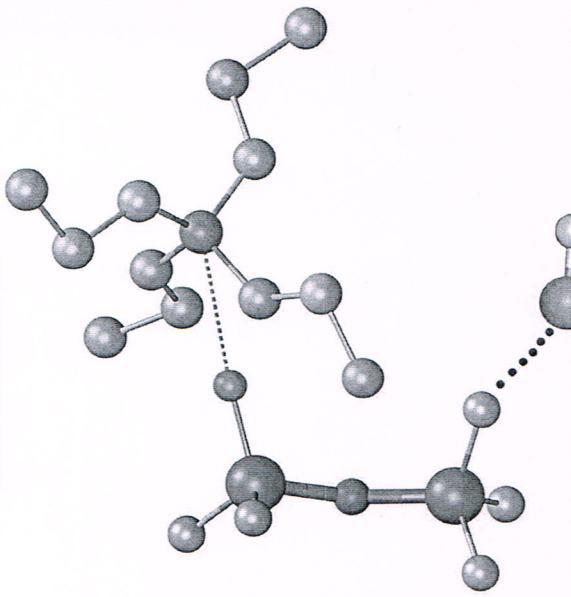
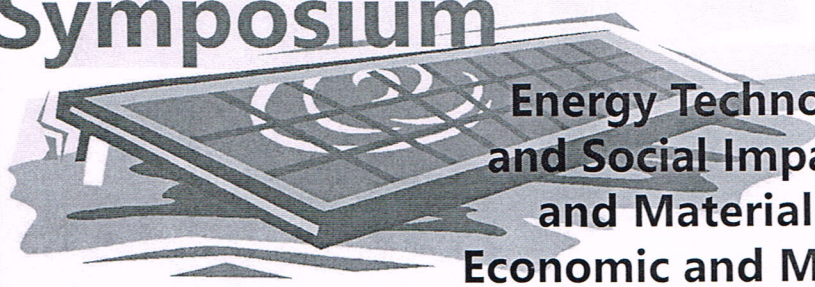
Proceedings

11th Eco-Energy and Materials Science and Engineering Symposium





Energy Technology, Environmental and Social Impact, Nanotechnology and Material Technology, Energy Economic and Management, Nuclear Technology, New Technology, Automotive Composite, and Other

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CONTENT

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Determination of the encapsulated octadecane in polymer capsule by gel permeation chromatography

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Abstract -*In this research, the determination of octadecane (OD) in polymer capsule by gel permeation chromatography (GPC) compared with thermogravimetric analysis (TGA) was studied. For TGA analysis of OD emulsion, the statistic calculation represented low accurate and precise as % Recovery and %RSD are 75-112% and 6-17% respectively. In contrast, the more accurate and precise measurment can be obtained from GPC analysis in which %Recovery closed to 100% (103-119%) with narrower %RSD(0.67-1.16%) of all concentrations of OD emulsion. GPC was then used to measure the encapsulated OD in polymer capsule prepared at 3 ratios of 50:50, 70:30 and 80:20 of PMMA: OD (%w/w) using toluene as solvent. The obtained OD content was compared with OD amount from the preparation recipe. It was found that the % relative error was only 5-6%.*

Keywords: *Phase change material; Octadecane; Polymer capsule; Gel permeation chromatography*

1. INTRODUCTION

In recent year, microencapsulation of phase change materials (PCMs) or heat storage materials are widely used in various applications [1-7] such as greenhouses textile, Building and Agriculture. One group of the useful PCMs is Paraffin waxes which melt and crystallize at a wide range of temperatures. Paraffin waxes are nontoxic, non-corrosive, chemically inert and have no unpleasant odor. They have moderate thermal energy storage and a small volume change compared to the amount of heat able to be stored[8, 9]. To measure the latent heats of PCMs, differential scanning calorimeter (DSC) is generally used. It was found that the latent heats of the encapsulated PCMs are always lower than those of the bulk PCMs[10-16]. Therefore, the latent heats in the unit of joule per 1 g of PCMs (J/g-PCMs) were preferred to use in order to compare the latent heats of the encapsulated PCMs having different amounts in the capsule particles and also bulk PCMs. The quantitative analysis of PCMs in the capsules is then an important. In the previous work, TGA was used to measure encapsulated PCMs. However, this technique seems less reproducibility especially in the case of some polymer shell and PCMs core in which the degradation curves of them may overlap resulting in unreliable of the obtained data. It is well known that separation technique is one of the famous techniques for quantitative analysis. It is able to separate each analyte in the sample using the appropriate column and mobile phase solution before detected by the suitable detector. Gel permeation chromatography (GPC) is one of the separation techniques. Normally, it is used to measure the molecular weight of the polymer using tetrahydrofuran (THF) as a mobile phase. PCMs as octadecane (OD) are easily soluble in THF.

