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Fully bio-originated latent heat storing calcium alginate microcapsules with high coconut oil loading

Bence Németh[a,b], Ágnes S. Németh[a], Aurél Ujhidy[a], Judit Tóth[a,b], László Trif[b], János Gyenis[a], Tivadar Feczkó[a,b,*]

[a] Research Institute of Biomolecular and Chemical Engineering, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary
[b] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., H-1117 Budapest, Hungary

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ABSTRACT

Latent heat storing calcium alginate microcapsules were manufactured by a repeated interfacial coacervation/crosslinking method. By using a high-viscosity sodium alginate for the capsule formation, the paraffin phase change material (PCM) content was substantially enhanced related to the recently developed procedure. The maximization of PCM loading was achieved using experimental design for paraffin containing microcapsules. The microcomposites were optimized for 81.5% PCM content with uniform size of 2.20 ± 0.14 mm. In some applications e.g. packaging, the biodegradable character of the materials is especially beneficial, hence for the manufacture of entirely eco-friendly heat storing microcomposites coconut oil PCM was microencapsulated by the same procedure. The process originally developed and optimized for paraffin was scaled-up by two orders of magnitude, accordingly, the outstanding PCM content was reproduced also with coconut oil (average value 81.1%). The high PCM content was reflected also in the heat storing capacity measured by differential scanning calorimetry. The easily upscalable, spherical and core/shell structured, entirely biocompatible microcapsules with thermally stable calcium alginate coating could be developed for industrial application.

1. Introduction

Nowadays, energy storage systems are essential for reducing the fossil fuel consumption, and hence contributing to environmentally friendly energy use. Latent heat thermal energy storage is one of the most efficient ways of storing thermal energy. The latent heat energy storage in phase change materials provides much higher energy storage density than that achieved by sensible heat (Zhang et al., 2012). To improve energy utilization efficiency, the PCMs have been extensively applied in textiles, buildings, therapies, packing and spacecraft (Hu et al., 2013). Most important requirements towards PCMs are the cost-effectiveness, no corrosion to the container and easy preparation with desirable dimensions. Microencapsulated PCM can considerably enlarge the heat transfer area, reduce the PCMs reactivity with the outer environment, avoid subcooling or incongruent melting, and control the changes in the volume during melting and freezing (Zhang et al., 2012). The so-called slurry phase materials that are developed to improve the heat capacity of solar thermal collectors include phase change materials encapsulated by suspended particles, which remain in the liquid state of the fluid at a macroscopic scale during the phase change process (Serale et al., 2016). Form-stable PCMs can also provide some of the above mentioned benefits of PCM microparticles, however, in some applications to evade PCM leaking they should be also supplied by a protecting layer on the surface (Feczko et al., 2016). Shell material plays an important role in the heat transfer feature and mechanical strength of all the PCM entrapping microcapsules. The shell material should have sufficient structural and thermal strength to withstand numerous phase change cycles of PCM, and it must not react with the PCM (Salunkhe and Shembekar, 2012). It can also improve the compatibility of PCMs that cannot be directly immersed in certain applications, such as food storage and building cooling/heating. Although polymeric shell prevents the leakage of liquid PCMs, due to its low thermal conductivity it reduces substantially the rate of heat storage (Sarı and Karaipekli, 2007). Thus, the most important task is to decrease the mass of encapsulating material parallel with avoiding the loss of shell mechanical strength.

To our knowledge, PCM microcapsules that originate completely from biological sources have not been synthesized so far. There are

* Corresponding author at: Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., H-1117 Budapest, Hungary.
E-mail addresses: nemeth.bence@mukki.richem.hu (B. Németh), szemes@mukki.richem.hu (Á.S. Németh), ujhidy@mukki.richem.hu (A. Ujhidy), toth@mukki.richem.hu (J. Tóth), trif.laszlo@ttk.mta.hu (L. Trif), gyenis@mukki.richem.hu (J. Gyenis), feczko@mukki.richem.hu (T. Feczkó).

