Polymer Bulletin 47, 457-463 (2002)

Polymer Bulletin

PMMA microcapsules containing water-soluble dyes obtained by double emulsion/solvent evaporation technique

N.Zydowicz, E. Nzimba-Ganyanad, N.Zydowicz (✉)

Laboratoire des Matériaux Polymères et Biomatériaux, UMR CNRS 5627,
Université Claude Bernard Lyon1, 43 Bd du 11 Novembre 1918 F-69622 Villeurbanne Cedex, France
e-mail : zydowicz@matplast.univ-lyon.fr**,** Fax **:** +33 (0)4 72 43 12 49

Received: 13 July 2001/Revised version: 23 October 2001/ Accepted: 23 October 2001

Summary

The aim of this study was to prepare microcaspules containing a water-soluble dye used in textile industry. These microcapsules must be stable during the time and no release of the dye must be observed during their stocking. The difficulty of this work lies in the water-solubility of the dye which does not allow a classical oil-in-water solvent evaporation and furthermore, the dye presents a certain solubility with volatile solvents classically used in solvent evaporation technique. Thus a double emulsion based encapsulation process was developped and allowed the encapsulation of the dye. The observation by optical microscopy and scanning electron microscopy showed well-spherical microcapsules with mean diameter around 30 μm, smooth surface and no porous membrane.

Introduction

Solvent evaporation technique allows the encapsulation of various active principles and is widely used in the field of pharmacy and drug release, even if this technique often involves chlorinated solvent [1-3]. In fact, the high volatility of the solvents induces very low residual solvent rates after the drying of microcapsules. This technique is classically adapted to the encapsulation of lipophilic active principles with an oil-in-water emulsion [4]. Double water-oil-water emulsions were developped for the encapsulation of hydrophilic drugs [2-4]. The interest of this double emulsion process lies not only in the possibility of hydrophilic drugs encapsulation but also in the formation of liquid core and solid shells particles contrarily to oil-in-water emulsion solvent evaporation which leads to the formation of microspheres. The present paper deals with the encapsulation of a water-soluble dye by double emulsion (w/o/w) solvent evaporation technique. The polymer is polymethylemethacrylate (PMMA) and the solvent is methylene chloride. The microcaspules are characterized by optical and scanning electron microscopies, static laser light scattering, thermal

gravimetric analysis and differential scanning calorimetry. The dye release from the microcapsules is followed by UV-visible spectroscopy.

Materials and methods

Methylene chloride was supplied by Aldrich (+ 99%).
Polyvinylalcohol, 88% hydrolyzed, Mw = 22,000 g/mol was supplied from Aldrich.
Amorphous polymethylmethacrylate was kindly supplied by AtoFina. The number average molecular weight determined by Size Exclusion Chromatography was found equal to 90,000 g/mol (polystyrene calibration).
The dye is a vinylsulfone type with a maximal absorption wavelength at 430 nm.
The size distribution of the microcapsules was determined on a Mastersizer MS 2000 (Malvern Instruments).
The stability of the emulsion and the observation of the microcapsules were controlled by using a Leiz Wetzlar optical microscope in the transmission mode and photographs were obtained by instantaneous digitalization by means of a Sony hyper HAD video.
Scanning electron microscopy (SEM) experiments were performed on a Hitachi S800 at 10 kVolt after coating with gold-palladium (Hummer II Coater).
Thermal gravimetric analysis : Samples weighing 2 – 10 mg were heated at 10°C/min from 25°C to 250°C in a stream of Helium in the microbalance of a TGA 2950 Du Pont Instruments thermal gravimetric analyser.
Differential Scanning Calorimetry : Samples weighing 5 – 10 mg were heated from – 80°C to 250 °C in sealed capsules in a stream of Helium in the oven of a DSC 2920 Modulated DSC TA Instruments.
Size Exclusion Chromatography – PMMA was analyzed on styragel columns (10^3 and 10^5 A) connected to a Waters 410 (Waters-Millipore) differential refractometer, using methylene chloride as eluent.
UV-visible spectrometry experiments were conducted on a KONTRON instrument at the maximal absorption wavelength of the dye (λ = 430 nm).

