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BIODEGRADABLE POLY(L-LACTIC ACID) MICROCAPSULE CONTAINING HEAT STORAGE MATERIAL: INFLUENCE OF POLYMER MOLECULAR WEIGHT ON ENCAPSULATION EFFICIENCY

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ABSTRACT

Microcapsule containing heat storage or phase change materials is useful in various applications. It provides a larger heat transfer area and controls the volume change of phase change materials during phase transition. Most polymer shells used in microcapsule are petrochemical-based polymers which is a growing concern about their impact on the environment. Therefore, in this work, biodegradable polymer as a poly(l)-lactic acid (PLLA) was implemented as the polymer shell to encapsulated octadecane (OD), a kind of phase change materials, by a simple emulsion evaporation method. Influence of PLLA molecular weight on the encapsulation efficiency and colloidal stability of microcapsule was studied. The spherical microcapsules with a size range ca. 5-50 μm were obtained in all molecular weights of PLLA. However, at higher molecular weights (54,000, 77,000 and 145,000 g/mol), some OD escaped from the droplets during solvent evaporation due to higher internal viscosity therein where polymer chains hardly diffused to precipitate on the droplet interface. In contrast, using the lowest molecular weight (24,000 g/mol), approximately 86 wt% microcapsule yields with about 100 %encapsulation and high colloidal stability were obtained which were much higher than those (44, 36 and 11% for 54,000, 77,000 and 146,000 g/mol, respectively) of higher molecular weights. In addition, latent heats of the encapsulated OD (200 J/g-OD) were closed to those (230 J/g-OD) of bulk OD. Based on high encapsulation efficiency, this biodegradable microcapsule would enhance environmental sustainability for thermal energy storage applications.

Keywords: Poly(l-lactic acid); Heat storage materials; Microcapsule; Simple emulsion evaporation method

INTRODUCTION

Phase change materials are used in many industrial applications such as solar heat storage, air conditioning of building and thermal adaptable fibers[1]. Paraffin wax is one of the most attractive phase change materials. It melts and crystallizes which can absorb and release energy, respectively, at a wide range of temperature. Because of their moderate thermal energy storage and low thermal conductivity, paraffin is then encapsulated within the polymer shell to increase surface area for providing a larger heat transfer before the practical application. Numerous polymer shells are used to fabricate paraffin microcapsules such as polystyrene[2, 3], poly(styrene-*co*-methyl methacrylate) [4], polydivinylbenzene[5, 6], poly(styrene-*co*-divinylbenzene) [7], poly(methyl methacrylate) [8] and poly(methyl methacrylate-*co*-methyl acrylate-*co*-methacrylic acid) [9]. However, most of them are petrochemical-based polymers which are a growing concern about their impact on the environment [10, 11]. Biodegradable polymer as PLLA is then the good candidate to be used as the polymer shell of paraffin microcapsules**.** Because of its non-toxicity and environmental friendly, it is applied for a various applications such as biomedical, pharmaceutical, food packaging and agricultural industries [12, 13]**.** To the best of our knowledge, there are a few researches using PLLA as phase change materials microcapsule shell. From our previous work [14], we have successfully prepared microcapsule containing urea using PLLA as a polymer shell by a simple emulsion evaporation method. Because urea can soluble in water, $water_1$ (containing urea) in oil (containing polymer) in $water_2$ system was prepared in order to increase the encapsulation efficiency. In addition, PLLA was successfully used to encapsulate more hydrophobic material as vitamin E [15] using oil in water

emulsion system with a simple emulsion evaporation method. Therefore, it would be possible to prepare paraffin microcapsule using PLLA as a polymer shell where paraffin and PLLA are dissolved in good solvent as an oil phase before being dispersed in the continuous (water) phase having surfactant. Paraffin microcapsule would be obtained based on an internal phase separation mechanism. Because PLLA is more hydrophilic than that of paraffin, it should diffuse from the polymer solution droplet to the droplet interface during the solvent evaporation to form polymer shell.

