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Research Article

Porous Poly(methyl methacrylate) Microsphere via Suspension Polymerization: Synthesis, Characterizations, and the Effect of Triglycerides as Porogen

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Abstract: Porous microspheres with interconnected internal and external pores can provide a large specific surface area, making them excellent adsorbents for various applications such as controlled drug release, chromatography, tissue engineering scaffolds, and blood purification. Poly(methyl methacrylate) (PMMA) has been globally utilized in many medical applications (e.g., adsorbents, drug delivery, dental implants, etc.) due to its unique properties including good thermal and chemical stability, biocompatibility, and hemocompatibility. In this work, we developed a method to prepare PMMA porous microspheres using triglycerides as porogen via suspension polymerization yielding particle size of 300-500 µm with a specific surface area as high as 281 $m^2 \cdot g^{-1}$. In addition, we also investigated the effect of triglycerides ranging from short-, medium-, and long-chain triglycerides as a porogen, which can influence the morphology and mechanical stability of the microspheres. The microspheres were characterized through an optical microscope and scanning electron microscope on morphology. In addition, pore size, pore volume, and specific surface area were calculated by BET method. The porosity of the microspheres was observed to be dependent on the type of triglycerides, where the short chain provided the highest porosity and the long chain provided the lowest porosity.

Keywords: Porous microspheres, Poly(methyl methacrylate) (PMMA), Triglycerides porogen, Suspension polymerization

1. Introduction

Polymeric porous microspheres have been utilized in many medical applications (e.g., adsorbents, drug delivery, dental implants, etc.). Among various polymers, poly(methyl methacrylate) (PMMA) possesses unique properties, including non-degradability, good thermal stability, biocompatibility, and hemocompatibility [1] which is suitable for medical applications. PMMA microspheres are already utilized in some medical applications. For example, orthopedic infections such as prosthetic joint infections (PJI) and chronic osteomyelitis were treated by using antibiotic-

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loaded PMMA beads [2]. Additional modification with 10% cyclodextrin of PMMA microspheres was demonstrated to help steadily and prolong the duration of antimicrobial activity of antibiotics [3]. PMMA microsphere, approximately 50 µm was also loaded with silver and doxycycline for antimicrobial action in dental care [4].

Various methods are available for PMMA microsphere preparation, such as emulsion polymerization, suspension polymerization, and seed swelling polymerization. Each method has its own unique features, depending on the applications. Drug delivery systems were primarily synthesized through emulsion polymerization due to their unique qualities such as nano-sizes, large surface area per unit volume, improved adsorption, and increased dispersion of active drugs [5]. While in the adsorbent application, the microspheres are usually prepared using suspension polymerization due to preparing uncomplicated, simple to regulate the polymerization conditions [6] and obtain large particle sizes [7]. The seed swelling polymerization technique can provide monodisperse porous microspheres and large particle sizes for highly porous microspheres which can be used in liquid chromatography as stationary phase material [8].

Currently, PMMA porous microspheres have not been studied for hemoperfusion despite the known excellent properties, including biocompatibility, nontoxicity, and biological safety [9]. Typically, the material is based on polystyrene (PS). For example, an inorganic-organic co-crosslinked network between vinyltriethoxysiline (VTES) functionalized hydroxyapatite nanoparticles (V-HAP) and non-ionic styrene divinylbenzene (PS-DVB) resins in ranges of 300-500 µm through suspension polymerization for effective removal of bilirubin was developed by Yamin Chai et al. [10]. The 300-500 µm size range is suitable for hemoperfusion due to the proper pressure which less effect to components of blood and high flow speed for fast treatment. Moreover, styrene-divinylbenzene porous microspheres were synthesized via suspension polymerization using toluene, cyclohexanol, and heptane as porogen utilized in cosmetics or pharmaceuticals applications [11]. The results demonstrated particle size in the range of 5-50 µm and specific surface area in the range of 40-180 $m^2 \cdot g^{-1}$ [11]. The selection of porogens to create porous structure is very important. In this work, three different triglycerides were chosen due to their high boiling point, suitable for high temperature initiated polymerization and their different in size and viscosity in order to observe the effect on porosity of the porous microsphere.

In this work, we aim to develop a method for preparing PMMA porous microspheres using triglycerides as porogen, including short-, medium-, and long-chain triglycerides, through suspension polymerization with a particle size of 300-500 µm which is suitable for various applications e.g., drug delivery [12], hemoperfusion [10], etc. Moreover, the difference in chain length and viscosity of each type of triglycerides was a key parameter affecting droplet size [13] and porous. The porosity of microspheres occurred during the polymerization due to phase separation which is driven by porogens. Therefore, the porosity is expected to depend on the types of triglycerides. The impact of triglycerides varying from short-, medium- and long-chain triglycerides as porogen, were investigated including their surface area, morphology, and mechanical stability of the microspheres.

2. Methodology

2.1 Materials

Methyl methacrylate (stabilized with 6-tert-Butyl-2,4-xylenol) (MMA, >99.8% grade) was obtained from Tokyo Chemical Industry Co., Ltd. Japan (TCI). Pentaerythritol tetraacrylate (Catalog no. 408263) was purchased from Sigma Aldrich, USA. Whey protein isolate (WPI) under the tradename Provon 292, was purchased from Glanbia Nutritionals, Inc. (Carlsbad, CA, USA), 1,1′ -Azobis(cyclohexanecarbonitrile) (98% grade) was obtained from Sigma Aldrich, USA. Tributyrin (97% grade) was purchased from Sigma Aldrich, USA. MCT oil (Food grade) was obtained from Vicchi Enterprises Co., Ltd. Thailand. Soybean oil was purchased from Thai Vegetable Oil Public Company Limited. Ethanol (99.8% grade) was obtained from Fisher Chemical, Thailand. These reagents were used without further purification.