Preparation of microcapsules

Microcaspules were prepared in a Sovirel reactor of 500 mL equipped with an impeller stirrer. 15 mg of dye were dissolved in 1 mL of water and 0.8 g of polymer were dissolved separately in 20 mL of methylene chloride. The two solutions were then mixed under vigorous stirring (Ultra Turrax, 20 000 rpm) for two minutes to form a water-in-oil emulsion. This emulsion was then rapidly poured in 200 mL of a 4% (w/w) PVA solution and stirred for one and half an hour at 600 rpm under 150 mm Hg vacuum. The hardened microparticles were collected by centrifugation at 2000 rpm during 10 min, washed and centrifuged four times with 100 mL of distilled water and dried at room temperature.

Determination of the encapsulation yield and the dye release.

The serum of each centrifugation cycle was then analyzed in UV-visible in order to determine the amount of the dye release during the washing step. The amount of dye leached into the external phase during the microcapsules preparation was obtained by

analysing the external phase by UV-visible spectrometry. The dye loading of the microcapsules was determined spectrophotometrically from a calibration curve of the dye absorption at λ= 430 nm after dissolving the microcapsules (13 mg) in 5 mL methylene chloride and extraction with 5 mL water.

Results and discussion

Size and morpholgy of microcapsules

The PMMA microcapsules present a bimodal size distribution with a mean diameter around 30μm. The major distribution, relatively narrow, is centered around the mean diameter, the minor one around 4 μm (Figure 1).

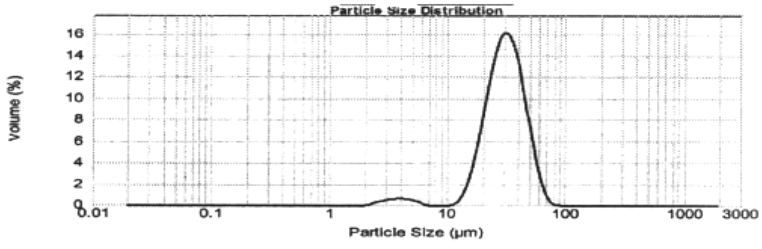


Figure 1 : Size distribution obtained by Laser light diffraction of PMMA microcapsules produced by W-O-W emulsion.

Optical micrographs of microparticles prepared by W/O/W emulsion are very informative on the morpholgy of the microparticles. As the dye is yellow, it allows first to discriminate the microparticles containing the aqueous dye solution and some other which are empty (Figure 2).

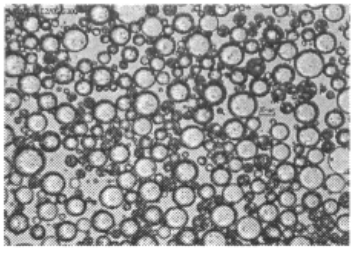


Figure 2 : Optical micrograph of PMMA microcapsules produced by O-W-O emulsion

This observation can be explained by the partial solubility of the dye in the organic phase which induces then the extraction of the dye by water (external phase) during the evaporation step. On another hand, it is interesting to note that most of the microparticles present a single internal cavity, corresponding to the type A of the droplet classification according to Florence *et al.* [5]. Thus the synthesized microparticles can be classified as monocompartmental microcapsules. SEM experiments allow to confirm the perfect spherical geometry of microcapsules (Figure

3a and b) and furthermore the investigation of the internal structure and the estimation of their shell thickness were performed after the cryofracture. Micrographs of fractured microcapsules reveal a single internal cavity, confirming the morphology observed by optical microscopy (Figure 3c). This confirms that the association of water and methylene chloride as double emulsion solvents is perfectly adapted in terms of boiling point, as it was pointing out by Loxley *et al.* [6]. A minimal difference of boiling point between the solvents is necessary to form liquid core-shell particles, that means microcapsules, otherwise the particles are uniform throughout. The internal wall appears slightly smooth like external wall, suggesting a homogeneous diffusion of the organic solvent and optimal interfacial tensions during the synthesis. The shell thickness can be determined and is found to be
equal to 2,5 µ.