In this research, the preparation of paraffin microcapsule with PLLA and octadecane (OD) as a polymer shell and phase change material core, respectively, by oil in water emulsion with a simple emulsion evaporation method will be studied. In addition, influences of PLLA molecular weight and PLLA and OD ratio on the encapsulation efficiency and colloidal stability of microcapsule will be investigated.

EXPERIMENTAL

Materials

PLLA molecular weights of 77,000 and 145,000 g/mol were used as received from B. C. Polymers Marketing Co., Ltd. OD (Sigma-aldrich, USA; purity, 99%), poly(vinyl alcohol) (Aldrich, Wisconsin, USA; degree of saponification, 87-90%) and chloroform (RCI Labscan, Bangkok, Thailand; purity, 99.8%) were used as received. Ethylene glycol (Loba chemie, India; purity, 99.5%) was also used as received.

Preparation of low molecular weight PLLA

Glycolysis of commercial PLLA with molecular weight of 145,000 g/mol employing EG was carried out to break PLLA chains[16]. PLLA and ethylene glycol at 1:1 weight ratio were previously mixed and dissolved in chloroform (finally, 20 wt% of PLLA) before transfer to a round bottom flask and sealed with silicone rubber septum. The solution was purged with five vacuum/N_2 cycles finally in a N_2 atmosphere. The reaction was started at 175 °C with a stirring rate of 200 rpm and kept at 30 and 60 min. After the completion of reaction, PLLA short chains were purified by precipitation in methanol before dried overnight in a vacuum oven.

Microcapsule preparation

PLLA microcapsules encapsulated OD using various molecular weight s (24,000, 54,000, 77,000 and 145,000 g/mol) were prepared in oil in water system. Firstly, 2.50 g of PLLA was dissolved in 20 g of chloroform containing 2.50 g of OD as an oil phase. It was added to 45 ml poly(vinyl alcohol) aqueous solution (1% wt) and then homogenized at 5,000 rpm for 5 min to prepare polymer droplets in oil in water emulsion as shown in Fig 1. Thereafter, the obtained polymer droplets emulsion was stirred overnight to evaporate chloroform resulting in the formation of polymer microcapsules.

Table 1 Reagent amounts for the preparation of PLLA/OD microcapsules by a simple emulsion evaporation method

Phase	Ingredients			
Oil	PLLA (g)	2.00[a]	2.50[b]	3.00[a]
	OD (g)	3.00	2.50	2.00
	$CHCl_3$ (g)	20.00	20.00	20.00
Aqueous	PVA solution (1 wt%) (g)	45.00	45.00	45.00

[a] Molecular weight (g/mol): 24,000
[b] Molecular weight (g/mol): 24,000 54,000 77,000 and 145,000

Characterization of PLLA microcapsules

The microcapsules encapsulated OD were observed with an optical microscope (SK-100EB&SK-100ET, Seek, Seek Inter Co. Ltd. , Thailand) and scanning electron microscope (JSM-6510, JEOL, JEOL Ltd. , Japan) to study the morphology of the particle surface and shape. For scanning electron microscope observation, a few of dried microcapsules were placed on a nickel scanning electron microscope stub and dried before Au-coated. Weight- and number-average molecular weights (M_w and M_n, respectively) and M_w/M_n of PLLA were measured by gel permeation chromatography (Waters 2414, Waters, USA) with two poly(S/divinylbenzene) gel columns (Phenogel 5 x 10^3 and 5 x 10^5 Å (pores), 7.8 mm (i.d) x 30 cm (length), Phenomenex, USA) connected in series and using tetrahydrofuran as eluent. The flow rate of eluent was maintained at 1.0 mL/min with column temperature of 40 °C and elution was monitored with refractive index detector (RI 2414/Waters). The columns were calibrated with six standard PS samples (2.5 x 10^3- 6.0 x 10^5, M_w/M_n = 1.05-1.15). For the measurement of thermal properties, the microcapsules were washed with 2-propanol before dried in vacuum oven. The OD content in the dried washed microcapsules was direction determined by thermogravimetric analyzer (TGA, TGA 4000,

Perkin-Elmer, USA) at a heating rate of 5 °C/ min. The latent heats (ΔH_m and ΔH_c) (J/g-capsule) and the melting (T_m) and crystallization (T_c) temperatures of the encapsulated OD were measured with a differential scanning calorimeter (DSC, DSC 4000, Perkin-Elmer, USA) under a N_2 flow in a scanning temperature range of -20-40 °C and at a heating/ cooling rate of 5 °C/ min and shown as average values of three measurements.

