Preparation of lipophilic dye-loaded poly(vinyl alcohol) microcapsules and their characteristics

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Poly(vinyl alcohol) microcapsules cross-linked by benzaldehyde with different cross-link densities containing various amounts of the lipophilic dye, Sudan I, were prepared by the emulsion/cross linking technique. Optimal conditions of microencapsulation were found. The chemical structure of walls of microcapsules was examined by FTIR and by the method of chemical analysis. The content of benzal groups in the walls of microcapsules depended on the quantity of initial dye solution. The size and shape of the microcapsules were examined by optical microscope. The average size of microcapsules was 10 μm and the shape was found to be spherical. The thermal and pressure stability of microcapsules and glass transition temperature of their walls were determined by Hoeppler consistometer. A small decrease in the thermal and pressure stabilities of microcapsules was observed with an increase in the quantity of core material.

Key words: microcapsules, poly(vinyl alcohol), lipophilic dye, benzaldehyde

INTRODUCTION

Interest in the preparation, characterization and application of microcapsules in both academia and industry is immense. Microcapsules include such diverse products as coated powders and any type of particular material containing a solid, liquid or gaseous incipient. Microcapsules are manufactured from a wide range of monomeric and polymeric materials and by a large number of different polymerization techniques and microencapsulation processes. Appropriate combinations of starting materials and manufacturing methodology can be chosen to produce microcapsules having a wide variety of compositional and morphological characteristics [1]. Microcapsules may be used in various fields of industry, medicine, agriculture, hygiene, cosmetics.

Lipophilic materials (dyes, perfumes, fuel, pigments, organic materials) may be encapsulated by various single or combined methods: coacervation [2–6], polycondensation [7–12], extrusion [13], precipitation [14], spray-drying [15] and cross-linking [16]. Water-soluble natural polymers such as gelatin [2–5, 17, 18], starch [2, 15] and synthetic polymers [2, 6, 11, 12, 14, 17] were used for encapsulation of lipophilic material. Poly(vinyl alcohol) (PVA) as a synthetic polymer was used for producing microcapsules in many cases [2, 6, 11, 12, 17]. The walls of PVA microcapsules were hardened both by lowering the temperature of the mixture [6, 17] and by adding hardening agents [2]. For curing the walls of PVA there were used water-soluble aldehydes such as formaldehyde, glyoxal and glutaraldehyde, but not oil-soluble aldehydes.

The aim of this work was to find optimal conditions for preparation of poly(vinyl alcohol) microcapsules by using a combined emulsion/polymer cross-linking technique. Poly(vinyl alcohol) microcapsules must be cross-linked with benzaldehyde, and they must contain a lipophilic dye, 1-phenylazo-2-naphthol (Sudan I) solution in 1-decanol (as the lipophilic material model).

EXPERIMENTAL

Preparation of liphophilic dye-loaded PVA microcapsules (MC) was based on a coacervation/cross linking technique. As dispersing agents for lipophilic materials inorganic thiocianates were used [2]. The original technique was modified by cross-linking PVA with oil-soluble benzaldehyde instead of water-soluble aldehydes. For emulsification of lipophilic dye in PVA solution surfactants were used. To produce PVA microcapsules, 3.0 weight parts (w. p.) of PVA (viscosimetric molecular weight, MW = $7.3 \cdot 10^4$, [–$OCOCH_3$] = 14%) was dissolved in 80.7–93.7 w. p. of distilled water. As emulsifiers, there were added surfactants (0.03–3.30 w.

p.): Tween 80 (polyoxyethylene-sorbitan-monooleate), sodium oleate, sulfonol (alkylbenzene sulfonate sodium salt), poly(ethylene glycol) (PEG, MW = = 6000), sulfonol or PEG mixture with sulfonol. 2.0–11.0 w. p. of 1% solution of lipophilic dye, 1-phenylazo-2-naphthol (Sudan I) in 1-decanol was added as core material (CM) of microcapsules. The mixture was dispersed by mixing for 5 min at a temperature of 323 K. The rate of stirring was 1100 rpm. Benzaldehyde (1.1–4.4 w. p.) and 1.0 w. p. of conc. HCl were added for the cross-linking of PVA at the same temperature. The total amount of all the components in the initial reaction mixture was assumed to be equal to 100 w. p. The produced microcapsules were rinsed with hexane and dried at room temperature. The yield of microcapsules was calculated from the amount of the initial quantity of PVA, Sudan I solution and benzaldehyde. The quality of microcapsules was considered as good, if they were powdery and of white color. The size and shape of microcapsules was examined by using a LEITZ optical microscope.

