

Formation of Microcapsulated Aluminium Potassium Sulfate Dodecahydrate by Phase Separation Method

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RESEARCH ARTICLE

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Abstract

The aim of this study was to produce microencapsulated phase change materials (PCMs) by simple coacervation method. For PCM $KAl(SO_4)_2 \cdot 12H_2O$ (Alum) and for coating ethyl cellulose (EtC) and poly(methyl methacrylate) (PMMA) were selected. The spherical core particles of 1.25 – 2 mm size were prepared by pan granulation of Alum-water wet pellets. Shell coating was carried out by two different types of coacervation variants. Process I: EtC polymer coacervation was induced from cyclohexane solution reducing the temperature from 81 °C to 25 °C. The polymer shell on the Alum particles surface was incomplete, because during hardening the polymer coatings was shrunken. Process II: Formation of EtC and PMMA shell coating was induced on Alum core surface by solvent change method. The polymer shell was coacervated from their dichloromethane solution by hexane. The water permeability, i. e. the release of Alum was investigated by conductivity measurements.

Keywords

phase change materials, coacervation, encapsulation, aluminium potassium sulphate dodecahydrate

1 Introduction

Phase change materials are capable of storing and releasing large amounts of energy [1,2,3]. Heat is absorbed or released when the material changes from solid to liquid and vice versa; thus, PCMs are classified as latent heat storage devices. The materials for thermal heat store can be divided in two big groups: they are organics or inorganics [4,5]. Our model substance was aluminium potassium sulphate dodecahydrate which belongs to the inorganic PCM group as a salt hydrate beside other salts or metals. Usage of PCM materials often has physicochemical and mechanical problems as supercooling, leakage, corrosion, and the insufficient long term stability to thermal cycling [6,7]. Microencapsulation is probably the best solution for solving these problems. Microencapsulation is the packaging of micronized materials in the form of polymer capsules. For microencapsulation several methods are known [8,9]. They can be produced by physical and chemical conversions: for example by spray drying, prilling or fluid coating, and for chemical processes as in situ polymerization, surface polycondensation or coacervation. In our experiments the coacervation process was selected for the formation of the microcapsules. The term coacervation was introduced in 1929 by Bungenberg de Jong and Kruyt [10], for a process in which aqueous colloidal solutions separate into two liquid phases, one rich in colloid, i.e., the coacervate, and the other containing little colloid. Coacervation was subdivided into simple and complex coacervation. In simple coacervation, the polymer is salted out by electrolytes or desolvated by the addition of an antisolvent, or by an increase or decrease in temperature. Complex coacervation is essentially driven by the attractive forces of oppositely charged polymers [11,12]. The main features of the process: first a suspension of the core material and the shell polymer solution has to be prepared. Then supersaturation of the polymer has to be driven for phase separation of the colloid. The coating of the core material occurs and after hardening of the polymer shell the encapsulated core material can be obtained.

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2 Experimental

2.1 Materials

The chemicals used for the experiments were the followings: Aluminium potassium sulphate dodecahydrate (Alum, puriss, Molar Chemicals Ltd.), ethyl cellulose (EtC, viscosity 4 and 100 cP, Sigma-Aldrich Ltd.), poly(methyl methacrylate) (PMMA, $M_w = 15\ 000$, Sigma-Aldrich Ltd.), polyisobutylene (PIB, B10, BASF), and as solvents cyclohexane, hexane and dichloromethane (A. R., VWR International Ltd.).

2.2 Preparation of the core material

Alum powder and water was mixed in the weight ratio of 23:3, than extruded to 1.5-2.5 mm big pellets which were spheronized to 1.25 – 2.0 mm granules in pan granulator ($d = 0.5\ m$) than dried at 40 °C.

2.3 Coacervation by temperature reduction

For apparatus a three-necked flask equipped with reflux condenser and a Teflon blade propeller was used. The mixture of EtC and PIB solution was heated in a water bath to 81 °C for dissolution, then the core particles were added to the solution. The solution was cooled down to 45 °C with natural cooling (30 min), then with ice bath to 25 °C. Stirring rate of 450 rpm was used for reflux and 300 rpm for cooling. After 15 minutes stirring at 25 °C the suspension was filtered, then washed two times with 25 ml hexane for hardening. The used concentration range was between 2-12 wt/wt % for EtC (viscosity 100 cP), and 6 and 10 wt/wt % for PIB. The amount of Alum was 1.63 g, and the mass of the solution was always adjusted by cyclohexane to 31.24 g. The form, the distribution and the polymer covering of the particles were seen by taking optical microscope photo images of the filtered particles.

