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SYNTHESIS AND CHARACTERIZATION OF POLYMERIC MICROSPHERES BY USING SUSPENSION POLYMERIZATION TECHNIQUE

Hiung Yin Yap[1], Chin Fhong Soon[1], Nik Hisyamudin Muhd Nor[3], Muhammad Sharil Saripan[1], Mohd Zainizan Sahdan[2] and Kian Sek Tee[1]
[1]Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia
[2]Biosensor and Bioengineering Laboratory, MiNT-SRC, Universiti Tun Hussein Onn Malaysia, Parit Raja, Johor, Malaysia
[3]Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Johor, Malaysia
E-Mail: soon@uthm.edu.my

ABSTRACT

Poly-dimethylsiloxane (PDMS) is commonly used to fabricate microfluidic devices, micro-lens and biosensors. The biocompatibility of PDMS allows it to be applied in biomedical field. In this paper, suspension polymerization technique was employed to fabricate microspheres of PDMS. Solution of PDMS was prepared by adding curing agent into the base elastomer. The un-cured PDMS was heated at 40 °C and stirred from 500 to 800 rpm in order to polymerize the polymer at various stirring speed in the presence of a surfactant which consists of distilled water and poly-vinyl alcohol. The result showed that the size of the PDMS microspheres was highly variable and slightly influenced by the speed of stirring. These elastomeric microspheres can be stained by dissolving red food dye in Toluene. The microspheres produced may be applicable to biosensing that do not require standardization of microsphere size.

Keywords: PDMS, microspheres, suspension polymerization.

INTRODUCTION

Poly-dimethylsiloxane (PDMS) is a silicone based polymer that is found in domestic products such as lubricants, sealants and medical products [1]. It is also used in scientific research for the fabrication of microfluidic devices due to its excellent properties that are non-toxic, transparent and chemically inert [2]. In biochemistry sensing, the treated PDMS microspheres absorbed selected sensing agents from the local environment [3].

There are many methods that can be used to fabricate microspheres such as microfluidic, suspension and solvent evaporation techniques. From the previous work that had done by other researchers, the suspension polymerization technique was used to fabricate polymeric microspheres by varied the temperature or concentration of polymer [4]. However, speed of stir was manipulated in the suspension polymerization technique was never been discussed in previous work. Free radical polymerization is a method of polymerization in which the polymer forms by the successive addition of free radical module. Suspension polymerization technique is one of the free radical polymerization technique used to fabricate microspheres in a simple fabrication setup [4-5]. The technique is similar to emulsification polymerization technique that requires a shear force to disperse immiscible fluid before the monomer is solidified [7]. The solidification of the monomer led to the formation of dispersed polymer [6]. This technique may not be suitable to monomers that are highly soluble. Monomers that are partially soluble in water will need more complex stabilizer solution to polymerize it [4,7]. Poly-vinyl alcohol (PVA) is one of the stabilizers which is widely used to assist microspheres to create a membrane (outer layer) before the microspheres polymerized [9].

PDMS is a hydrophobic polymer. Hence, dye is difficult to diffuse into it. An alternative methods can be used to stain PDMS with a sensing agent [9-10]. Previous literature [2] shows that PDMS microspheres could be stained by mixing Toluene and a sensing dye (Porphyrin) to the PDMS elastomer before addition of curing agent. Porphyrin is a sensing agent for detection of oxygen based on optical changes.

MATERIALS AND METHOD

Suspension polymerization of PDMS microspheres

Figure-1 shows the experimental setup for the suspension polymerization technique. A flat bottomed Erlenmeyer flask was filled with 250 ml of distilled water. The flask was immersed in a water bath pre-heated to 40 ^{o}C on a hot plate with a magnetic bar. The Sylgard 184 PDMS elastomer and curing agent obtained from Dow Corning Corp was used in this experiment. 1.5 ml of monomer and 1.0 ml of curing agent at a ratio of 6:4 were dripped into the pre-warmed distilled water. After that, the poly-vinyl alcohol was slowly poured inside the stirred solution as a stabilizer. The Erlenmeyer flask was purged with nitrogen gas during the stirring of mixed solution. Similar mixtures of monomer with curing agent were prepared and stirred at 500, 600, 700 and 800 rpm using a magnetic bar. After six hours of stirring at a constant temperature of 40 ^{o}C and different constant stirring speed, PDMS mixtures turned into solid beads.

