

Development of a precipitation method intended for the entrapment of hydrated salt

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Abstract

Microcapsules loaded by sodium phosphate dodecahydrate (DSP) were prepared according to the solvent evaporation–precipitation method using chloroform as solvent and cellulose acetate butyrate (CAB) cross-linked by methylene diisocyanate (MDI) as coating polymer. The effects of the preparation conditions on the capsule morphology and the entrapment efficiency of water-soluble materials were investigated. A mechanism of the process of wall formation material is also suggested depending on the ratio of CAB/MDI introduced. A competition between the hydroxyl functions of CAB and water to react with an isocyanate might occur to form the microcapsule shell. An increase of the amount of MDI promoted urethane linkages whereas urea and urethane linkages decreased by increasing the CAB amount. Furthermore, the encapsulation yield was found to be linked to the CAB and MDI concentrations and optimal when the ratio (MDI to CAB) was in the range of 0.4–1.

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1. Introduction

Preparation of uniform polymeric microcapsules in the 1–10 μm size range has received great attention in recent years and more especially for their use in textile area (Erkan & Sariisik, 2004; Nelson, 1991, 2002). Amongst these applications, the incorporation of microencapsulated phase change materials (PCMs) has attracted great interest to improve thermal insulation (Leitch & Tassinari, 2000; Pause, 1995). Until now, only organic PCMs have been encapsulated (Hawladar, Uddin, & Khin, 2003; Yoshizawa, Kamio, Hirabayashi, Jacobson, & Kitamura, 2004; Zhang, Tao, Yick, & Wang, 2004). It has been found that the possible use of salt hydrates and their supercooling property can be exploited for specialized thermal storage

applications (Hirano & Saitoh, 2002; Hirano, Saitoh, Oya, & Yamazaki, 2001; Sandnes & Rekstad, 2006). Furthermore, a step of encapsulation with a semi-impermeable coating is necessary to improve their performance since hydrated salts are sensible to moisture (Canbazoğlu, Şahin-Aslan, Ekmekyapar, Aksoy, & Akarsu, 2005).

The functional performance of the microcapsules depends on the morphology, the chemical nature and the surface characteristics of the polymeric shell influenced by the process parameters (Yadav, Suresh, & Khilar, 1990). The choice of a particular process is determined by the solubility characteristics of the active compound and the shell material. Cellulose derivatives have been widely used in the preparation of water-soluble microencapsulated compound. Microencapsulation processes using cellulose acetate butyrate (CAB) as coating material include emulsion solvent evaporation (Arnaud, Boue, & Chaumeil, 1996; El Bahri & Taverdet, 2006; Obeidat & Price, 2005;

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Torres, Boado, Blanco, & Vila-Jato, 1998), spray drying (Giunchedi, Conti, Maggi, & Conte, 1994), and precipitation (Rege et al., 1999).

In a solvent evaporation technique, morphology of CAB microcapsules is affected by the solvent choice and its evaporation temperature. Indeed, a high temperature allows a rapid shell formation characterized by a homogeneous and porous structure with large pores, while at low temperature a more compacted heterogeneous porous structure is obtained (Fundueanu et al., 2005). Besides, the pressure created by the swelling of the core component is sufficient to cause rupture of the CAB shell.

The thermo-chemical and physical properties of the CAB polymeric film can be improved by cross-linking CAB with a diisocyanate (Uda & Hijikigawa, 1988). The cellulosic compound is cross-linked through the formation of urethane bonds. Laskar, Vidal, Fichet, Gauthier, and Teyszié (2004) have observed that the required molar ratio of cross-linker (diisocyanate) to free OH groups in cellulose to obtain a network decreased with the increase of CAB amount. This result suggests two ways of cross-linking amongst the amount of CAB, inter or intra chains.

