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Preparation of double layered shell microparticles containing an acid dye by a melt dispersion–coacervation technique

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ABSTRACT

Two types of microparticles with a double layered shell containing an acid dye were prepared by using a melt dispersion–coacervation process. The surface morphology and the composition of the microcapsules were investigated using scanning electron microscope (SEM), and Fourier-transform infrared spectroscope (FTIR) respectively. The results showed that the loading content and morphologies strongly depend on the composition, the protective colloid, as well as on the outer polymeric shell and the way the solvent solubilizes it. The thermo-physical properties strongly depend on the nature of the core content and the synthesis conditions. Factors affecting the release performance of the microcapsules were investigated and the results are presented in this paper.

1. Introduction

The application of microencapsulated dye technology in textile dyeing and printing has been investigated since early 90s [1]. Microcapsules are tiny particles in the size range of 1 µm to 2 mm surrounding functional materials with a polymer shell. The release properties of the polymer that forms the shell depends on the class of the wall materials, but also on the microencapsulation methods, on the physico-chemical parameters of the process, on the mean particle size and on the membrane thickness [2,3]. In recent years, composite microparticles comprising of polymeric matrixes embedded with dye have attracted much interest in the field of dyeing textiles [4].

The water-soluble anionic dyes, which are one of the most important groups of dyes used in the textile dyeing industries, are used to dye fabrics like wool, nylon and silk. Microencapsulation of dyes allows them to be protected from the outside environment. It also allows them to have a reduced reactivity and so ensures good dyeing characteristics [4]. Up to now, reactive and dispersed dye were essentially encapsulated by interfacial polymerization in polyurea and polyurethane shell [5–10] or in a liposomic structures [11] whereas acid dyes were only entrapped in a liposomic structure [12,13].

Core-shell microcapsules have been investigated widely and significant promise for providing new functionalities was shown. Thus, many “smart” microparticles have been synthesized to act in response to the change in environmental stimuli, e.g. temperature [14–17], pH[18], light [19,20], electric [21] or magnetic field [22], and other stimuli. The microparticles using a single polymer shell present certain numbers of disadvantages including an initial burst, caused by the release of the active substance trapped on the surface during the encapsulation process and a low encapsulation efficiently for highly water soluble compound. The addition of a second polymer layer to a polymeric microparticle to form a two-layered structure may overcome these limitations. Thus these structures may provide the opportunity to improve the thermal conductivity and stability of the particles [23,24]. Furthermore, the selection of the appropriate core and the appropriate shell polymer chemistries plays an important role to control the release of the active substance [25] and to incorporate the particles on a substrate [26]. One of the possible ways to achieve the linkage on a textile substrate is to fuse the outer thermoplastic wall by a “hot-melt” process.

Various approaches have been designed to prepare this two-layered polymer blend structure to obtain required properties. One method entails a polymer–polymer phase separation of a binary blend of polymer solutions, which results in the formation of double walled microparticles [27]. Another method is to encapsulate active substance in microparticles using conventional microencapsulation technique and then coat these particles with a second polymer. With the formation of the outer coating, the active substance diffusion and the burst effect during the process are reduced since no active substance is entrapped on the surface of the particles [28].

Gander et al. [29] have shown that the morphology of the microparticles depended on the polymer solvent system. One method predicting the solubility of a solute in a solvent is to compare their solubility parameters. Thus, a good solvent for a solute such as a polymer has a solubility parameter close to that of the solute's one.

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Hildebrand or partial Hansen solubility parameters (δ_t, δ_d, δ_p, δ_h) can be used for predicting polymer/solvent properties.

In this work, we have checked the ability to synthesize microcapsules containing acid dye with an uncoloured shell: once the microcapsules are applied on the textile support, the colorant is released by melting the microcapsule shells forming specks which can penetrate the textile. The microparticles were prepared using a melt dispersion-coating method. Gelatin, a natural macromolecule, is widely used in biomedical and biotechnological applications and is a good candidate for preparation of microspheres and microcapsules for the purpose of controlled release applications of drugs. The aim of this study was to prepare microcapsules containing a water-soluble dye used in the textile industry which changes colour irreversibly according to the external environmental conditions. Microencapsulated acid dyes have been characterised in terms of thermal properties measured by Differential Scanning Calorimeter (*DSC*), morphological structure (SEM), chemical composition (FTIR) and colour differences (E^*) using spectrophotometer.

2. Experimental

2.1. Materials

Commercial grade dye AR57 (Nylosan Red EBL) was supplied by Clariant-Switzerland and used without further purification. Carnauba wax, poly(vinyl alcohol) (M.W. 95000, 95% hydrolysed), gelatine used as emulsifiers and span 85, employed as surfactant, were purchased from Acros Organics and Aldrich, respectively. Carnauba wax belongs to the naturally occurring waxes of vegetable origin, which constitutes mainly high molecular weight esters [30,31]. Low density polyethylene (PE) and polystyrene (PS) were obtained from Elf Atochem and BP chemicals respectively. Toluene, Chloroform and Petroleum ether from Aldrich are used as received.