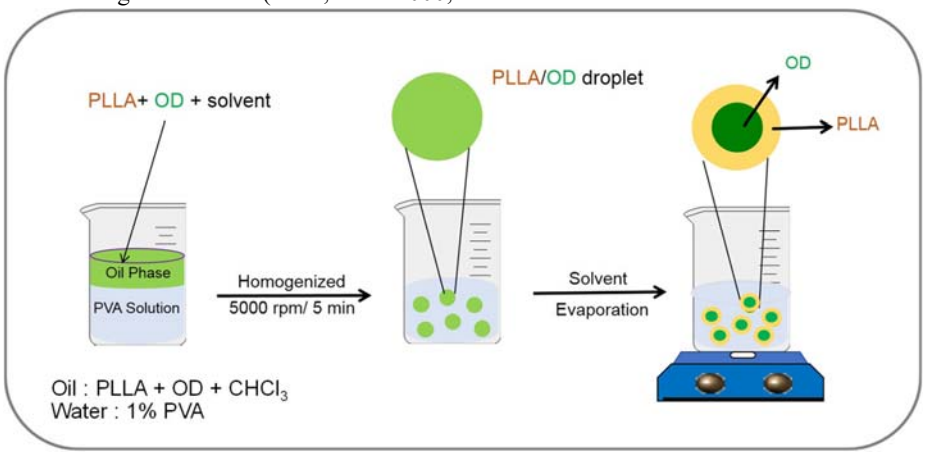

Fig. 1 Schematic diagram for the preparation of PLLA microcapsules containing OD prepared by a simple emulsion evaporation method

ΔH_m* and ΔH_c* (J/ g-OD) were, respectively, obtained using the following equation (1) from the ΔH_m and ΔH_c (J/ g-capsule) and the OD content in each washed microcapsule (% loading) obtained from the thermogravimetric analysis, which did not contain unencapsulated OD.

$$A = [B / C] \times 100 \quad \ldots\ldots(1)$$

Where

A = ΔH_m* and ΔH_c* of the encapsulated OD in unit of joules per 1 g of encapsulated OD (J/g-OD)

B = ΔH_m and ΔH_c of the encapsulated OD in unit of joules per 1 g of microcapsule (J/ g-capsule) measured with differential scanning calorimeter

C = % loading (experiment) of OD in the washed microcapsules measured with thermogravimetric analysis

The theoretical % loading of OD in the washed microcapsules was calculated by equation (2)

$$\%\ \text{Loading (theory)} = [W_{wax}/(W_{wax} + W_{PLLA})] \times 100 \quad \ldots\ldots(2)$$

Where W_{wax} and W_{PLLA} are weights of OD and PLLA, respectively, in the preparation recipes shown in Table 1.

Encapsulation efficiency (%) of OD was calculated using the equation (3).

$$\text{Encapsulation efficiency (\%)} = [\%\text{loading (experiment)}/\%\ \text{loading (theory)}] \times 100 \quad \ldots\ldots(3)$$

RESULTS AND DISCUSSION

One of the main driving forces for microcapsule preparation based on internal phase separation mechanism is viscosity inside polymer solution droplet. To the best of our knowledge, when the polymer chains smoothly diffuse to the droplet-water interface, the microcapsule with high encapsulation would be obtained. The amount of polymer chain reached to the droplet-water interface decrease with internal viscosity. In this work, various molecular weights of PLLA were used to encapsulate OD in which using higher molecular weights was expected to obtain high capsule shell strength. However, this parameter was optimized based on both encapsulation efficiency and shell strength. The low molecular weights PLLA were obtained by glycolysis of high molecular weight PLLA (145,000 g/mol) with various times at 30 and 60 min. It was found that the molecular weight of PLLA significantly decreased to 54,000 and 24,000 g/ mol for the reaction times of 30 and 60 min, respectively, as shown in Fig. 1. It is due to the depolymerization of PLLA by ethylene glycol to form shorter chain of hydroxyl (OH) -terminated PLLA where PLLA molecular weight decreased with the reaction time [16, 17].