In a water in oil polycondensation system to prepare polyurethane network, it is known that the reaction of isocyanate groups with water molecules during the capsule formation forms also urea cross-linkings. This formation depends on the water molecules diffusion through the polyurethane network and could influence the thermal properties controlling the permeation properties of the microcapsules. In this work, the synthesis and characterization of poly(urea-urethane) microcapsules are studied using different amount of cellulose acetate butyrate and diphenyl methylene diisocyanate (MDI). The experimental procedure is derived from an interfacial polycondensation used for the polyurethane microcapsule preparation. The objective of this work was to investigate the influence of incorporated CAB and MDI amounts on chemical structure of microcapsules by Fourier-transform infrared spectroscopy (FTIR) analysis.

2. Experimental

2.1. Materials

Cellulose acetate butyrate (CAB) (13.5%-wt acetyl and 38%-wt butyryl content, average Mn ca. 30,000) and diphenyl methylene diisocyanate (MDI) (Suprasec 2030, Hüntsmann ICI; blend of MDI isomers, 4,4'-diphenyl methylene diisocyanate principally) used as shell-forming monomers were obtained from Aldrich and Huntsman ICI. Sodium phosphate dodecahydrate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (DSP) was employed as core material. Nonionic surfactant, Span[®] 85 (sorbitan trioleate) and poly(ethylene glycol)dioleate (PEG 400 dioleate) were purchased from Aldrich, and used as emulsifier. Toluene and chloroform were of reagent grade and used without further purification.

2.2. Preparation of microcapsules

The preparation of the microcapsules was carried out according to the following method. 12.5 ml of an aqueous phase containing 15 g of hydrated salt were emulsified at a stirring rate of 8500 rpm with a homogenizer (ultra tur-rax[®], Ika, Germany) at room temperature in 50 ml of an organic phase. The organic phase was prepared by dissolving the surfactant in a nonvolatile solvent, e.g. toluene. After 15 min, when the expected droplet size of the emulsion was reached, a solution containing 0, 0.625, 1.25, 2.5, 5 and 10%-wt of CAB previously solubilized in 30 ml of a volatile solvent (chloroform) is added. The mixture was stirred continuously using a blade stirrer at a lower speed (600 rpm) under ambient pressure and the temperature was increased at 1 °C/min until 60 °C to allow the progressive evaporation of volatile solvent. The complete cross-linking of the microcapsules was carried on by a drop-wise addition of a solution containing 0.5, 1, 2, 5, and 10%-wt of MDI in toluene, until the polycondensation was complete (2 h). The resultant microcapsules were recovered by filtration and washed with toluene to remove remaining MDI and dried at room temperature for one night.

The encapsulation yield was calculated as the ratio of the mass of microcapsules shell [after correction of salt content determined by thermogravimetric analysis (TGA) (Table 2)] obtained at the end of the process and the mass of initial substances added including CAB and MDI.

2.3. Analysis of the microcapsules

The structure of the shell polymer was analyzed by FT-IR spectra. Samples were ground and mixed with KBr to make pellets. FT-IR spectra in the transmission mode were recorded using a Nicolet Nexus, connected to a PC, in which the number of scan was 32 and the resolution was 4 cm^{-1} .

To put an interpretation on a more quantitative basis, we performed the de-convolution of the spectra using peakfit 4.0 software (Jandel, San Rafael, CA) in the $1575\text{--}1800\text{ cm}^{-1}$ region into Gaussian peaks. These wavenumbers were used as initial parameters for curve fitting with Gaussian component peaks. Position, bandwidths, and amplitudes of the peaks were varied until: (i) the resulting bands shifted by no more than 4 cm^{-1} from the initial parameters, (ii) all the peaks had reasonable half-widths ($<20\text{--}25\text{ cm}^{-1}$) and (iii) good agreement between the calculated sum of all components and the experimental spectra was achieved ($r^2 > .99$). The results of four independent experiments were averaged.

The relative contents of different absorption bands of elements were estimated by dividing the areas of individual peaks, assigned to particular secondary structure, by the whole area of the resulting ester band.

The thermal behavior of the particles was recorded using a TA instrument type DSC 2920 piloted on PC with

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