The quantity of core material in microcapsules was estimated by extraction with acetone in a Soxhlet extractor. The solid residue was dried at room temperature. The quantity of core material was calculated as a difference between the weight of sample before extraction and after it. The quantity of benzal groups in the walls of microcapsules was estimated after extraction according to [19].

The thermal and pressure stabilities of microcapsules were determined with a Hoeppler consistometer [19]. The used load was 0.750 kG and the rate of increase of the temperature was 1 K/min.

RESULTS AND DISCUSSION

A combined emulsion/polymer cross-linking technique was used to prepare PVA microcapsules containing different quantities of core material, solution of the liphophilic dye, Sudan I employed as a model material. Various solvents were used for dissolving the lipophilic dye. High yields and a good quality of microcapsules (powdery consistence and white color) were obtained when Sudan I was dissolved in 1-decanol or ricinus oil. The quality of microcapsules was poor when Sudan I was dissolved in toluene or cyclohexane. Such results can be explained by a thermodynamic affinity between the used solvents and PVA. 1-Decanol or ricinus oil contain hydroxyl groups, therefore they have a higher affinity to PVA than toluene or cyclohexane. The quality of microcapsules depended on the initial quantity of dye solution. If this content was less than 2.0 or more than 11.0 w. p., the quality of microcapsules would become worse. The quantity of core material in microcapsules depended on the initial quantity of dye solution and was in the range of 36–75% (Fig. 1). The yields of microcapsules depended on the initial quantity of dye as well (Fig. 2). The best yield (65%) was obtained when the initial quantity of dye solution was 5 w. p. The content of the lipophilic dye in microcapsules in such a case was 66% (Fig. 1).

Oil-soluble benzaldehyde was used for curing the microcapsules' walls formed from PVA. Cross-linking of polymer chains in the droplets was accomplished by diffusion of benzaldehyde. It is an instantaneous reaction and leads to immediate formation of microcapsules from the dispersed droplets. The reaction resulted in intermolecular and intramolecular benzal groups which were indicated by IR spectra. The IR spectra of PVA had the following distinct absorption bands: the O–H stretching at 2944 and 3434 cm^{-1}, the C–O stretching at 1098 cm^{-1}, and the C–O stretching of acetate group at 1267 cm^{-1}. The cross-linked PVA also showed phenyl group absorption peaks at 701, 752 and 1455 cm^{-1}. Microcapsules with various degrees of cross-linking in the

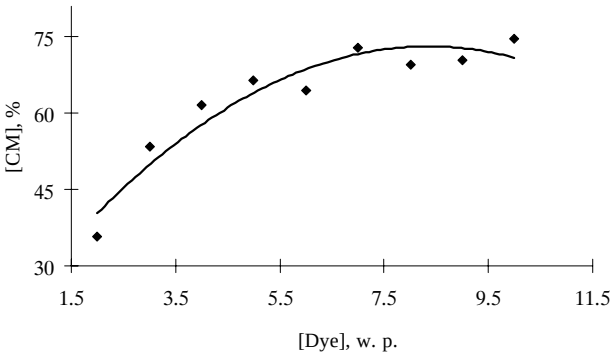

Fig. 1. Content of core material in microcapsules as a function of initial quantity of dye ([Tween 80] = 0.3 w. p., [BA] = = 2.2 w. p.)

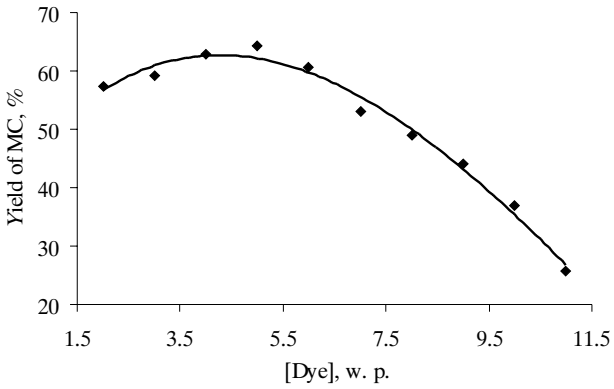

Fig. 2. *Y*ield of microcapsules as a function of initial quantity of dye ([Tween 80] = 0.3 w. p., [BA] = 2.2 w. p.)