2.2. Methods

2.2.1. Solvent selection

Carnauba wax was used as the encapsulating material. Ten organic solvents having a Hansen solubility parameter of 14–27 MPa$^{1/2}$ were screened for polymer solvency (Table 1). 1 g of carnauba wax was added to test tubes containing 10 ml of the test organic solvent. The test tubes were agitated during 2 h at 50 °C. Solubility of carnauba was judged by visual examination. Solvents were classified into four groups: good solvents that formed clear wax solutions; intermediately good solvents that formed turbid wax solutions; intermediately poor solvents that were marginally able to swell the wax; and poor solvents in which the carnauba wax remained intact.

The Hansen solubility parameters consist of three components, with a dispersion term δ_D, a polar term δ_P, and a hydrogen-bonding term δ_H, which together make up the total solubility parameter δ_t, and their relationship can be expressed as in Eqs. (1) and (2):

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

$$\delta_t = \sqrt{\frac{E}{V}} \tag{2}$$

Where, E is the vaporization energy of the solvent, and V is the molar volume of a solvent. Solubility parameters are not available for carnauba wax. In this case, the calculation of Hansen solubility parameters can be estimated by incremental methods. There are based on group attraction constants F_{Di} and F_{Pi}, for dispersion and polar components, and group cohesion energies E_{Hi}. The contributions of the different groups to the cohesion energy and the molar volume have been published by Fedors [32] and corresponding solubility parameters can be calculated by means of Eqs. (3), (4) and (5).

Table 1
Solubility parameter components of various solvents and interaction radius.

Solvent	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	R_{ij}
Acetone	15.5	10.4	7.0	19.9	11.2
Chloroform	17.8	3.1	5.7	18.9	4.9
Cyclohexane	16.8	0	0.2	16.8	2.2
Dichloromethane	18.2	6.3	6.1	20.2	7.6
Ethanol	15.8	8.8	19.4	26.5	19.1
Ethyl acetate	15.8	5.3	7.2	18.2	7.0
Hexane	14.9	0.0	0.0	14.9	4.1
Petroleum ether	15.2	0.0	0.0	15.2	3.7
Toluene	18.0	1.4	2.0	18.2	3.0
Xylene	17.8	1	3.1	18.1	2.6

$$\delta_d = \frac{\Sigma_i F_{Di}}{\Sigma_i V_i} \tag{3}$$

$$\delta_p = \frac{\sqrt{\Sigma_i F_{Pi}{}^2}}{\Sigma_i V_i} \tag{4}$$

$$\delta_H = \sqrt{\frac{\Sigma_i E_{Hi}}{\Sigma_i V_i}} \tag{5}$$

The chemical composition of carnauba is complex, and the different components can be fallen into five classes such as fatty acids, ω-hydroxy fatty acids, alcohols, α,ω-diols and cinammic acids [33]. Thus, in this study, to calculate the solubility parameters from Hansen theory, we consider that carnauba wax is composed almost entirely of esters of C_{24}, C_{26} and C_{28} carboxylic acids and C_{30}, C_{32} and C_{34} straight-chained primary alcohols and contains more essentially myricyl cerotate ($C_{25}H_{51}COOC_{30}H_{61}$) and small quantities of free cerotic acid ($CH_3(CH_2)_{24}COOH$) and myricyl alcohol ($C_{30}H_{61}OH$) [33].

Furthermore, according to Hansen, the region of good solubility can be characterized by the distance between solvent and polymer and defined as a sphere in the three-dimensional space of the solubility parameters. The corresponding interaction radius for solvent i and polymer j is therefore given by Eq. (6):

$$R_{ij} = \left[4\left(\delta_{d,i} - \delta_{d,j}\right)^2 + \left(\delta_{p,i} - \delta_{p,j}\right)^2 + \left(\delta_{h,i} - \delta_{h,j}\right)^2\right]^{\frac{1}{2}} \tag{6}$$

This means that a polymer is probably soluble in a solvent if the Hansen parameters for the solvent lie within the solubility sphere for the polymer. In order to predict the solubility, the distance R_{ij} must be less than the interaction radius of the polymer, R_j. Here, we replaced the polymer by carnauba wax. Thus, the calculated Hansen solubility parameters of carnauba wax are $\delta_d = 16.6$ MPa$^{1/2}$, $\delta_p = 0.5$ MPa$^{1/2}$, $\delta_h = 2.3$ MPa$^{1/2}$ and $\delta_t = 16.8$ MPa$^{1/2}$.

2.2.2. Preparation of double-walled microparticles

The microencapsulation of an acid dye was carried out in a 500 ml three neck round-bottomed flask equipped with a mechanical stirrer by a melt dispersion–coacervation technique. Typical procedure for the preparation of double layered shell microcapsules was divided in two steps in which firstly, spherical particles were prepared by using carnauba according to the w/o melt dispersion method, and secondly these later were entrapped with a surrounding polymer either PS or PE by a coacervation-phase separation technique induced by the addition of a non-solvent either ethanol or water (Fig. 1).

2.2.2.1. Preparation of microparticles. 40 ml of an aqueous phase containing an acid dye solution (1%-wt) and 0, 0.33, 0.66, 1.33 or 3.33%-wt of gelatin were emulsified at 900 rpm with a mechanical