The PDMS microspheres formed were collected in a 15 ml tube by using a centrifuge at a rotation speed of 3000 rpm for 5 min. Subsequently, the distilled water was discarded and the PDMS microspheres were collected on a filter paper and allowed to air dried. PDMS are highly adhesive and sifting technique used to sort out the various

sizes of PDMS microspheres is not feasible. The experiments were repeated 3 times and 100 of samples were randomly removed for determination of the diameter.

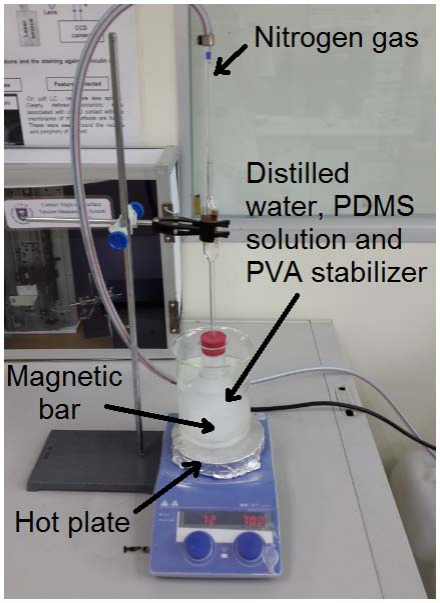

Figure-1. Experiment setup for suspension polymerization technique.

Doping red food dye into the PDMS microspheres

For the fabrication of stained PDMS microspheres, red food dye was used. First, the PDMS elastomer was added into a mixture which consists of 40 mg/ml of red food dye dissolved in Toluene. The mixture was heated at 90 °C for a day to evaporate the Toluene and left with the red dye that was mixed well in the PDMS elastomer. After the PDMS elastomer with red dye had been mixed, PDMS curing agent was added to the mixtures and then dripped into an Erlenmeyer flask that was filled with 250 ml of distilled water to synthesize microspheres using suspension polymerization technique. Similar elastomer to curing agent ratio at 6:4 was used. In the experiment, the parameters such as the speed of stirrer and temperature were set constant at 40 °C and 600 rpm, respectively.

Determining the absorbance spectrum of PDMS microspheres

The stained and unstained PDMS microspheres in red food dye were analyzed using a Fisher Scientific Multiskan Go microplate reader. The two samples of stained and un-stained microspheres were placed in 2 wells of a 96-well plate and analyzed in a range of spectrum from 200 to 850 nm at a resolution of 1 nm wavelength. This is used to determine the peak absorbance of the dyed microspheres.

Field emission-scanning electron microscopy

Field Emission-Scanning Electron Microscopy (FE-SEM) is one of the high-end equipments that are commonly used to observe the morphology of solid samples in micro and nano size. FE-SEM is a microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source [12]. The electrons bombard the surface of sample in order to generate photons, characteristic X-ray, back-scattered electrons and secondary electrons. Via the detection of these signals, the image of sample can be observed on the microscope. Therefore, the sample needs to be conductive in order for the detector to receive the reflected primary electron. Non-conductive materials such as PDMS microspheres were coated with gold or platinum target by using a JEOL JFC-1600 Auto Fine Coater powered at 20 mA in 20 s. Before loading sample into the FE-SEM, the sample was mounted on the mounting stub using double-sided carbon tape and grounded using double-sided copper tape. Sample with grounding will reduce the residue charges that can affect quality of the images. After the sample was prepared, the mounting stub was inserted into the sample holder and the sample was pushed into the specimen chamber using a stainless steel rod. After the sample was loaded, the vent valve was closed and the chamber was pumped into vacuum. This is to avoid unwanted particle to interrupt with the primary electron during the scanning process. In order to scan the sample, the minimum working distance set was approximately 4 mm. The distance can be calculated using formula, Z (Height between substrate and tip) = WD (Working distance) + H (Height of substrate). The FE-SEM is capable to scan in 3 different modes such as Secondary Electron Image (SEI), Lower Secondary Electron Image (LEI) or Low Angle Backscatter Imaging (LABE). Secondary Electron Image (SEI) mode was used to scan the SEM images of PDMS microspheres.