Therefore, it is possible to measure amount of OD in polymer capsule. In this work, GPC is firstly implemented to measure PCMs in the polymer capsule having PMMA and OD as the shell and the core, respectively, compared to TGA technique. The accuracy and precision of the measurement will be studied.

2. EXPERIMENTAL

2.1 Materials

Methyl methacrylate (MMA; Aldrich, Wisconsin, USA; purity, 99%) were purified by pass through the column packed with basic aluminium oxide. The purified monomers were stored in a refrigerator. Potassium persulfate (KPS; Aldrich, Wisconsin, USA) was purified by recrystallization. OD (Aldrich, Wisconsin, USA; 99.5%) was used as received. Polyvinyl alcohol (PVA) (Aldrich, Wisconsin, USA; degree of saponification, 87–90%) was used as received. Tetrahydrofuran (THF) (QReC, Auckland, New Zealand; HPLC grade) was used as received.

2.2 Synthesis of PMMA

Polymethyl methacrylate (PMMA) was prepared by emulsion polymerization[17]. The polymerizations were carried out at 70°C for 24 hours with a stirring rate of 200 rpm. The monomer (30 g) and water (250 g) were charged into the reactors and then purged with N_2 for 30 min. The polymerizations were initiated by the addition (20 g) of KPS aqueous solution (1.2 wt%). The obtained PMMA latex was dried overnight at 70 ^{0}C before using to prepare polymer capsule in the next step.

2.3 PMMA capsule preparation

PMMA capsule containing OD was prepared by solvent evaporation method in oil in water (o/w) system[18] as shown in Fig. 1. Firstly, OD and PMMA were dissolved in toluene as the dispersed or the oil phase.Secondly, the oil phase was then dispersed into the continuous or aqueous phase containing PVA using homogenizers at 5,000 rpm/ 5 min resulting in homogeneously oil droplet emulsion. The reagent amount was shown in table 1. After evaporation of the solvent inside the oil droplet, the capsule having PMMA and OD as shell and core, respectively, would be obtained.

To compare OD measurement between GPC and TGA, the artificial OD emulsions with various OD concentrations (1, 2.5 and 5% wt) were prepared. OD and PVA solution 1% (w/v) were mixed using homogenizer at 5000 rpm for 5min.

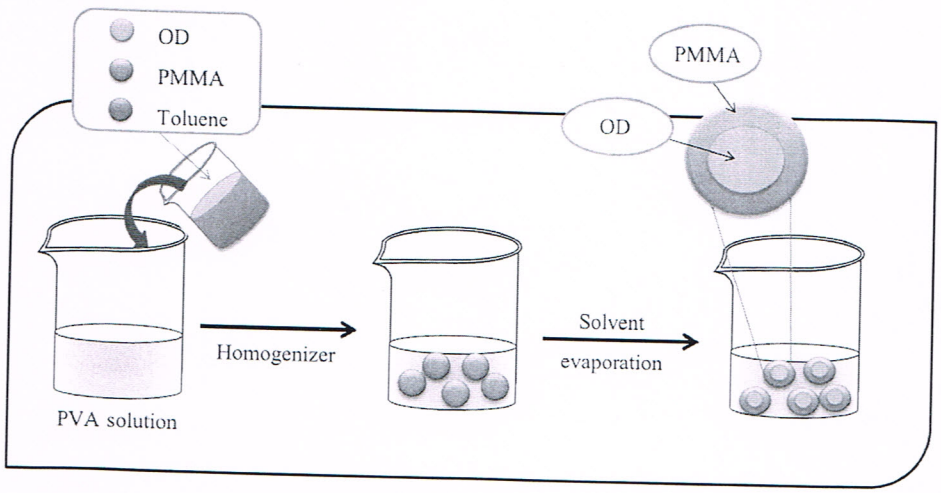

Fig. 1. schematic of polymer capsule encapsulated octadecane preparation

Table 1. Reagent amount for the preparation of PMMA encapsuletd OD by solvent evaporation mthod