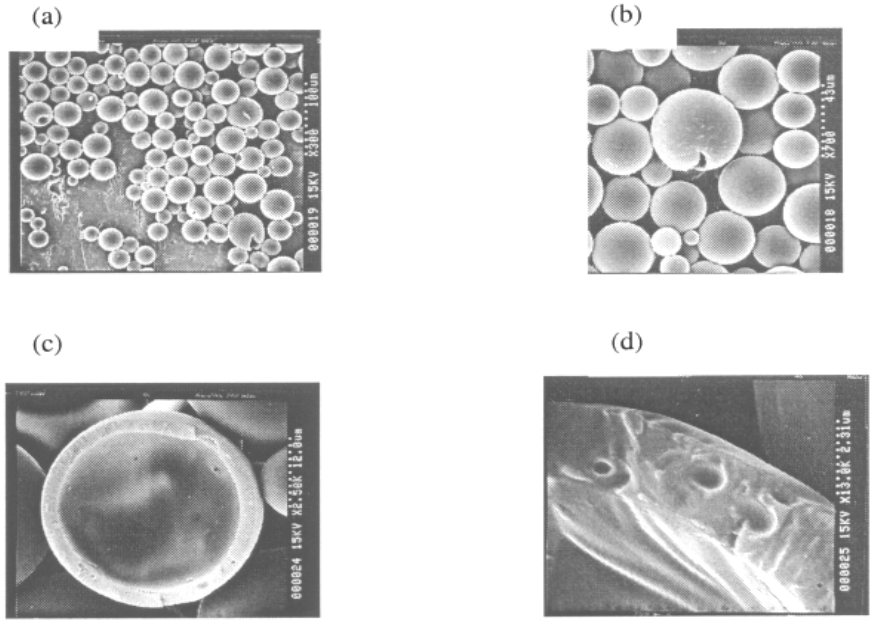


Figure 3 : Electron micrograph of PMMA microcapsules produced by O-W-O emulsion

It is possible to determine the ratio Vs/Vt from the equation (Eq.1) [6] with a mean radius equal to 32 µm (r) and a mean thickness of the microcaspules of 2.33 µm (t).

$$\frac{Vs}{Vt} = \frac{r^3 - (r-t)^3}{r^3} \qquad (1)$$

Vs = volume of the shell

Vt = total volume

t = thickness of the microcapsule

r = radius of the microcapsule

The ratio is found to be equal to 0.203, that means that the volume of the polymer represents 20.3% of the total volume of the microcapsules.
Some small holes of few hundred nanometers can be observed in the thickness of the wall (Figure 3d). Some of them can be attributed to bubbles formed during the solvent loss through the shell. The largest holes could correspond to multicompartmental particles, that means another morphology than the major one.
Optical micrographs of microcapsules collected after 4 washing-centrifugation cycles were recorded (Figure 4). It is very interesting to notice that some of them are broken, showing hollow cavity. This behaviour at washing-centrifugation cycles is interesting from the point of view of dyeing applications for which the desired type of dye release should be obtained by disruption of the microcapsules.