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some studies dealing with microencapsulation of naturally formed PCMs. Konuklu et al. (2014a, 2014b) microencapsulated caprylic acid (octanoic acid) and decanoic acid with urea-formaldehyde-, melamine-formaldehyde- and urea-melamine-formaldehyde resins by the coacervation method, and caprylic acid using polystyrene shell material by the emulsion polymerization method (Konuklu and Paksoy, 2017). Palmitic acid was entrapped by some groups using organic (Doguscu et al., 2017) or inorganic (Cao et al., 2014) shells. These fatty acids are environmentally friendly, since they can be obtained from vegetable and animal oils. Decanoic acid can be derived from coconut oil, which is abundant in tropical countries. Coconut oil has suitable melting temperature, high latent heat capacity, little or no super cooling during the phase transition, non-toxicity and non-corrosivity against metal containers. In the other approach, the carrier material is of biological origin, for example chitosan, a low-price and eco-friendly polymer, was used to synthesize graphene-based carbon aerogel that was filled with 1-hexadecanol in order to prepare a form-stable PCM for thermal energy storage (Fang et al., 2017). Silk fibroin was utilized for embedment of paraffin PCM (Luo et al., 2016). n-octadecane microcapsules with gelatin-gum arabic shell were prepared by complex coacervation and crosslinking with glutaraldehyde (Li et al., 2012). As a carrier calcium alginate is favourable, e.g. it was used to entrap paraffin wax Rubitherm RT27 by a simple co-extrusion minifluidic device (Liang et al., 2014). n-octadecane shape stabilized with calcium alginate matrix was embedded in acrylic-based copolymer capsules (Li et al., 2013). Calcium alginate was also used to incorporate shape-stabilized phase change materials (Wang et al., 2011). Thus, in former studies exclusively either the PCM or the shell material originated from biological sources.

Bio-originated PCMs such as soybean oils, coconut oils, palm oils, and beef tallow (Jeong et al., 2013) have high latent heat of fusion, good thermal stability, and no toxicity, similarly to paraffin, and are also suitable for microencapsulation. However, most paraffins are flammable, while bio-originated PCMs have considerably higher ignition resistance. Since bio-based PCMs are fully hydrogenated, they are not sensitive to oxidation. Their melting point can be adjusted in a wide temperature range, from −23 °C up to 78 °C, hence they can be suited to various application fields in various climatic condition. They possess low vapor pressure, self-nucleating behavior, safety, and commercial availability at low cost (Kang et al., 2015). The eco-friendly shell material promotes the environmental sustainability as well, because it can be degraded into non-toxic materials, hence it becomes a competitive alternative to conventional petroleum-based polymers in various applications.

Recently, we have developed a method for preparing alginate microcapsules containing paraffin by the method of repeated interfacial coacervation/crosslinking (Nemeth et al., 2015). In this work, the PCM loading was enormously improved by using a high-viscosity sodium alginate for forming the capsules. Moreover, the paraffin was substituted by coconut oil in order to prepare fully eco-friendly PCM containing microcomposites. Beside the characterization of size, structure and chemical composition, thermal analysis of the microcapsules was thoroughly performed too.

2. Material and methods

2.1. Materials

Sodium alginate (viscosity at 25 °C, concentration 2 w/v%: 950 mPa s) was bought from Cargill (US). $CaCl_2{\cdot}2H_2O$ was purchased from Sigma-Aldrich, paraffin with melting temperature interval 55–57 °C was kindly provided by the MOL Plc, Hungary. Coconut oil was obtained from Soya Group Ltd., Hungary. Petroleum ether (boiling temperature 60–62 °C) was purchased from Lach-Ner s.r.o., Nercetovice, Czech Republic. All chemicals were of analytical grade and were used as purchased. For preparation of all aqueous solutions distilled water was used.