2.4 Coacervation by solvent change

0.25 g Alum core particles were soaked in 10 ml hexane for 15 min. The particles were separated by filtering, then immersed into the polymer solution, then let to stay at 4 °C for 20 minutes. After separation the coating were hardened by soaking the capsules again in hexane. The particles were filtered and dried in air. For polymer solution EtC (9 wt/v %, visc. 4 cp) and PMMA (2, 4, 10 wt/v %) in dichloromethane were used.

2.5 Salt release study

Salt release in water from the encapsulated particles was investigated in a 150 ml double-jacketed beaker which was connected to a thermostat. 100 g distilled water which conductivity was adjusted to a starting value of 50 μS was filled into the baker. 5 pieces of the capsules packed in 100 μm filter bag were immersed into the water. The temperature was kept at 25 °C, the solution was stirred with magnetic bar by 500 rpm. The conductivity was measured with a Radelkis OK097P electrode contacted to a Radelkis OK-114 conductometer, and its voltage output was

connected to a digital multi meter. The measured digital signals were transmitted to a PC.

3 Results and discussion

3.1 Coacervation by temperature reduction

The concentrations of the components are important parameters for the coacervation process: according to Benita and Donbrow [13] coacervated particles can be waited between a concentration range of 6-12 % for PIB, and 2-20 % for EtC. PIB took part in the process as a protective colloid. Experiments were first carried out without granules for investigating only the polymer coacervation process to determine the conditions for the encapsulation process. Coacervated particles with roundish shape and almost uniform size distribution were aimed. The concentrations of the components and the characteristics of the coacervated particles based on the photo images are listed in Table 1.

Table 1 The composition of the experimental solutions and the particles shape got from coacervation by temperature reduction

Sample	c_{EtC} , wt/wt %	c_{PIB} , wt/wt %	m_{Alum} , g	Particle shape*
CT(6)1	2	6	0	F
CT(6)2	4	6	0	E+R
CT(6)3	5	6	0	E+R
CT(6)4	6	6	0	E+R
CT(6)5	8	6	0	E+R
CT(6)6	12	6	0	F
CT(10)1	2	10	0	E
CT(10)2	4	10	0	E
CT(10)3	5	10	0	E+R
CT(10)4	6	10	0	E+R
CT(10)5	8	10	0	E+R
CT(10)6	12	10	0	F
CT(10)7	6	10	1.63	-
CT(10)8	3	10	1.63	-

c_{EtC} : concentration of EtC, c_{PIB} : concentration of PIB,

*particle shape for coacervated polymer particles :

F: formless, E: elongated, R: roundish

In the first series of experiments the concentration of PIB was constant 6 wt/wt % (CT(6)1-6), the particle shape and size distribution changed greatly within a range of 2-12 wt/wt % of EtC. In the second series the PIB concentration was 10 wt/wt % (CT(10)1-6), and the most roundish particle, and the relatively narrow distribution, similarly to the previous experiments, were obtained at EtC concentration of 6 and 8 wt/wt %. Two examples are showed on Fig. 1. For the coating process 10 wt/wt % of PIB and 6 and 8 wt/wt % of EtC were selected.

The granules obtained with 6 wt/wt % ETC and 10 wt/wt % PIB are demonstrated on the Fig. 2a. The granules and the shell polymers are both white coloured. To differentiate them a simple

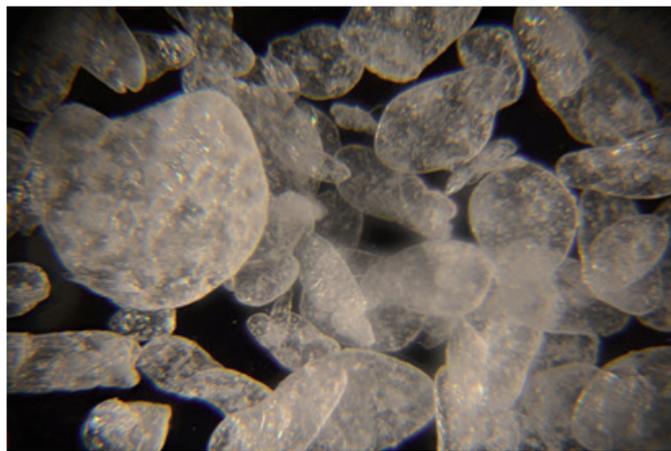
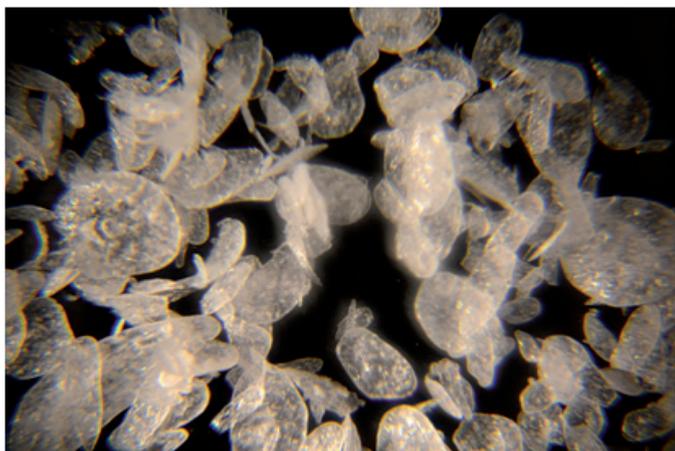