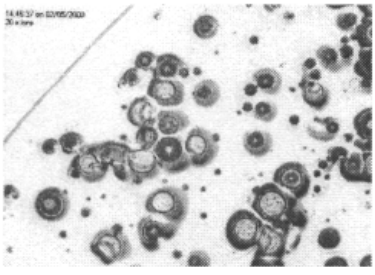
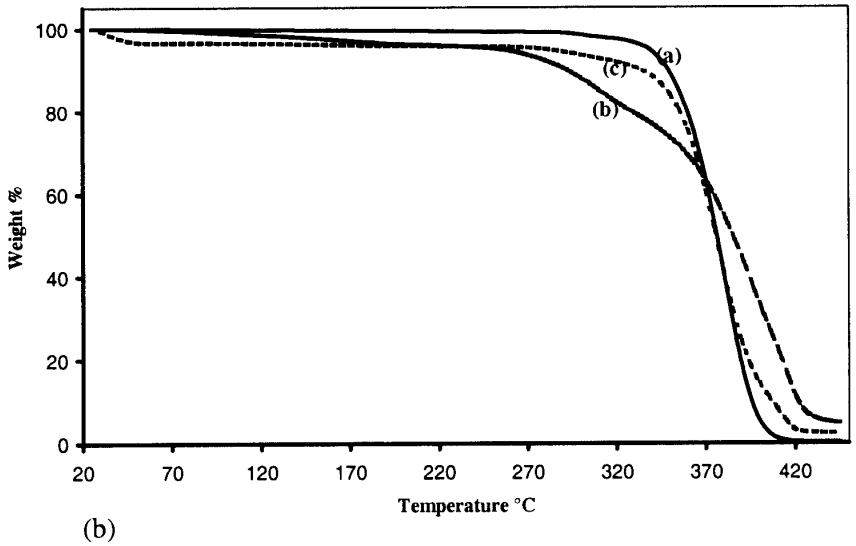


Figure 4 : Optical micrograph of PMMA microcapsules collected after 4 washing-centrifugation cycles

DSC thermogramm of raw PMMA confirms its amorphous character with a glass temperature (Tg) at 105°C. The DSC experiments on PMMA microcapsules after washing-centrifugation cycles confirm that the polymer morphology is not changed during the encapsulation process (Tg = 106.7°C). The presence of an endothermic peak at 64.2°C could correspond to the evaporation of the methylene chloride retained in the microcapsules. The difference between this experimental value and the theoretical one (39.8°C) is due to the entrapment of the methylene chloride. This phenomenon has been already observed [7]. The enthalpy of this peak allows to estimate the amount of solvent retained in the microcapsules around 0.12%. This result was confirmed by elementar analysis of microcapsules which showed the presence of 0. 19% (w/w) of atomic chlorine.
The thermal behaviour of the PMMA microcapsules is very close to the one of PMMA (Figure 5). We can only notice a difference before 100°C with a weight loss of 4.2% probably due to the loss of water and dye. The weak difference of weight loss between PMMA microcapsules collected before (Figure 5a - (b)) and after washing-centrifugation cycles (Figure 5a - (c)) is probably due to a difference of drying at room temperature and thus is not significant. It is more interesting to observe if thermogravimetric analysis allows to estimate the presence of surfactant adsorbed at the capsules surface and the influence of washing on its adsorption. That could be done roughly if we compare the weight loss curves of PVA and microcapsules (Figure 5b – (d) and (b) and (c)) before the degradation temperature of PMMA. In fact, we can notice that the (d) curve profile is more similar to (b) than (c), suggesting that the amount of PVA adsorbed at the surface of the capsules collected after washing-

centrifugation cycles is lower, meaning that washing is efficient on the desorption of the surfactant from the capsules surface.

(a)



(b)