Ingredient	PMMA : OD		
	50:50	70:30	80:20
PMMA (g)	1.0	1.4	1.6
THF (g)	10.0	10.0	10.0
OD (g)	1.0	0.4	0.4
1%(w/w) of PVA solution (g)	18.0	18.0	18.0

Characterizations

The prepared capsules were observed with an optical microscope (OM) (SK-100EB & SK-100ET, Seek, Seek Inter Co. Ltd., Thailand) and scanning electron microscope (SEM) (JSM-6510, JEOL, JEOL Ltd., Japan) to investigate the inner structure of the microcapsules and the morphology of the surface, respectively. For the SEM observations, one drop of the polymer suspension was placed on a nickel SEM stub and dried before being coated with Au. The OD content in the microcapsule was determined by both Gel permeation chromatography (GPC) (Water 2414, Water, USA) and thermogravimetric analyzer (TGA) (TGA 4000, Perkin-Elmer, USA). For TGA analysis, the required amount of sample was measured in the ceramic sample holder using a heating rate of 55°C min^{-1} from 30 to 400 ^{0} C. For GPC measurement, the sample solutions (1%wt) in THF were injected to GPC system consist of two poly(styrene divinylbenzene) gel columns (Phenogel $5 \cdot 10^3$ and $5 \cdot 10^5$ A, 7.8 mm i.d x 30 cm, Phenomenex, USA) connected in series. The flow rate of THF as eluent was maintained at 1.0 ml/min with column temperature of 40°C and elution was monitored with refractive index detector.

3. RESULT AND DISCUSSION

To compare the efficiency of OD measurement between TGA and GPC techniques, the artificial OD emulsions with the different concentrations were prepared. In the case of TGA analysis, the samples are directly measured for 5 times of each OD concentration comparing to the bulk OD. It was found that the degradation temperature (155-220 °C) of all concentrations of OD emulsion accorded to that of the bulk OD (135-225°C) as shown in Fig. 2. The increase of degradation temperature of OD emulsion higher than of bulk OD would due to the encapsulation. From percent weight loss, the percent recoveries of all OD concentrations were obtained (111.86, 75.14 and 77.08% for 1, 2.5 and 5 %wt, respectively). From these data, TGA analyses seem to be less accuracy especially in the case of higher concentration. Moreover, the reproducibility is also investigated in the term of %relative standard deviation (%RSD) compared to that of the theory (Horwitz equation; predicted RSD)[19]. The experiment %RSDs (12.12, 18.65 and 5.64% for 1, 2.5 and 5 %wt, respectively) of all OD concentrations are higher than those of the theory as the Horwitz ratio (experimental %RSD/ predicted RSD) of 8.91, 11.88 and 2.85 for 1, 2.5 and 5 %wt, respectively. In general, the reproducibility of analytical method would be accepted when the experiment %RSD lower than that of the theory. Therefore, from the results indicated that the reproducibility of TGA analysis is unacceptable.

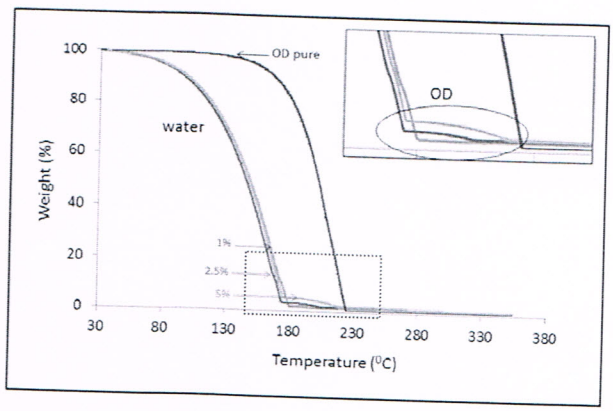

Fig. 2. TGA thermogram showed the degradation temperature of OD solution at 1, 2.5 and 5% wt.

For GPC analysis, the OD emulsions were dried and then dissolved in THF before GPC measurement. In contrast to TGA analysis, GPC analysis of the same OD emulsion samples represent more accurate and precise than those of TGA analysis. The percent recovery (119, 119 and 103 for 1, 2.5 and 5 %wt, respectively) of all concentrations of OD closed to 100%. Moreover, the experiment %RSDs (0.84, 0.67 and 1.16 for 1, 2.5 and 5 %wt, respectively) are lower than those of predicted RSD as the Horwitz ratio giving lower than 1 (0.63, 0.51 and 0.87 for 1, 2.5 and 5 %wt, respectively). From all results, it can be conclude that the determination of OD with GPC is more accurate and precise than those of TGA. Therefore, GPC was selected for OD measurement in polymer capsule in the further work.