2.2 Preparation of poly(methyl methacrylate) microspheres

Poly(methyl methacrylate) (PMMA) microspheres were prepared through oil-in-water suspension polymerization using ratio of aqueous phase to oil phase (85:15). Firstly, 1 wt.% of whey protein in deionized water (DI) was prepared for an aqueous phase. For an oil phase, methyl methacrylate as a monomer, pentaerythritol tetraacrylate (20 wt.% of monomer) as a crosslinker, azobis(cyclohexanecarbonitrile) (2.72 wt.% of monomer) as an initiator, and triglyceride (tributyrin, MCT oil, or soybean oil: 20-70 wt.% of total oil phase) were added to another vial, followed by purging under nitrogen for 5 min. After that, the oil phase was transferred into the aqueous phase, and they were continuously stirred using a magnetic stirrer and occasionally sonicated (ultrasonic bath, GT-SONIC-D6) for 3 min at room temperature to obtain the suspension. After that, the suspension was heated to 85±5 °C to initiate the polymerization and continuously stirred at 300 rpm for 35 min. The temperature was maintained above 80 °C. Afterwards, the generated PMMA microspheres were collected using centrifugation at 2300 rpm (MSE Centaur 2, MSB20.CX1.5). The microspheres were washed three times with ethanol, followed by DI water four times. Finally, the PMMA microspheres are dried under vacuum at below -60 °C for two days. The scheme of preparing PMMA microspheres was shown in Figure 1.

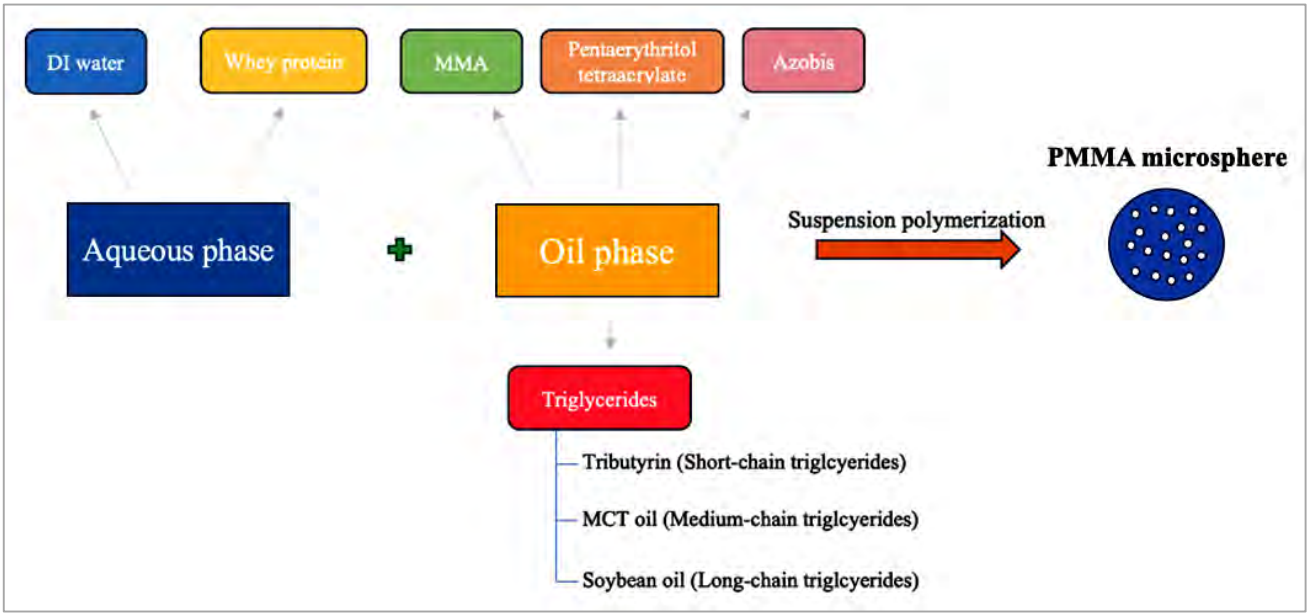

Figure 1 Scheme of preparing PMMA microspheres.

2.3 Characterization of the microspheres

The morphology of the microspheres was gold-coated before determined by a scanning electron microscope (SEM, HITACHI, SU3500-Horiba X-maxN). An analysis was conducted at magnifications of 10,000X. The optical microscope (OLYMPUS, CX31) was utilized to acquire the macroscopic morphology of the microspheres. The bead sizes were measured from the observed particles (n=10) under optical microscope and the imageJ software was used to measure the size of the particles from the images. The specific surface areas, the average pore diameter, and the pore volume were evaluated by Brunauer-Emmett-Teller (BET) surface area analysis using nitrogen gas at 80 °C for 24 h through the Micromeritics 3Flex instrument.

2.4 Mechanical strength

0.5 grams of the microspheres were stirred at 1000 rpm for 24 h at room temperature in a beaker that contained 15 ml of water [14,15]. After that, broken microspheres were sieved through a mesh size 100 and weighed. The breakage rate was calculated as follows

$$\text{Breakage rate (\%)} = W_A/W_B \times 100 \quad (1)$$

where W_A and W_B are weights of broken and total microspheres, respectively. This experiment was carried out at three times.