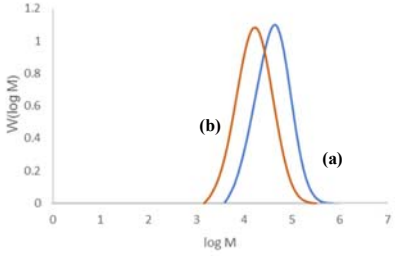

Fig. 2 Molecular weight distribution of PLLA (Mw 145,000) after glycolysis at various times (min): (a) 30 and (b) 60

The PLLA/ OD solution droplets dispersed in poly(vinyl alcohol) aqueous solution (1 wt%) were obtained with the homogenization. As seen in Fig. 3, the PLLA chains with higher molecular weights seemed incomplete miscible in $CHCl_3$ containing OD especially for 77,000 (Fig. 3c) and 145,000 g/mol (Fig. 3d) where the PLLA/ OD solution droplets contained dark domains. After $CHCl_3$ removal, PLLA chains homogeneously distributed throughout the microcapsule due to high internal viscosity. This then resulted in low microcapsule yield where numerous microparticle without OD were obtained. In contrast, for lower molecular weights of PLLA, both PLLA/OD solution droplets, (Fig. 3a and b) and microcapsule (Fig. 3a' and b') were clearly transparent. Based on the theoretical total density of microcapsule (~1; densities of OD and PLLA are 0.78 and 1.22 g/mol, respectively) at the ratio of PLLA:OD of 1: 1, the microcapsule should be floated on the top layer of the suspension. The suspension photos of PLLA/OD microcapsules with various PLLA molecular weights were shown in Fig. 4. For the three higher molecular weights (Fig. 4b-d), three parts i.e. top, middle and bottom layers of the suspensions were clearly observed where small amounts of microcapsules floating on the top layer were obtained. The PLLA dispersed and precipitated in the medium and the bottom would be the broken particle and the PLLA particle without OD, respectively. In contrast, most of PLLA/OD microcapsules floated on the top layer for the lowest molecular weight (24,000 g/ mol) of PLLA (Fig. 4a) . The amounts of PLLA/ OD microcapsules at the top layer separating from each suspension were measured by gravimetry. It was found that the amounts of PLLA/OD microcapsules prepared by various PLLA molecular weights were 11, 36, 44 and 86 wt% (based on the original of PLLA and OD) for 145,000, 77,000, 54,000 and 24,000 g/ mol, respectively. This indicates that the obtained microcapsules increased with the decrease of PLLA molecular weight. From these results, PLLA molecular weight of 24,000 g/ mol was selected to be used as the polymer shell for further study. The PLLA: OD ratio will be investigated in order to obtain large amount of PLLA/ OD microcapsules.