Table 1
Paraffin content and capsule size as a function of experimental conditions (sodium alginate- and calcium chloride concentrations, contact time) using 3 factors Box-Behnken design with 1 block, 15 runs and 3 repetitions in centrum point (C).

Run #	Sodium alginate concentration (%)	Calcium chloride concentration (%)	Contact time (min)	Paraffin weight ratio (%)	Mean capsule size (mm)
1	3.5	4.0	13.0	52.44	2.29 ± 0.13
2	3.5	4.0	1.0	71.76	2.19 ± 0.13
3	2.0	1.0	1.0	78.22	2.24 ± 0.19
4	3.5	1.0	7.0	72.03	2.29 ± 0.21
5	0.5	4.0	1.0	81.53	2.17 ± 0.17
6	0.5	1.0	7.0	75.97	2.28 ± 0.17
7C	2.0	4.0	7.0	62.28	2.27 ± 0.12
8	2.0	1.0	13.0	69.18	2.22 ± 0.17
9	2.0	7.0	1.0	69.10	2.27 ± 0.12
10C	2.0	4.0	7.0	59.21	2.15 ± 0.10
11C	2.0	4.0	7.0	58.84	2.12 ± 0.14
12	0.5	4.0	13.0	64.10	2.01 ± 0.10
13	2.0	7.0	13.0	52.71	2.21 ± 0.13
14	0.5	7.0	7.0	67.16	2.19 ± 0.16
15	3.5	7.0	7.0	40.69	2.12 ± 0.13

2.2. Methods

2.2.1. Capsule preparation

The microcomposite preparation was optimized using paraffin PCM, and the detailed process was described in our recent study (Nemeth et al., 2015). Compared to this cited work it was found that the application of a sodium alginate with higher viscosity (950 mPa s related to the former 14 mPa s, at 25 °C, concentration 2%) results in substantially higher PCM loading in the capsules. Due to the fact, that the process parameters also changed significantly, hence they need to be presented here (Table 1). Briefly, an oil-in-water emulsion was formed by mixing 8.1 g solid paraffin with 45 g sodium alginate solution (concentration: 2.0%) in distilled water at 65 °C. After paraffin melting, it was emulsified into the aqueous phase by sonication for 3 × 30 s with Vibra cell VCX130 (Sonics and Materials Inc., Newtown, USA) sonicator using 40% of its 130 W maximal power. The formulated oil-in-water emulsion was dropped into a gently stirred 500 g solution containing 4% $CaCl_2$. After the gelation time (30 min), the particles were transferred into another $CaCl_2$ solution of various concentrations (minimum value: 1.0%, medium value: 4.0%, maximum value: 7.0%) to provide excess Ca^{2+} ions near the surface region of core particles. The core particles were filtered from the gelling solution and added into the gently stirred sodium alginate solution (minimum value: 0.5%, medium value: 2.0%, maximum value: 3.5%) for the reaction time (minimum value: 1 min, medium value: 7 min, maximum value: 13 min). Finally, the raw capsules were removed and rinsed three times with distilled water. To solidify the microparticles, the prepared capsules were heated, while they were rolled on a hot stainless steel plate at 125 °C for 15 min.

3-level 3 factors Box-Behnken experimental design was carried out by the STATISTICA® software (Statsoft Inc. USA). 3 process variables, that is, sodium alginate- and $CaCl_2$ concentrations and contact time were found to affect considerably the paraffin content of the PCM containing microcapsules. The experimental program (Table 1) consisted of 15 runs, including 3 repetitions in the center (indicated with capital C in the Table). The concentrations of the first sodium alginate solution and the first calcium chloride concentrations were kept constant.

For the coconut oil microencapsulation the process was scaled-up. To 2.75 kg 2% sodium alginate solution at 50 °C 1.0 kg melted coconut oil was added, then it was homogenized by an industrial homogenizer (IKA Ultraturrax-40) for 10 min to produce a stable emulsion. The