Formation of polymeric microcapsules with encapsulated hexane by extraction-coacervation technique

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Abstract* – *The formation of polymer microcapsules containing encapsulated hexane on the basis of synthesized heterofunctional tetrapolymer as shell-building material using the developed "extraction-coacervation" method of microencapsulation was performed. The effect of process parameters on the final size of microcapsules and efficiency of hexane encapsulation was studied.

Key words – heterofunctional tetrapolymer, microcapsules, microencapsulation.

I. Introduction

At present there are many methods of encapsulating of substances, that differs by the nature of core and shell materials of microcapsules (MC), disperse medium, the method of obtaining encapsulating shell, MC size etc. The main requirements for successful microencapsulation are: a) high yield and encapsulation efficiency; b) the quality and profile of microspheres (MC) have to be reproduced in definite limits, c) MC should not make agglomerates. There are known different methods, such as removal of the solvent by emulsification, polymeric division of phases, spray drying, and grinding techniques that can satisfy mentioned requirements. But they are not always suitable in its general form.

The promising methods of microencapsulation of hydrophobic substances with the use of organic solvents are currently the method of the solvent removal at the emulsification of solution and the method of separation of the organic phase (coacervation in the disperse phase).

However, these methods have several disadvantages. In the first case, the rate of removal of the solvent influences on the basic characteristics of microspheres – fast removal leads to the formation of porous structures on the surface of MC and polymer solidification in shapeless state. The solvent removal by extraction method is faster (typically takes less than 30 minutes) than the process of evaporation and thus formed MC by above method are more porous and shapeless [1]. Solvents used in micro-encapsulation by emulsion solvent removal, especially those containing chlorine (dichloromethane, chloroform) may remain in MC as impurities. Replacement of toxic solvents containing chlorine with less toxic, such as ethyl acetate (EAC), a mixture EAC / acetone or ethyl formiate is a promising direction [2].

The second method allowed to form MC with encapsulated peptide (nafarelin acetate) for parenteral use in industrial scale [3]. This process occurs by reducing the solubility of polymers dissolved in an organic solvent, by temperature changing or by the addition of the third component – coacervating substance that reacts with organic solvent, but not with polymer [4]. During coacervation the phase equilibrium is never reached. Therefore, the composition and process parameters have a significant effect on the kinetics of the process and, ultimately, onto the properties of MC. In addition, the droplets of coacervate are usually sticky and clump together before the end of the phase separation process or before curing. Hence, the system tends to form agglomerates [5].

We have developed a new method – "extraction-coacervation" microencapsulation method [6], which effectively combines the above-mentioned techniques and allowes to avoid these shortcomings. On the one hand, the use of EAC as the solvent that allows to extract it during the dispersion is characteristic for the method of removal of the solvent in the case of solution emulsification. On the other hand, the use of heterofunctional tetrapolymer as coacervate substance and as the main shell-building material is inherent to the method of separation of the organic phase (coacervation in the dispersed phase).

II. Materials and methods

Materials.

The following materials were used in this work: polyvinyl alcohol (PVA) (POVAL JP-18) was used as a stabilizer of o/w dispersions; EAC, hexane (HEX), toluene were analytical-grade and were used as supplied; water was bidistilled; heterofunctional copolymer ABSM-5311 (HFC) has been synthesized via radical copolymerization of acrylonitrile, butyl methacrylate, styrene and maleic anhydride [7] and was used as the shell-building material of the microspheres.

Analysis.

Micrographs of MC were obtained using optical microscope Karl Ceiss and scanning electron microscope JEM-200A. The particle number average (D_N), and weight average size (D_W), polydispersity index (k_p) were determined using statistical treatment of micrographs (the size of 500-700 MC was measured for each sample).

Determination of encapsulated HEX have been carried out by chromatographic analysis of MC dissolved in EAC with the aim of Selmihrom-1 gas-liquid chromatography. Analysis was performed using an internal standard. As the standard for the quantitative determination of HEX in the sample was used toluene.