PMMA capsules encapsulated OD was prepared at 3 ratios of PMMA: OD (50:50, 70:30 and 80:20 %w/w) using toluene as solvent. The transparent spherical polymer solution droplets were obtained (Fig. 3 A-C). After solvent evaporation, the dark polymer capsules (Fig. A'-C') were obtained. Although, the optical micrograph is not clear to observe the capsule formation, the smooth outer surfaceas of the capsules were observed by SEM (Fig. 4) which indicated that the OD would exist in the capsule. The incomplete encapsulated OD capsule would represent the rough surface which accorded to the polydivinyl benzene/natural rubber capsule containing OD in the previous work[12]. The PMMA/OD capsule then was used to measure the OD content by GPC. The GPC chromatogram of PMMA/OD capsule (Fig. 5C) represented two peaks in which are the PMMA and OD peaks at the retention time of 13.5 and 21.5 min, respectively. The retention time of those peaks are accorded with the original OD (Fig. 5A) and PMMA (Fig. 5B). This indicated that the PMMA/OD capsule was successfully prepared. The amount of encapsulated OD is able to obtain from the OD peak area of the capsule compared to those of OD standard curve. At the various ratios between PMMA and OD, the amount of OD measured by GPC closed to the theoritical value (OD in the recipe) as the % relative error representing 5.00-6.00% with the small %RSD (1.88-3.39) as show in the Table 2.

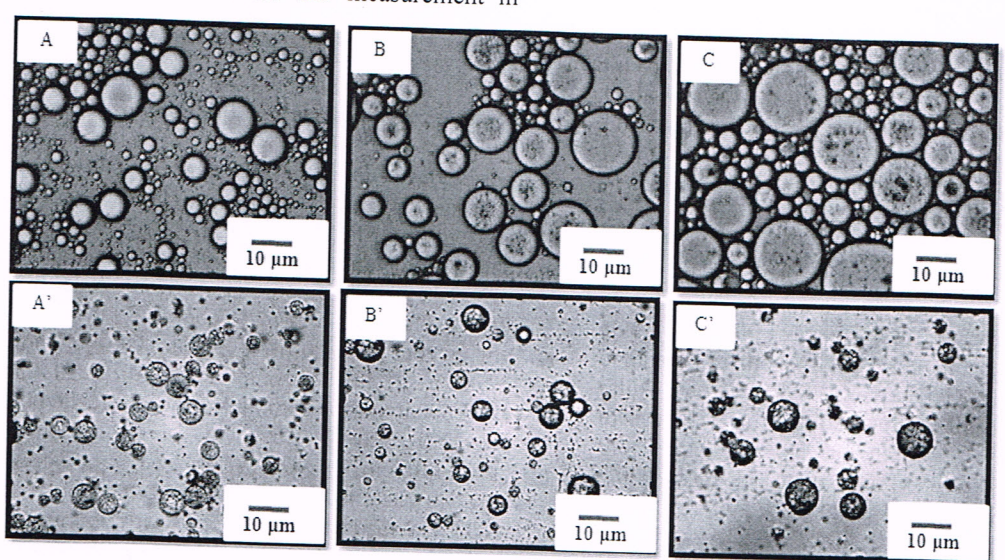

Fig. 3. The optical micrograph of polymer capsule encapsulated octadecane before and after evaporation solvent, the PMMA: OD (%w/w); A, A') 50:50 B, B') 70:30 and C, C') 80:20 respectively