3. Results and discussion

Effect of each type of triglycerides on particle size and pore size

The PMMA porous microspheres were prepared using simple suspension polymerization. Three types of triglycerides (tributyrin (T) (short-chain triglycerides), MCT oil (M) (medium-chain triglycerides), and soybean oil (S) (long-chain triglycerides)) were used as a porogen during the polymerization. The amount of the porogen added to the oil phase will play a significant role in the surface area and mechanical strength of the microsphere. The high content of the porogen might provide more porosity, but it could also loosen the mechanical integrity. Therefore, the influence of each triglyceride type on morphology, particle size, pore size, and pore volume of PMMA porous microspheres was examined. The study investigated over four different content of triglycerides (20 wt.%, 40 wt.%, 50 wt.%, and 70 wt.%). We began this work with two hypotheses. Firstly, we hypothesized that the type of triglyceride will affect pore size due to the difference in molecular weight. Therefore, long-chain triglycerides are expected to yield the largest pore size. On the other hand, short-chain triglycerides should provide the smallest pore size. However, the BET results suggested that there was no significant effect of the triglyceride type on the pore size, which yielded a similar size of 2 nm (Figure S1). The type of the triglyceride was found to affect the size of the microsphere in which tributyrin provided the smallest size, while the other two yielded similar sizes over 1,000 µm. The change in size could contribute to the difference in viscosity of the triglycerides resulting in the different oil droplet sizes during the suspension polymerization. However, the amount of triglyceride at 70 wt.% of each type of triglyceride demonstrated smaller particle size than others which could be due to the excess amount of triglyceride which diluted the monomer and crosslinker during the polymerization leading to the formation of less dense microsphere. Therefore, beads were broken while forming. From Figure S2, tributyrin at 20 wt.% (T2), 40 wt.% (T4), 50 wt.% (T5), and 70 wt.% (T7) demonstrated particle size that was increased from approximately 400 µm at 20 wt.% to 800 µm at 50 wt.% and decreased to 296 µm at 70 wt.%. Next, MCT oil at 20 wt.% (M2), 40 wt.% (M4), 50 wt.% (M5), and 70 wt.% (M7) demonstrated particle size that was increased from approximately 1100 µm at 20 wt.% to 1470 µm at 50 wt.% and decreased to 288 µm at 70 wt.%. Finally, soybean oil at 20 wt.% (S2), 40 wt.% (S4), 50 wt.% (S5), and 70 wt.% (S7) demonstrated particle size that was increased from approximately 1200 µm at 20 wt.% to 1450 µm at 40 wt.% and decreased to 500 µm at 50 wt.% and 70 wt.%. The data was concluded in Table 1.

Effect of each type of triglycerides on specific surface area and pore volume

For the second hypothesis, the high content of triglyceride in the oil phase is predicted to improve specific surface area and porosity. Thereby, the amount of triglyceride at 70 wt.% of each type of triglycerides should yield the largest specific surface area and pore volume. From Figures S3 and S4, the BET results mostly agreed with the hypothesis. The pore volume of tributyrin was observed in the range of 0.08 cm^3/g to 0.13 cm^3/g, MCT oil was in the range of 0.02 cm^3/g to 0.08 cm^3/g, and soybean oil was in the range of 0.0002 cm^3/g to 0.009 cm^3/g. Meanwhile, the specific surface area of tributyrin was increased from 174 m^2/g to 281 m^2/g at 20 wt.% – 50 wt.%. Conversely, at 70 wt.% it decreased to 257 m^2/g. In addition, MCT oil and soybean oil increased from 41 m^2/g to 166 m^2/g and 0.54 m^2/g to 19.7 m^2/g, respectively according to the increase of the content of triglyceride. By increasing the content of the porogen, their specific surface area was increased. The size of the microspheres was also increased along with the amount of porogen. Typically, the larger microspheres provide lower specific area than the smaller one per weight ratio. Thus, these results suggested that increasing the porogen content can enhance the formation of high-porosity microspheres. Interestingly, tributyrin yielded the highest specific area of 281 m^2/g and soybean oil gave the lowest specific area of microspheres. The results indicated that the type of porogen can play a significant role in porous

microsphere formation. Tributyrin has the lowest viscosity among the other which can provide a better solubility rate during the polymerization. Since the viscose solvent has a poor interaction with the solute, the phase separation or polymer precipitation might occur during the microsphere formation for the other porogens causing the low specific area material.

Table 1 Effect of different amounts of each type of triglyceride on specific area, pore volume, pore size, and particle size of poly(methyl methacrylate) particles compared with CytoSorb (commercial product was approved from Food and Drug Administration (FDA) [16])

Sample	Triglyceride amount (wt.%)	Average size (μm)	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
T2	20	451 ± 50	174	0.083	1.95
T4	40	538 ± 78	263	0.127	1.94
T5	50	815 ± 56	281	0.135	1.93
T7	70	296 ± 66*	257	0.126	1.96
M2	20	1188 ± 102	41	0.020	1.95
M4	40	1460 ± 10	84	0.041	1.95
M5	50	1461 ± 10	112	0.054	1.95
M7	70	288 ± 78*	166	0.083	2.00
S2	20	1206 ± 84	0.54	0.0002	1.79
S4	40	1459 ± 5	6.88	0.0034	1.98
S5	50	511 ± 14*	14.1	0.0068	1.94
S7	70	506 ± 138*	19.7	0.0094	1.92
CytoSorb [17]	-	450	850	1.91	5.93

* Debris size and irregular shape size

Effect of each type of triglycerides on morphology

In term of microsphere morphology, the spherical shape was found in most formulas with some fragments and debris that might have come from the broken microsphere. No broken microspheres were observed in all samples from 20 wt.% of the porogen. From Figure 2 showed an increase in the particle size of the porous PMMA microsphere using each type of triglycerides at 20 wt.% as porogen. Furthermore, from Figure 3 demonstrated the morphology of tributyrin at 20 wt.% to 70 wt.% was observed with a larger spherical shape from the optical microscope and a larger pore from SEM according to the increasing content of tributyrin (Figure S7). Meanwhile, Figures S5 and S6 show that both MCT oil and soybean oil exhibit a larger spherical shape and a larger pore as the triglyceride content rises (Figures S8 and S9). However, at 70 wt.% of the three types of triglycerides showed debris of microspheres. In addition, the porosity of three types of triglycerides showed from the highest to lowest according to short-, medium-, and long-chain triglycerides, respectively. The results confirmed the high mechanical strength of those samples. The more debris was found when the amount of porogen increased. This was because the microspheres became more porous, leading to weak mechanical strength. The number of microspheres was found to be significantly lower in the system of 70 wt.% porogen, indicating low mechanical stability and poor conditions for forming porous microspheres. Cross-sectional images from SEM exhibited similar morphology for all samples confirming the forming of a highly porous microsphere.