Concentration of HEX in the sample was determined by averaging the results of at least three chromatograms. Calculations were performed as follows:

$$C_{\text{HEX}} = \frac{m_{\text{st.}} \cdot S_{\text{HEX}} \cdot k}{m_{\text{s.}} \cdot S_{\text{st.}}} \qquad (1)$$

where C_{HEX} – concentration of HEX, which is determined, weight share; $m_{\text{st.}}$ and $m_{\text{s.}}$ – weight of standard and sample, g; $S_{\text{st.}}$ and S_{HEX} – peaks area of the standard and HEX, which is determined; k – coefficient of chromatographic.

Efficiency of microencapsulation of HEX was determined by the formula:

$$E = \frac{C_{HEX}}{C_{HEX\,(teor.)}} \cdot 100\%$$

where E – efficiency microencapsulation of HEX, %; C_{HEX} – HEX concentration determined by chromatographic analysis; $C_{HEX(theor.)}$ – concentration of HEX in prepared organic solution for microencapsulation.

III. Results and Discussion

Designed "extraction-coacervation" microencapsulation method involves the preparation separately: 1. aqueous solution of the stabilizing system comprising EAC and PVA; 2. oleo-phase – solution of shell material MC (copolymer) and substance that have to be encapsulated (in this case HEX) in EAC.

Solutions of aqueous and organic phases are mixed and dispersed to form an "oil in water" dispersion. After the dispersion formation water was added slowly to the system for extraction EAC out of drops of organic phase. As a result of organic solvent extraction and the phase separation of the polymer-organic solvent system, droplets of the organic phase are gradually transformed into spherical MC with solid polymer shell and encapsulated HEX.

1% aqueous solution of PVA saturated with EAC and 12% solution of HFC in EAC with HEX (30% with respect to copolymer) were prepared. Dispersion and formation of microcapsules have been carried out at a temperature of 298 K at various mixing speeds and phase ratios of [polymer solution] to [aqueous phase].

One can see that resulting MC possess strictly spherical shape, and the agglomeration of particles is not observed (Fig. 1).

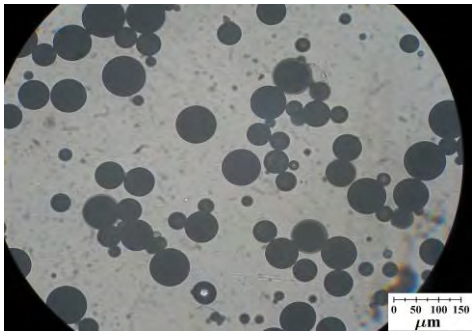

Fig. 1. Micrograph of MC that encapsulated by HEX

Table 1 presents the results of the study of dependence of the synthesized MC colloidal-chemical properties on process parameters. The change of phase ratio influences the size and size distribution of MC.

Thus, weight-average diameter of the MC is from 58 to 100 μm at the phase ratio 1:15, and k_p – 1,34-1,77, while at phase ratio 1:7,5 MC diameter was from 63 to 97 μm and k_p – 1,4-1,6.

Increasing dispersion speed, as expected, causes the decrease of MC number-average and weight-average diameters and polydispersity index. Obviously, this is due to the decrease of particle size at the stage of dispersion formation by increasing the intensity of mixing.

Efficiency of encapsulation decreases with increasing dispersion rate. At this as it was already mentioned, MC size decreases and, consequently, at the same concentrations of reagents the total surface area increases. As a result, the thickness of polymer shell decreases, which leads to more rapid loss of volatile encapsulated substance as compared with MC of larger size.

TABLE 1

CONDITIONS FOR THE FORMATION AND CHARACTERISTICS OF MC

Phase ratio	Dispertion rate (rpm)	D_N (μm)	D_W (μm)	k_p	E, %
1:15	450	56,8	100,7	1,77	-
	600	53,7	77,6	1,44	-
	700	43,3	58,0	1,34	-
1:7,5	450	59,3	97,1	1,64	28,0
	600	45,3	70,9	1,57	15,4
	700	45,1	63,0	1,40	5,4

Conclusion

So, the study of the formation of MC with encapsulated HEX by developed "extraction-coacervation" method of microencapsulation has been carried out. MC with strictly spherical shape, that do not form agglomerates have been obtained. The dependence of colloidal-chemical properties of the synthesized MC on process parameters has been studied. It is shown that increasing the dispersion speed causes decreasing number-average and weight-average size of MC and reducing the polydispersity index. At the same time, the efficiency of encapsulation decreases with increasing the speed dispersion.

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