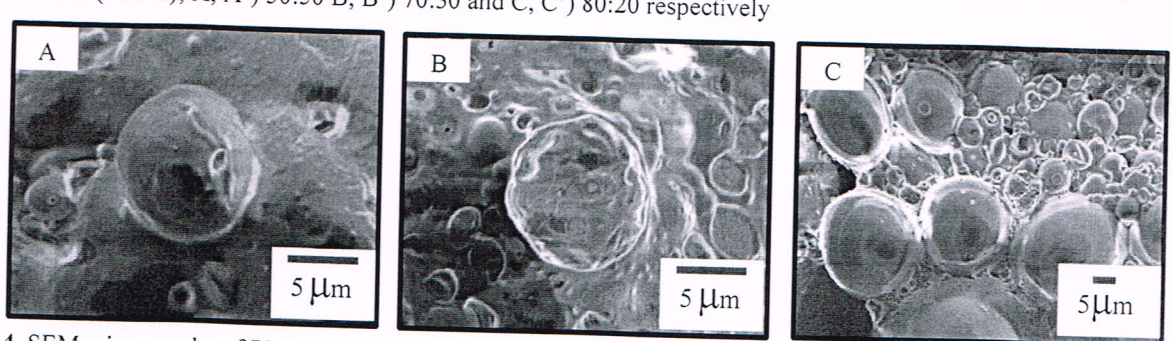

Fig. 4. SEM micrographs of PMMA capsule containing OD prepared by sovent evaporation technique with various ratios of PMMA: OD (%w/w): A) 50:50 B) 70:30 and C) 80:20

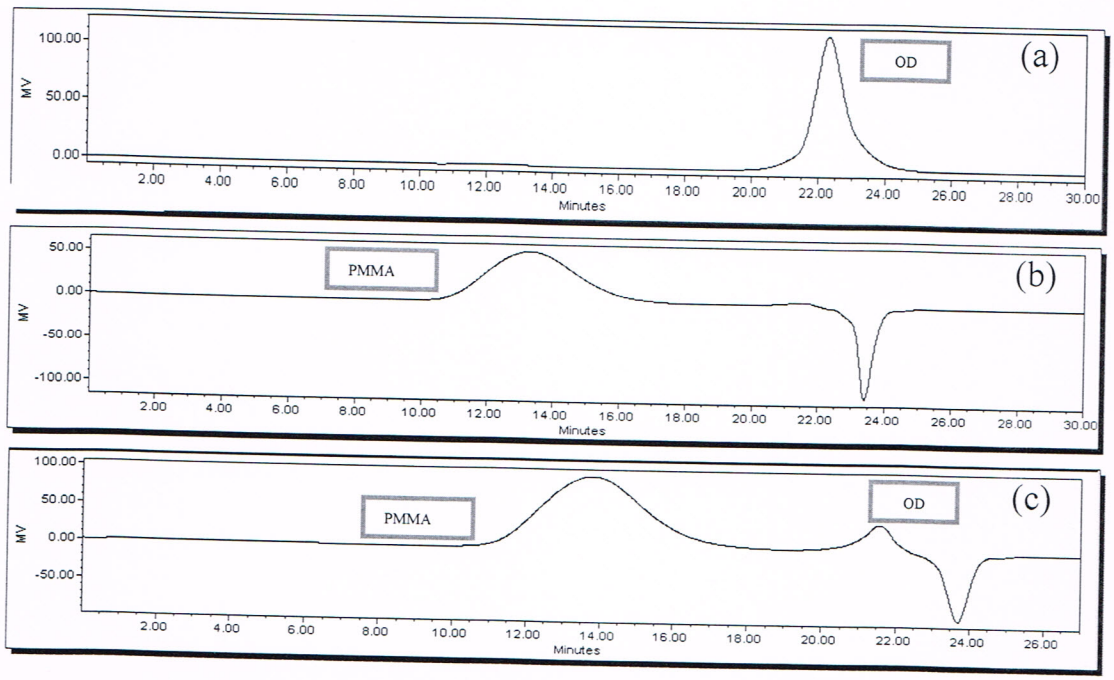

Fig. 5. GPC chromatograms of (a) OD (b) PMMA and (c) encapsulated octadecane insided the capsule

Table 2. The amount of encapsulated OD was measured with GPC

PMMA: OD (%w/w)	OD (g)		%relative error
	Theory	Experiment (%RSD*)	
50:50	0.050	0.053(3.01)	6.00
70:30	0.060	0.063(3.39)	5.00
80:20	0.060	0.063(1.88)	5.00

Remark: * N=3

4. CONCLUSION

In this research, GPC was firstly implemented to measure OD content in the polymer capsule compared to the convensional technique as TGA. It can be conclude that GPC analysis represents more accurate and precise than those of TGA. From these results, GPC can be used for not only molecular weight of polymer measurement but also for measurement of PCMs content as OD in the capsule. This technique would be useful for various polymer capsules containing PCMs as paraffin waxes.

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