increased, viscosity is increased.

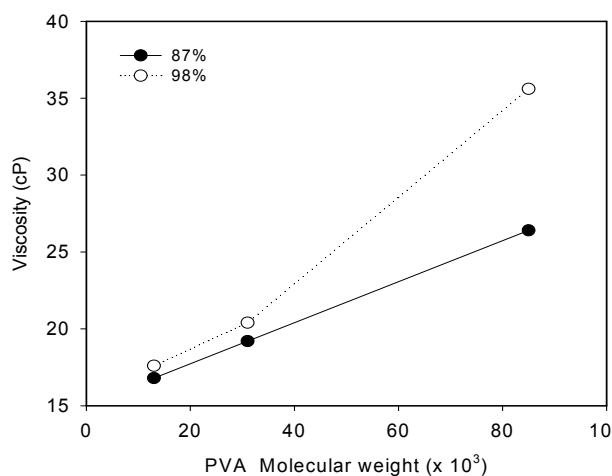


Fig. 2. Viscosity of poly(vinyl alcohol) aqueous solutions at 20°C. [●, PVA-87; ○, PVA-98]

Fig. 3 shows mean particle size of polyurea microcapsules prepared at different molecular weights and degree of hydrolysis of the stabilizing agent. To investigate the effects of the stabilizing agent on the various physical properties of microcapsules, this study used poly(vinyl alcohol) with molecular weights of, 13000, 31000, and 85000 (PVA1, PVA2 and PVA3) for 87% and 98% of hydrolysis.

The mean particle size increases when the molecular weight of PVA increases from 31000 to 85000. Also, it is noticed that the solution with a

98% of hydrolysis shows a higher mean particle size than that of 87%. It is related that the strong gel networks are formed by hydrogen bonding. Consequently, the mean particle size of the PVA with a higher degree of hydrolysis 98% is enhanced due to the increase of the agglomerates between the particles.

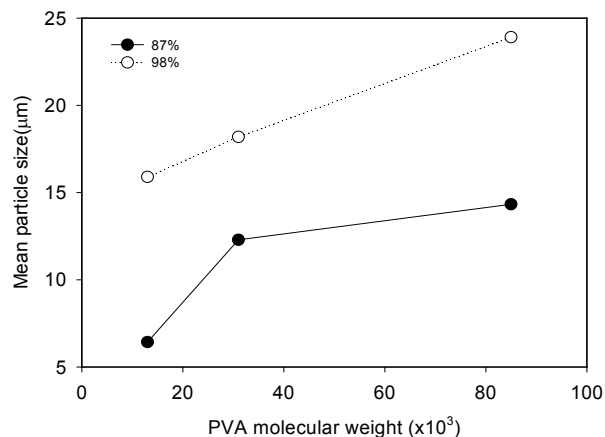


Fig. 3. Mean particle size of microcapsules prepared at different conditions of the stabilizing agent.

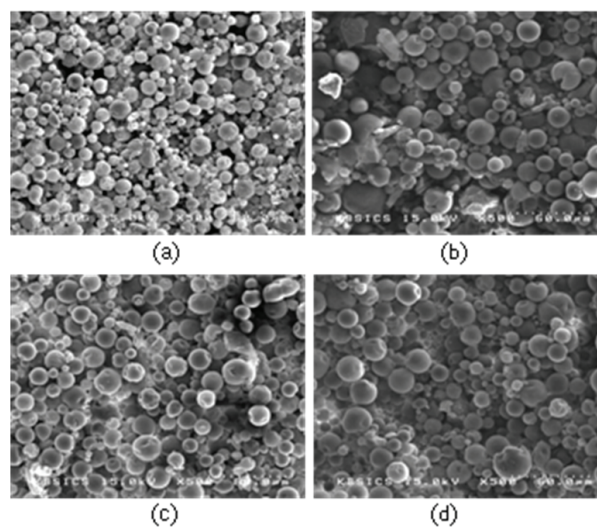


Fig. 4. SEM photographs of microcapsules prepared at different conditions of the stabilizing agent. [(a) PVA1-87, (b) PVA1-98, (c) PVA3-87, (d) PVA3-98]

4. REFERENCE

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