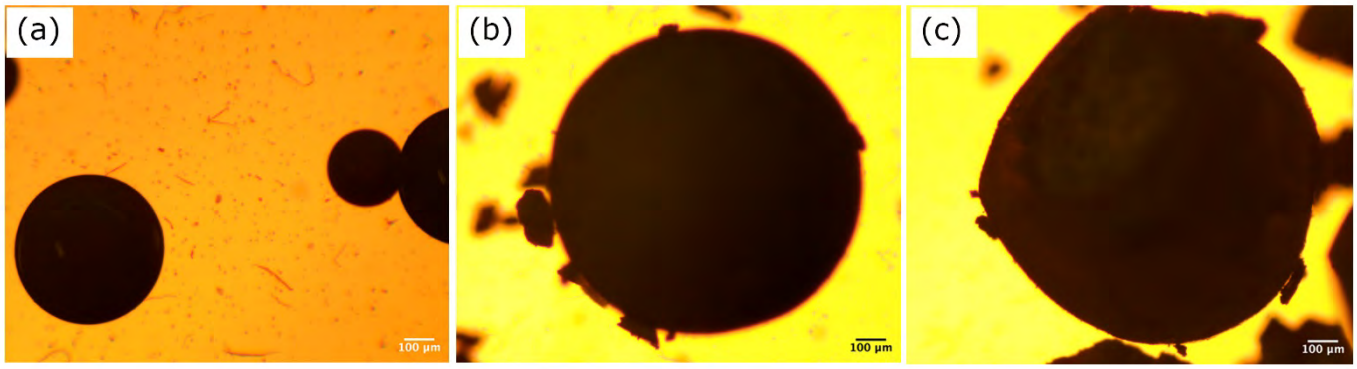

Figure 2 (a) PMMA microsphere using tributyrin, (b) MCT oil, and (c) Soybean oil 20 wt.%, respectively at 4X by an optical microscope.

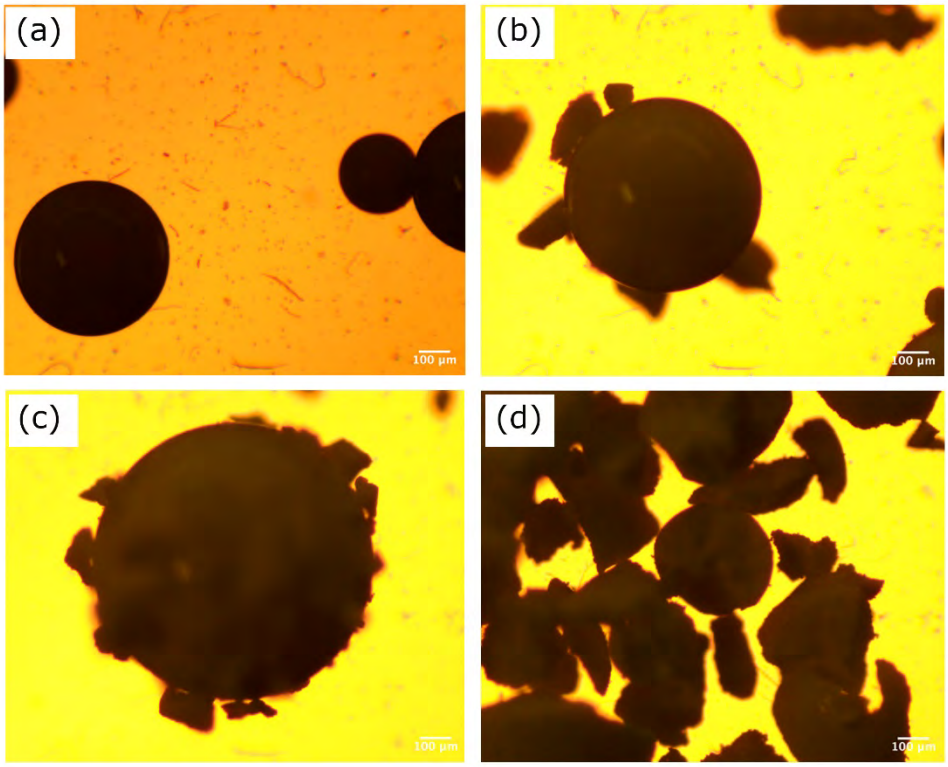

Figure 3 (a) PMMA microsphere using tributyrin 20 wt.%, (b) 40 wt.%, (c) 50 wt.%, and (d) 70 wt.% at 4X by an optical microscope.

Effect of each type of triglycerides on mechanical stability

PMMA microspheres are intended to be used as an adsorbent in hemoperfusion applications. Therefore, PMMA microspheres T4 and T5, which have the highest specific surface area, were selected for further investigation. Mechanical stability was examined for T4 and T5 by measuring the breakage rate compared with CytoSorb. The result demonstrated the breakage of 40 wt.%, 50 wt.% of tributyrin, and CytoSorb of 11±15%, 26±12%, and 0.58±0.3%, respectively (Table 2).