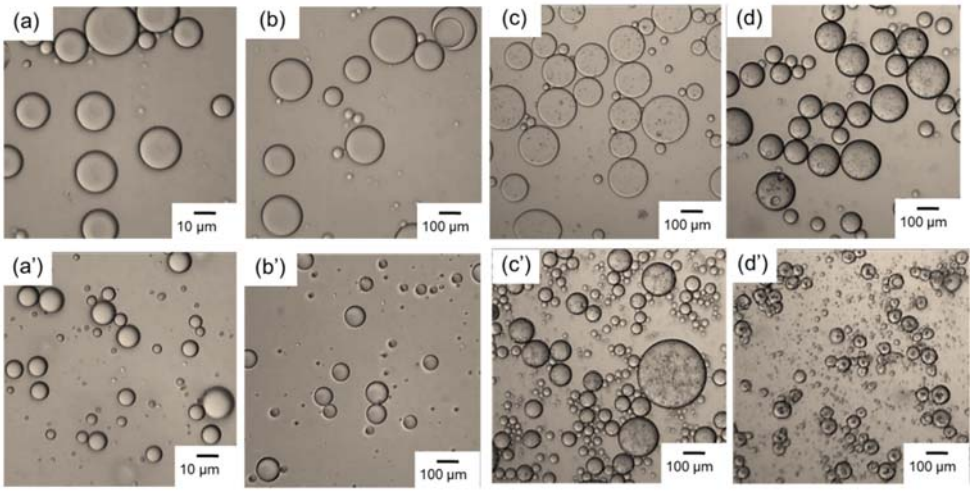

Fig. 3 Optical micrographs of PLLA/OD droplets (a-d) and microcapsules (a'-d') prepared by a simple emulsion evaporation method using different PLLA molecular weights (g/mol): (a and a') 24,000; (b and b') 54,000); (c and c') 77,000 and (d and d') 145,000

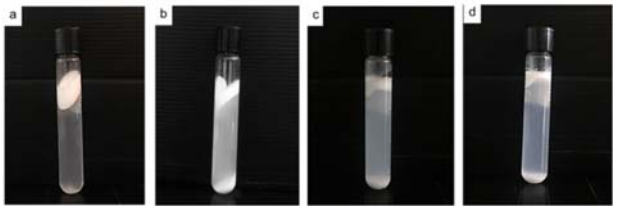

Fig. 4 Suspension photos of PLLA/OD microcapsules after centrifugation at 3,000 rpm using different PLLA molecular weights (g/mol): (a) 24,000; (b) 54,000); (c) 77,000 and (d) 145,000

PLLA:OD ratio was varied at 40:60, 50:50 and 60:40 wt% using PLLA molecular weight of 24,000 g/mol. The suspensions of three conditions were shown in Fig. 5a-c. The densities of PLLA/OD microcapsule increased with PLLA content in which most (82 % related to original of PLLA and OD) of PLLA/OD microcapsules precipitated onto the bottom layer in the case of 60:40 wt%. However, this phenomenon was also observed for 40:60 wt%

of PLLA:OD (30 % related to original of PLLA and OD). The precipitated polymer is due to the polymer part of the broken microcapsule in which low content of PLLA was not enough to encapsulate OD. The microcapsule size and morphology of all PLLA:OD ratios were then observed by optical microscope as shown in Fig. 5a'-c'. It was found that uneven surface microcapsules (Fig. 5a') were observed with some broken particles in the case of 40:60 wt% of PLLA:OD according to the suspension photo. On the other hands, the spherical microcapsules were formed in the cases of 50:50 (Fig. 5b') and 60:40 wt% (Fig. 5c') without broken particle. This seems that the PLLA shell can completely envelope the OD core.

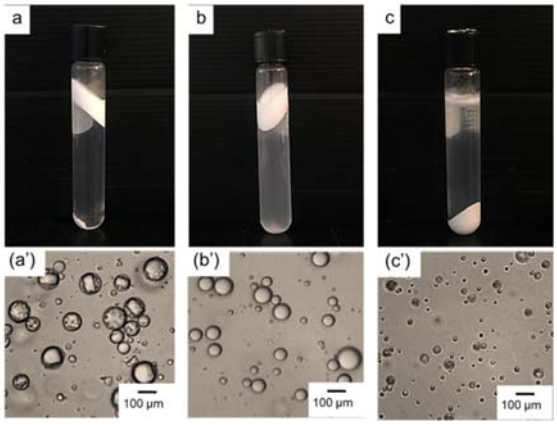

Fig. 5 Suspension photos (a-c) and optical photographs (a'-c') of PLLA/OD microcapsules using PLLA molecular weight of 24,000 g/mol after centrifugation at 3,000 rpm with different PLLA: OD ratios (wt%): (a and a') 40:60; (b and b') 50:50 and (c and c') 60:40