Fig. 1 Coacervated EtC (viscosity 100 cP) particles obtained by temperature reduction, sample CT(6)4: a, sample CT(10)5: b. The EtC coacervate particles produced with 10 wt/wt % PIB (Fig. 1b) are more roundish than the particles obtained with 6 wt/wt % PIB (Fig. 1a)

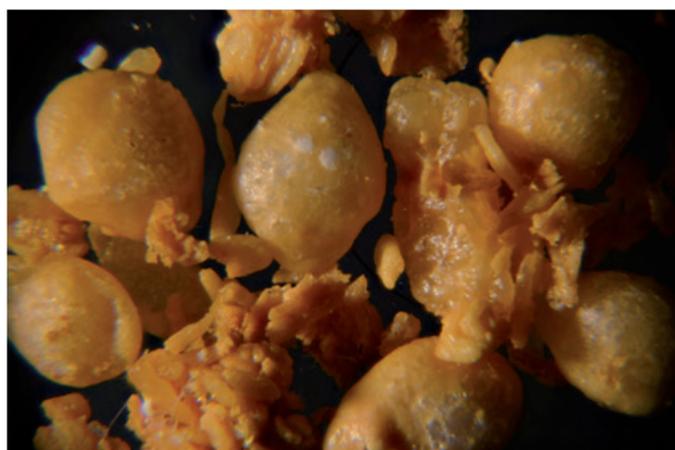


Fig. 2 Coated Alum particles formed by temperature reduction in the presence of 10 wt/wt % PIB. Sample CT(10)7: a, EtC concentration of 6 wt/wt % was too high, some part of the polymer coacervated separately. Sample CT(10)8: b, EtC concentration was 3 wt/wt %, the particles are covered by polymer, but the layer is not complete, the darker/yellowish colour shows the presence of the polymer

chemical reaction was used which is known in thin layer chromatography: the particles were immersed in Iodine vapour: the organic substances are getting a yellowish colour after oxidation, the salt is not affected. Thin coating can be recognized on the granules but some part of the polymer coacervated also separately as formless particles. (On Fig. 2a the smooth/yellow surface indicates the polymer). It was concluded that the concentration of the EtC was too high, that's why in the next experiments we used only concentration of 3 wt/wt % for EtC. The result can be seen on Fig. 2b. The granules are coated with the polymer but the coating is not continuous (the darker/yellow colour and the relatively smooth surface indicates the presence of the polymer). One reason can be the not proper ratio between the core and coating materials. On the other hand the sample was controlled before the hardening step: the particles were fully covered by polymer. It means that during hardening the gel-like coating layer has lost the cyclohexane solvent causing the reduction of its volume and thus shrinking. That's why we decided to change the process for coacervation made by solvent change.

3.2 Coacervation by solvent change

The driving force of the polymer coacervation by solvent change method is the decrease of solubility, which was generated by adding an antisolvent (i.e. a bad solvent) to the colloid solution. In our experiments dichloromethane and hexane were selected as solvent and antisolvent [14], respectively. For the encapsulation the so cold inverse method was used, i. e. the core particles were contacted first with the antisolvent (hexane). The core particles were produced by a granulation method, thus they were porous with rough surface, and they could take up the antisolvent. It means that the pores and the surface of the granules were filled or covered by hexane. In the next step the hexane on the surface of particles contacted with the polymer (EtC or PMMA) solution. Due to decrease in its solubility, polymer coacervate layer was formed on the surface of the granules. For hardening the soft coating, the capsules were immersed again in hexane, thus the good solvent dichloromethane were eliminated from the coating. The prepared coated samples and the used polymer concentration are summarized in Table 2.