walls and a different quantity of benzal groups (64.2–69.5%) were produced by employing various concentrations (1.1–4.4 w. p.) of benzaldehyde (Fig. 3). The lower the degree of cross linking, the more swellable the polymer walls. It was estimated that the content of benzal groups in the walls of microcapsules depended on the quantity of the initial dye solution (Fig. 4). An increase in the quantity of the initial dye solution from 2.0 to 4.0 w. p. resulted in an increase of the quantity of benzal groups from 62.0 to 68.0%. The further increase of initial dye solution from 5 to 10 w. p. resulted in a decrease of the quantity of benzal groups to 46.0%. It may be caused by the influence of dye solution on the cross-linking reaction of PVA. The best quality of microcapsules was obtained by using 2.2 w. p. of benzaldehyde, 0.3 w. p. of Tween 80 and 5.0 w. p. of dye solution. The yield of microcapsules in such conditions was 65% and the quantity of benzal groups was 66.5%.

For curing the walls of microcapsules, water-soluble glutaraldehyde was also used. Gel, but not microcapsules were formed by using 0.92–2.26 w. p. of glutaraldehyde. In this case cross-linking of PVA chains was accomplished by diffusion of aldehyde from the water.

Anionic and non-ionic surfactants were used as emulsifiers for microencapsulation. The presence of Tween 80 or sodium oleate in certain ranges of concentration gave microcapsules of good quality. Microcapsules of good quality were obtained when the concentration of Tween 80 was in the range from 0.25 to 1.00 w. p. or the concentration of sodium oleate was 0.5 w. p. The use of PEG, sulfonol or a PEG mixture with sulfonol in various proportions resulted in a medium or bad quality of microcapsules.

The shape of the prepared microcapsules was found to be spherical. The average particle size was 10 μm and particle size distribution was 5–35 μm.

The thermal and pressure stabilities of the microcapsules were determined with a Hoeppler consistometer. Two characteristic temperature values were estimated for microcapsules. The first temperature showed the thermal and pressure stabilities of microcapsules, *i. e*. their mechanical resistance found by determining their rupture temperature at a load

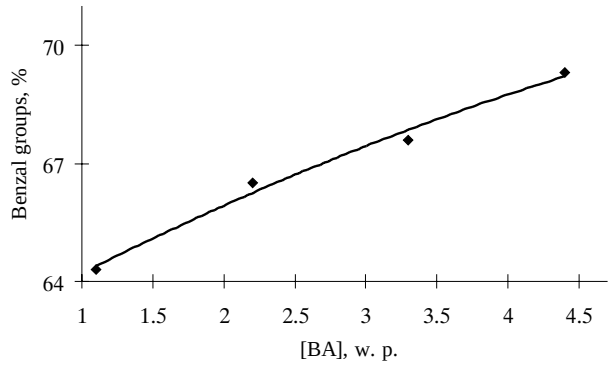

Fig. 3. Content of benzal groups in the walls of microcapsules as a function of initial quantity of benzaldehyde ([Tween 80] = 0.3 w. p., [CM] = 5.0 w. p.)

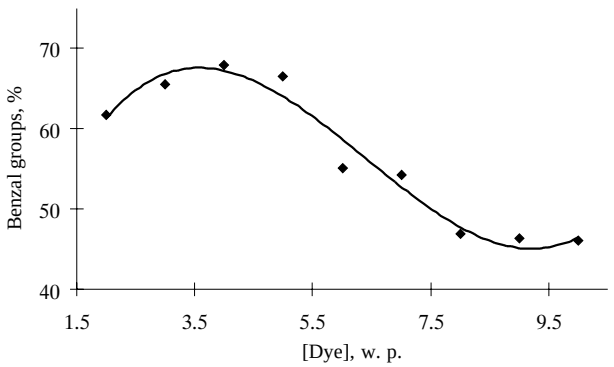

Fig. 4. Quantity of benzal groups in the walls of microcapsules as a function of initial quantity of dye ([Tween 80] = 0.3 w. p., [BA] = 2.2 w. p.)