Table 2 Compare the mechanical stability of poly(methyl methacrylate) microsphere and CytoSorb

Sample	Triglyceride amount (wt.%)	Breakage rate (%)
T4	40	11 ± 15
T5	50	26 ± 12
CytoSorb	-	0.58 ± 0.3

4. Conclusion

Porous poly(methyl methacrylate) microspheres in the range of 300 µm to 1,000 µm were successfully synthesized through suspension polymerization. The influence of three types of triglycerides, including tributyrin, MCT oil, and soybean oil was investigated. The short-chain triglyceride yielded the highest specific area up to 281 m^2/g with a size between 400 µm - 800 µm depending on the triglyceride content. Furthermore, the specific surface area was higher than styrene-divinylbenzene microspheres are 40-180 m^2/g [11]. The mechanical strength was directly linked to the porosity of the microspheres where the strength deteriorated in highly porous microspheres. The optimum microsphere in this work was T4 providing substantial porosity with a high specific area of up to 260 m^2/g but still had a slightly lower mechanical strength than CytoSorb.

Acknowledgment

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Supplementary Information

Porous Poly(methyl methacrylate) Microsphere via Suspension Polymerization: Synthesis, Characterizations, and the Effect of Triglycerides as Porogen

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Supporting figures

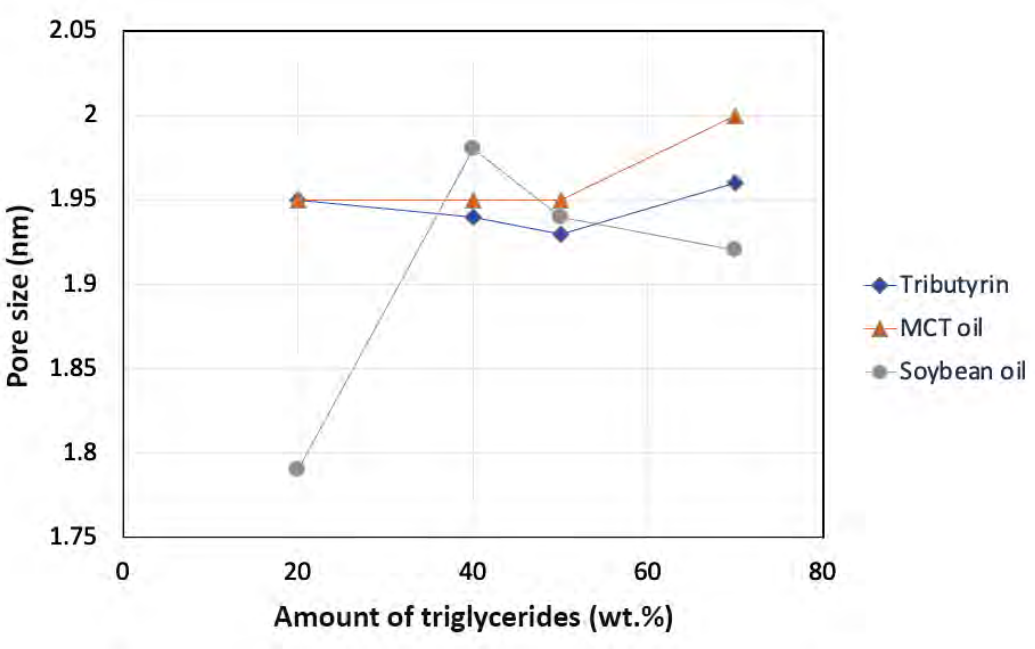

Figure S1. Effect of each type of triglycerides at 20 wt.%, 40 wt.%, 50 wt.%, and 70 wt.% on the pore size of PMMA microspheres

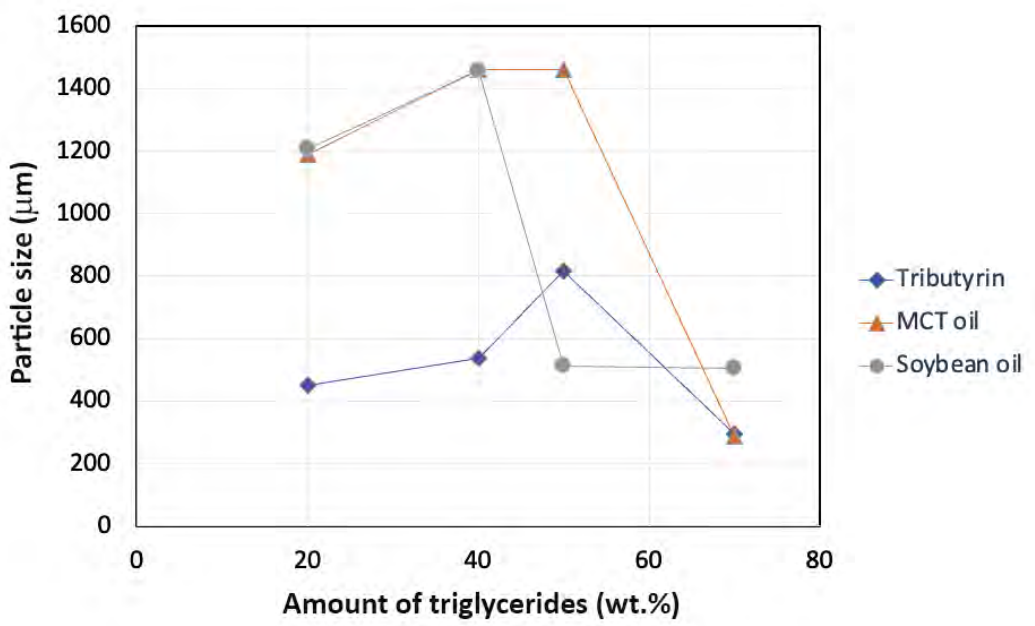

Figure S2. Effect of each type of triglycerides at 20 wt.%, 40 wt.%, 50 wt.%, and 70 wt.% on the particle size of PMMA microspheres