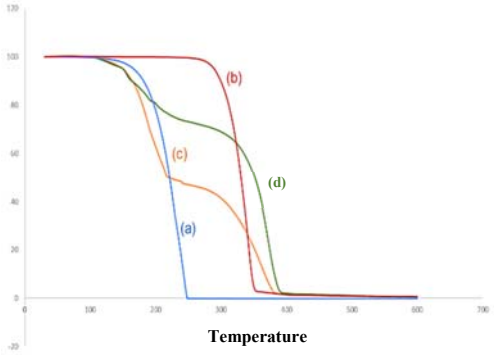

Fig. 6 Thermogravimetric analysis thermograms of (a) bulk OD, (b) PLLA and dried PLLA/OD microcapsules at PLLA:OD ratio (wt%) of (c) 50:50 and (d) 60:40

The degradation temperatures of bulk OD, PLLA and OD encapsulated in the PLLA microcapsules using PLLA:OD ratio of 50:50 and 60:40 were observed by thermogravimetric analysis and the thermograms are shown in Fig. 6. In the case of dried PLLA/OD microcapsules (Fig. 6c and d), the decomposition temperatures of OD (130-260°C) and PLLA (280-420°C) were shown in two respective steps. The degradation temperature of bulk OD (Fig. 6a) of 140-300°C was closed to that of the encapsulated OD. The thermogravimetric analysis thermograms confirmed that OD existed in the prepared microcapsules. In addition, in the case of 50:50, the experimental percent loading was 50% which was closed to the theoretical ones (50%) giving 100% encapsulation where the experimental percent loading was 27% giving only 65% encapsulation in the case of 60:40 ratio. This indicates that PLLA represented high efficiency to encapsulate OD.

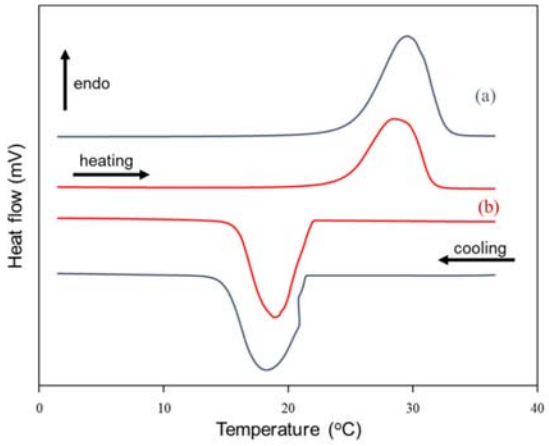

Fig. 7 Differential scanning calorimeter thermograms of (a) bulk OD and (b) the encapsulated OD in dried microcapsules at PLLA:OD ratio of 50:50 %w/w

The latent heats (J/g-OD and J/g-sample for bulk and encapsulated OD, respectively) of bulk OD (Fig. 7a) and the encapsulated OD (Fig. 7b) were obtained from the heating/cooling peak areas of differential scanning calorimeter thermograms. The latent heats (ΔH_m* = 197 and ΔH_c* = 196 J/g-OD) of the encapsulated OD were quite closed to those of bulk OD (ΔH_m* = 233 and ΔH_c* = 234 J/g-OD). It may be due to the hydrophilicity of PLLA increased the phase separation between polymer shell and OD core where the encapsulated OD behaved similar with bulk OD.

CONCLUSION

The spherical biodegradable poly(l)-lactic acid microcapsule containing octadecane with good colloidal stability was successfully prepared by a simple solvent evaporation method. The molecular weight of poly(l)-lactic acid affected on the formation of the microcapsule shell. The lower

molecular weight poly(l)-lactic acid formed the smoother shell than the higher ones based on lower internal viscosity. The latent heats of the encapsulated octadecane were closed to those of bulk octadecane. Therefore, the prepared polylactic acid/octadecane microcapsules were able to use in heat storage applications in place of petrochemical-based microcapsule.

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