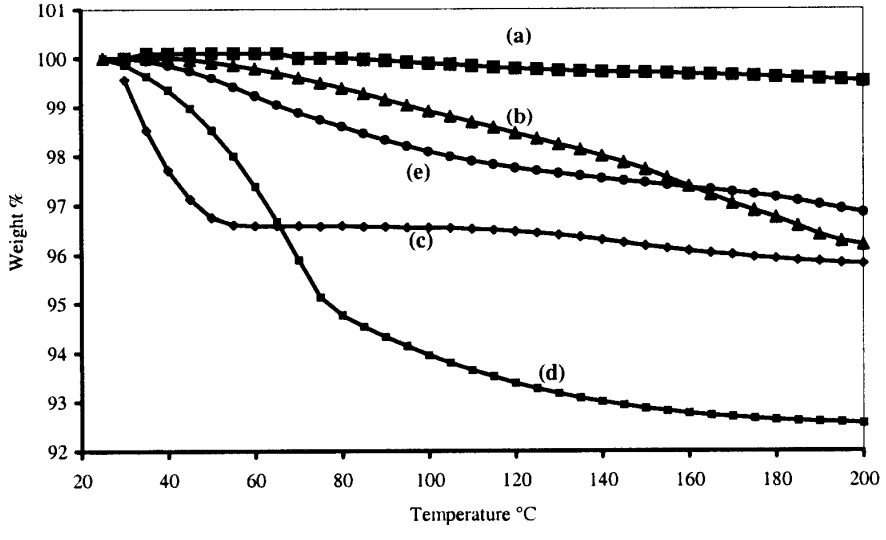


Figure 5a : Thermal behaviour of PMMA : (**a**) and PMMA microcapsules produced by O-W-O emulsion : (**b**) ; collected after 4 washing-centrifugation cycles : (**c**)

———— (**a** — • — (**b** ---------- (**c**)

Figure 5b : enlargement of **Figure 5a** : (**d**) : dye ; (**e**) : PVA

Determination of the encapsulation yield and study of the stocking behaviour of microcapsules

The UV spectrum of the dye collected after dissolution of the polymeric shell and water extraction of the dye is the same as the dye, confirming that the chromophoric power of the dye is not changed by the encapsulation process. The serum collected after the first washing-centrifugation cycle is still coloured whereas no colour is observed for the following cycles, suggesting that nearly no more dye is released from the capsules after the first cycle. The dye released during the first cycle, is certainly entrapped in the capsules wall during the evaporation process. The encapsulation yield (or encapsulation efficiency) is calculated as : actual dye content (m_a)/theoretical dye content (m_t) $\times$100% (m_t = 15 mg). The actual dye content (m_a) is obtained as $m_a = m_t - m_{fr}$ with (m_{fr}) corresponds to the dye amount, determined by UV, present in the serum collected at the end of the encapsulation. It is then found that 47.3% of the entire dye was encapsulated. The actual dye loading is calculated as [1] : actual dye content, mg/amount of microcapsules, mg $\times$100% and found equal to 0.5%, instead of 1.8% corresponding to theoretical dye loading. The release of the dye induced by 4 washing-centrifugation cycles and a storage at room temperature during 30 days is estimated about 7% of the loaded dye.

Conclusion

The encapsulation of a water-soluble dye by double W-O-W emulsion solvent evaporation was performed with an encapsulation rate of 47%. It was shown that the chromophoric power and thus the chemical structure of the dye was not changed nor damaged during the encapsulation process. Interesting morphology from the point of view of dyeing applications, of the capsules was observed : monocompartmental microcapsules were majoritary formed and the internal structure of the wall was particularly dense and smooth. This feature is desired for a stable storage behaviour. Mean diameter is equal to 30 μm. The residual chloride content is found to be very low, which is interesting from the point of view of environmental concerns. The increase of encapsulation rate could be improved by the optimisation of the amount of surfactant, the average number molecular weight of PMMA, and the initial concentrations of dye and polymer.

References

[1] M.Sriwongjanya, R.Bodmeier, (1997) Int. J. Pharm.158 : 29-38
[2] C.Witschi, E.Doelker, J.Control. Rel. 51 : 327-341 (1998)
[3] H.Huatan, J.H.Collett, D. Attwood, (1995) J. Microencapsulation 12(5) : 557-567
[4] P. Giunchedi, H.O.Alpar, U.Conte, (1998) J. Microencapsulation, 15(2) : 185-195
[5] D.Meyers, (1992) "Surfactant Science and Technology", 2nd Ed. VCH Publ :. 244
[6] A.Loxley, B.Vincent, (1998) J. Colloid Interface Sci, 208 : 49-62
[7] T.Ishizaka, M.Koishi, T.Kondo, (1979) J.Membr.Sci, 5 : 283-294