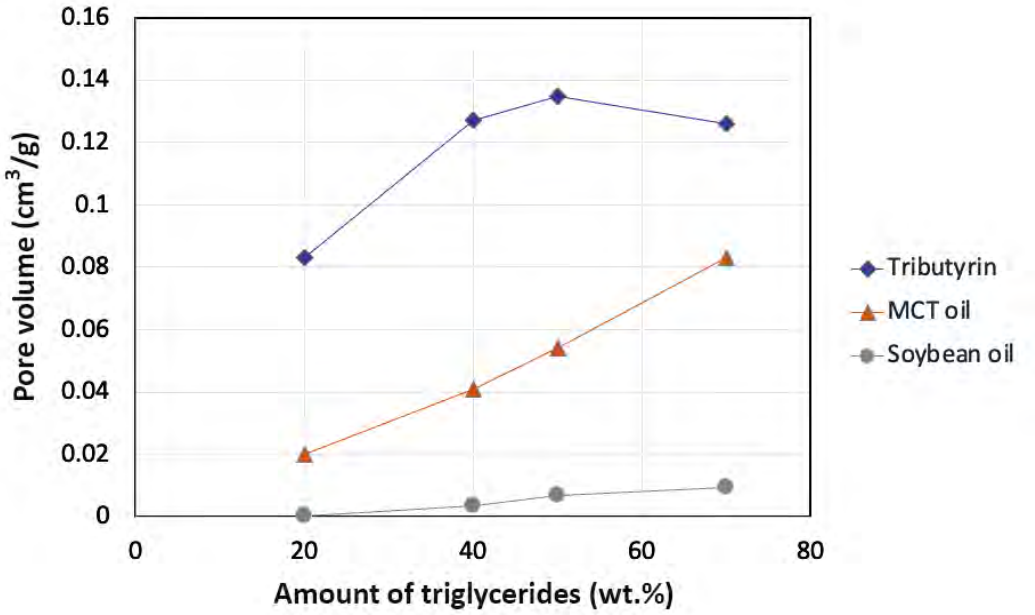

Figure S3. Effect of each type of triglycerides at 20 wt.%, 40 wt.%, 50 wt.%, and 70 wt.% on the pore volume of PMMA microspheres

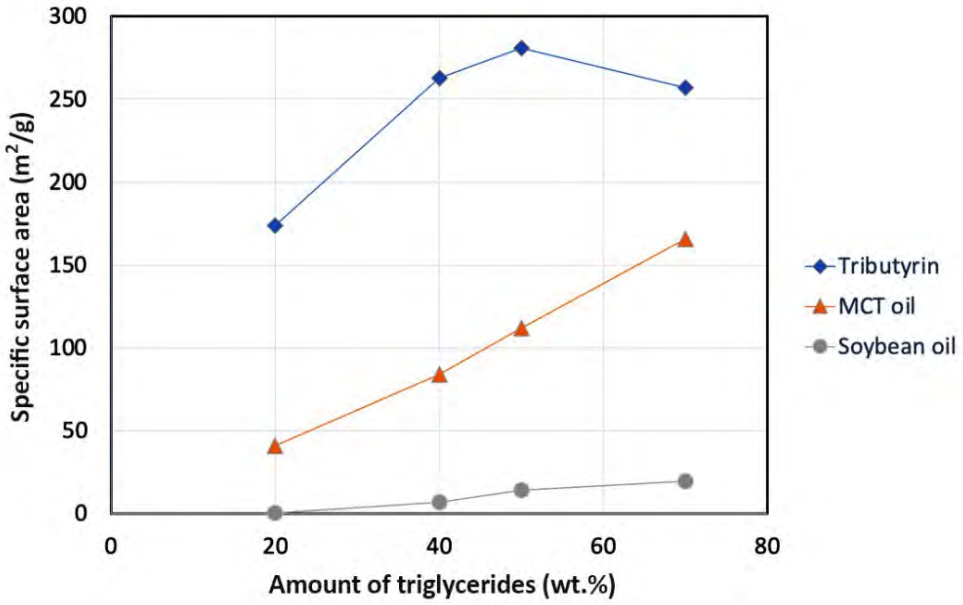

Figure S4. Effect of each type of triglycerides at 20 wt.%, 40 wt.%, 50 wt.%, and 70 wt.% on the specific surface area of PMMA microspheres