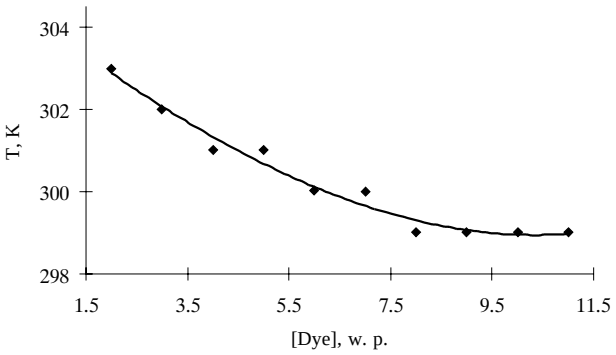

Fig. 5. Thermal stability of microcapsules as a function of initial quantity of dye ([Tween 80] = 0.3 w. p., [BA] = =2.2 w. p.)

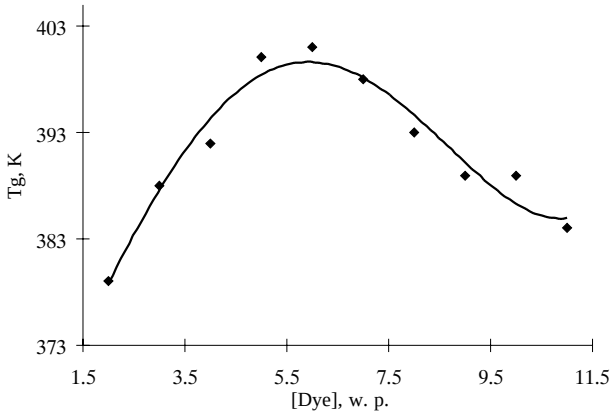

Fig. 6. Glass transition temperature of cross-linked PVA as a function of initial quantity of dye ([Tween 80] = 0.3 w. p., [BA] = 2.2 w. p.)

of 0.750 kG. Increasing the initial quantity of dye solution from 2.0 to 11.0 w. p. resulted in thinner walls and a lower thermal stability of microcapsules (Fig. 5). The second temperature value indicated the glass transition temperature (T_g) of cross-linked PVA (Fig. 6). T_g increased from 379 to 401 K with increasing the quantity of dye solution from 2.0 to 5.0 w. p., presumably because the walls of microcapsules were thinner and the possibility of benzaldehyde to diffuse across the walls was better. Further increasing the quantity of dye solution to 11.0 w. p. resulted in a decrease of T_g to 384 K. There was a correlation between these results and the content of benzal groups in the walls of microcapsules (Fig. 4).

CONCLUSIONS

1. Poly(vinyl alcohol) microcapsules cross-linked by benzaldehyde with 46.0–69.5% of benzal groups in the walls of microcapsules containing 36–75% of lipophilic dye, Sudan I, were prepared by the emulsion/cross linking technique. The best quality of microcapsules was obtained by using 2.2 w. p. of benzaldehyde, 0.3 w. p. of Tween 80 and 5.0 w. p. of lipophilic dye solution. The yield of microcapsules in such conditions was 65%, the content of lipophilic dye in microcapsules was 66% and the quantity of benzal groups in the walls was 66.5%.

2. A slight decrease in thermal and pressure stabilities of microcapsules was observed when increasing the quantity of core material.

3. Glass transition temperatures of the walls of microcapsules depended on the quantity of encapsulated dye solution. An excess of it (>5 w. p.) resulted in a decrease of cross-link densities of poly(vinyl alcohol) and glass transition temperatures of the walls.

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POLI(VINILO ALKOHOLIO) MIKROKAPSULIŲ SU ĮKAPSULIUOTU LIPOFILINIU DAŽIKLIU GAVIMAS IR TYRIMAS

S a n t r a u k a

Emulsijos/susiuvimo metodu gautos įvairaus susiuvimo poli(vinilo alkoholio) mikrokapsulės. Susiuvimo agentas – benzaldehidas. Įkapsuliuoti įvairūs lipofilinio dažiklio Sudano I kiekiai. Rastos optimalios mikrokapsuliavimo sąlygos. IR ir cheminės analizės metodu nustatyta mikrokapsulių sienelių cheminė sandara. Benzalinių grupių kiekis mikrokapsulių sienelėse priklauso nuo pradinio dažiklio tirpalo kiekio. Mikrokapsulių dydis ir forma įvertinti optiniu mikroskopu. Jų vidutinis dydis yra 10 μm, o forma – sferinė. Mikrokapsulių terminis stabilumas, mechaninis atsparumas ir jų sienelių stiklėjimo temperatūra nustatyta Heplerio konsistometru. Padidėjus įkapsuliuojamos medžiagos kiekiui, mikrokapsulių terminis stabilumas ir mechaninis atsparumas šiek tiek sumažėja.