Table 2 The concentration of the polymer solutions used for the coacervation made by solvent change

Sample	c_{EtC} , wt/v %	c_{PMMA} , wt/v %
CS1	-	2
CS2	-	4
CS3	-	10
CS4	9	-

c_{EtC} : concentration of EtC,
 c_{PMMA} : concentration of PMMA

The obtained encapsulated Alum particles can be seen in Fig. 3. As is seen on the images the particles coated with the inverse method show complete coating on the surfaces. But, especially, at samples CS3 fibres of polymer were also seen around or close to the capsules. The viscosity of the 10 wt/v % PMMA solution is high and the separation of the particles from the polymer solution was difficult.

3.3 Salt release study

To investigate the water permeability of the encapsulated phase change materials is very important because of the different applications. Especially, when the PCM is a salt or salt hydrate. When the coating is not water and/or moisture resistant

because of the osmotic pressure and the diffusion material transport takes place via the polymer membrane: water moves inside the capsules and oppositely the salt releases from the capsule core. The salt release was followed as a function of time by measuring the changes in conductivity, which indicates the change of the salt concentration in the water phase. It means if conductivity increases the coating is oozing, water moves inside the particles and the opposite direction salt releases to the water phases. The basis conductivity of the distilled water was adjusted to 50 μS because of the low sensitivity under this value. For comparison of the coatings permeability the reached conductivities at 200 minutes release time were used. For the calculation data of 5 parallel experiments was taking into account. Because of the particles inhomogeneity in their mass (particle size of the core granules were between 1.25-2.0 mm) the reached maximum and minimum conductivity values of the 5 parallel measurements at 200 minute time were compared instead of using the mean values of 5 measurements. Standard deviation (SD) of the data was also calculated as a characteristic value of the coating inhomogeneity. The data are demonstrated on Fig. 4. In case of PMMA capsules (CS1-3) the salt release depended on the concentration of the polymer solution. Using higher PMMA concentration the coating leakage was



Fig. 3 Coated Alum particles obtained by solvent change method: sample CS1: a (covered by 2 wt/v % PMMA, thin layer indicated by the light yellow colour), sample CS2: b (covered by 4 wt/v % PMMA, complete coating indicated by the dark yellow colour), sample CS3: c (covered by 10 wt/v % PMMA, complete coating but fibers of polymer are seen outside and around the capsules) and sample CS4: d (covered by 9 wt/v % EtC, complete coating can be seen)

moderate, taking into account that the starting conductivity was adjusted to 50 μS . The coating inhomogeneity also decreased, i. e. the SD values decreased by increasing polymer concentration. The most stable and homogeneous coating belonged to the capsules prepared by EtC polymer (CS4).

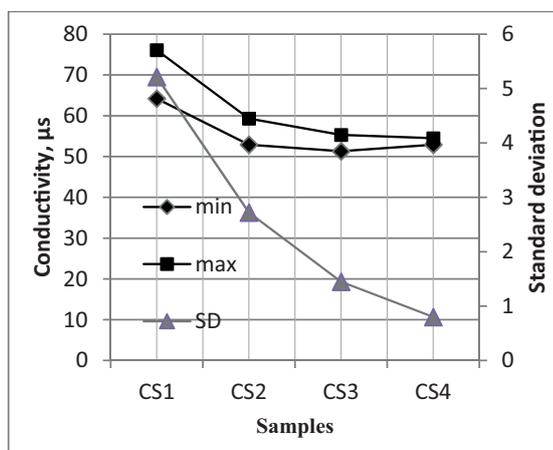


Fig. 4 Reached maximum (max) and minimum (min) values of conductivities within 5 parallel measurements investigated in water after 200 minutes release time of polymer coated Alum particles. Standard deviation (SD) of the conductivity data of 5 parallel measurements are depicted on the second vertical axis. The measured maximum and minimum values of conductivities and the SD data show the same tendency, i. e. the coating homogeneity increases with increasing polymer concentration of PMMA (samples CS1 – CS3). The lowest SD value belongs to the sample CS4 (coated with EtC) indicating that the individual particles have relatively uniform coating.

4 Conclusions

Microencapsulated aluminium potassium sulphate dodecahydrate particles were produced by two different simple coacervation methods. The coacervation of the polymers was induced by temperature reduction or by solvent change.

Using temperature reduction method the coating of the microcapsules was incomplete. During hardening the polymer was shrunken on the granules surface.

Using solvent change method whole covering of the granules was reached both in case of coating polymer EtC and PMMA. To investigate the salt release in water from the coating conductivity measurement was appropriate. The permeability of the coatings was different, depending on the polymer type and concentration. Moderate leakage and homogeneous coating was obtained when 9 wt/v % EtC (visc. 4) was used as coating solution.

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