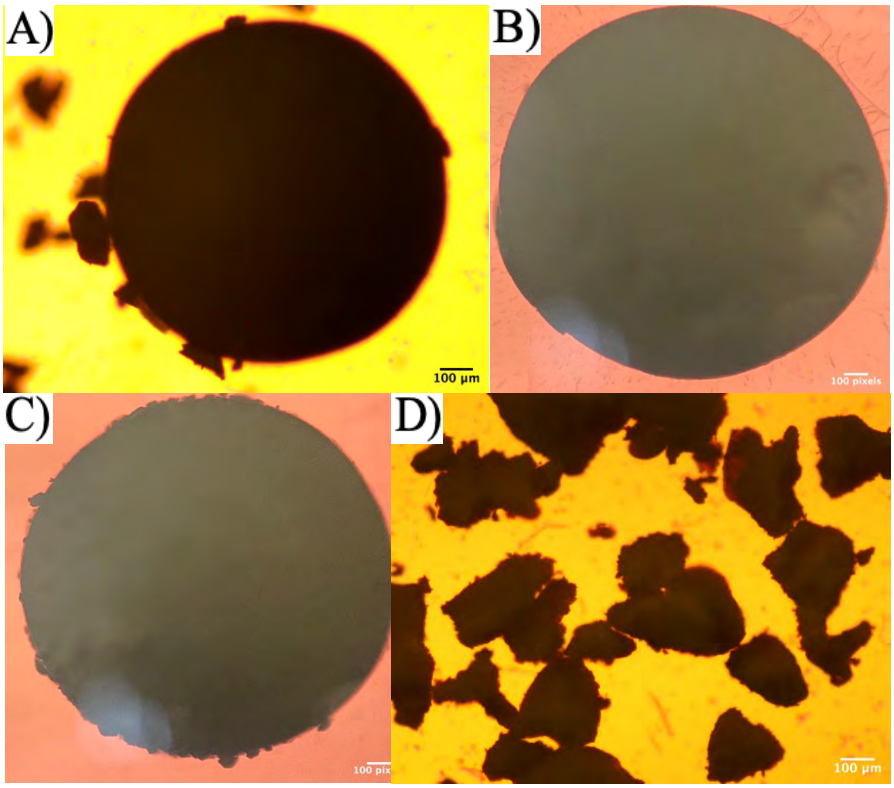

Figure S5. PMMA microsphere using MCT oil 20 wt.% (A) at 4X by an optical microscope, 40 wt.% (B) by camera phone, 50 wt.% (C) by camera phone and 70 wt.% (D) at 4X by an optical microscope

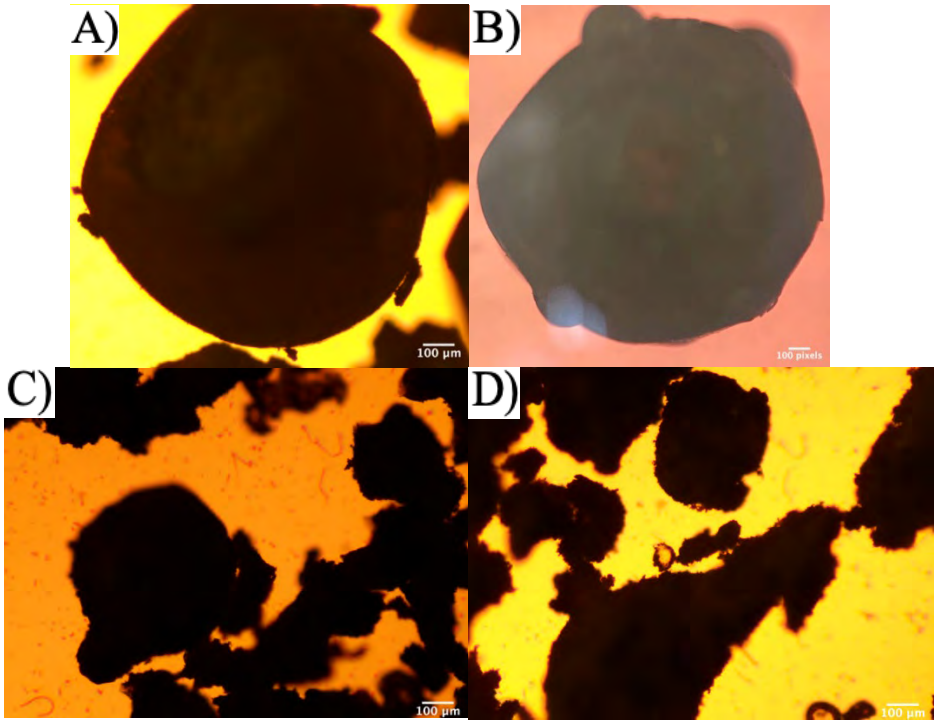

Figure S6. PMMA microsphere using soybean oil 20 wt.% (A) at 4X by an optical microscope, 40 wt.% (B) by camera phone, 50 wt.% (C) by at 4X by an optical microscope and 70 wt.% (D) at 4X by an optical microscope

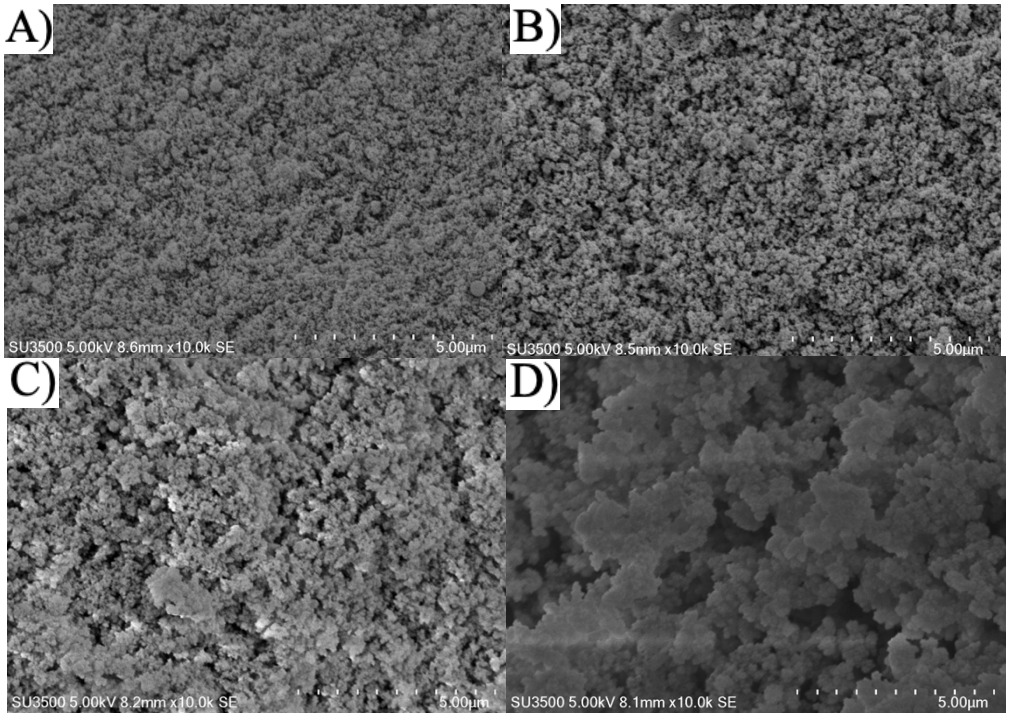

Figure S7. Cross-sectional of PMMA microsphere using tributyrin 20 wt.% (A), 40 wt.% (B), 50 wt.% (C) and 70 wt.% at 10000X by scanning electron microscope

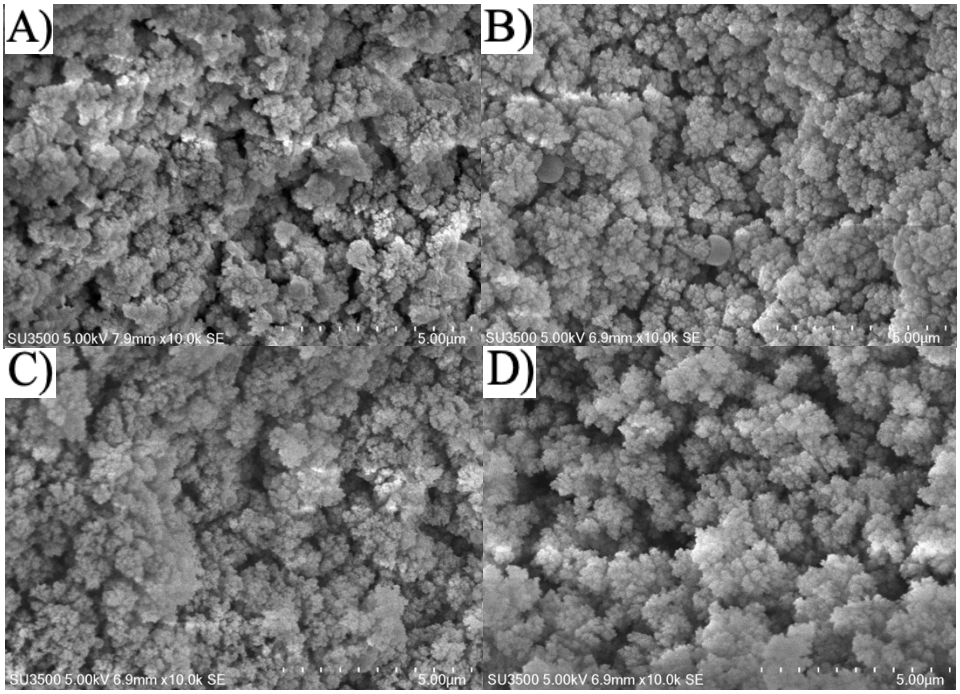

Figure S8. Cross-sectional of PMMA microsphere using MCT oil 20 wt.% (A), 40 wt.% (B), 50 wt.% (C) and 70 wt.% at 10000X by scanning electron microscope

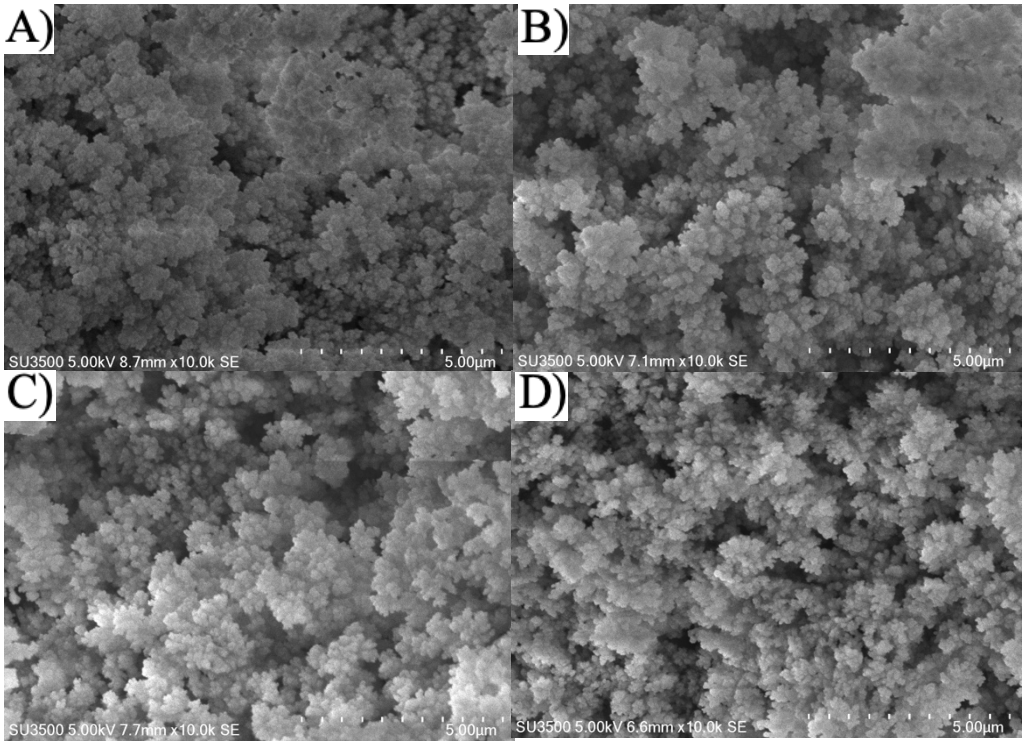

Figure S9. Cross-sectional of PMMA microsphere using soybean oil 20 wt.% (A), 40 wt.% (B), 50 wt.% (C) and 70 wt.% at 10000X by scanning electron microscope