RESULTS AND DISCUSSION

Diameter of PDMS microspheres

In this paper, the stirring speed was varied and the other parameters (temperature, concentration of solution and volume of surfactant) were set constant. Figure 2 shows the relationship between the stirring speed and the size of the microspheres. For the increment of speed at 500, 600, 700 and 800 rpm, PDMS microspheres were obtained in smaller diameter which is 331.69, 305.70, 285.83 and 234.95 µm, respectively. From the result that had obtained, the increment of the stirring speed was decreasing the standard deviation of the diameter of the microsphere (± 14.619, ± 13.576, ± 10.652 and ± 8.193) which means the size of microsphere was nearly consistent with each stirring speed from 500 to 800 rpm. The result shows the increasing of stirring speed will decrease the diameter of the microsphere.

PDMS microspheres stained in red

Figure-3 shows the absorbance spectrum of the unstained and stained microspheres. The stained PDMS microspheres have a peak absorbance (optical density = 2.3) at 505 nm in comparison to the PDMS microspheres which show low absorbance (optical density = 1.5) across the spectrum from 300 to 850 nm. Both stained and unstained PDMS microspheres absorbed light at ultra violet range. The optical properties of the microspheres revealed absorbance ability of the microspheres. The suspension polymerization method can be used to stain the PDMS with different concentration of sensing agent. Although PDMS microspheres cannot be stained after the PDMS microspheres are formed but the staining of the polymer can be achieved during the pre-polymerization stage.

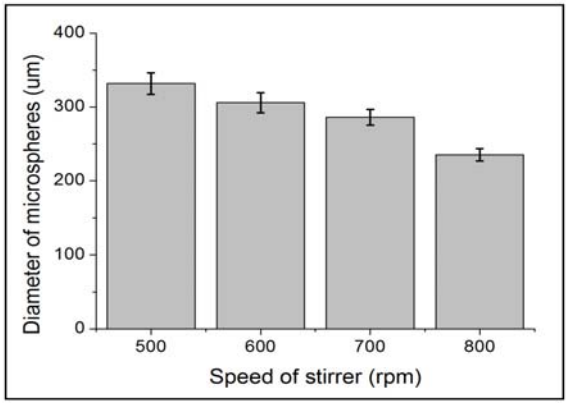

Figure-2. The diameter of the microspheres versus speed of stirrer.

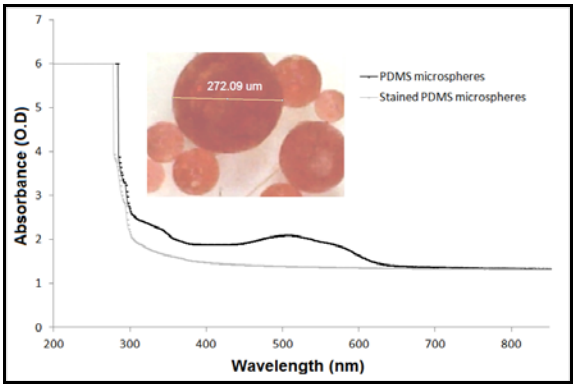

Figure-3. The absorbance spectrum of the stained microspheres. Inset: PDMS microspheres stained in red.

The surface morphology of PDMS microspheres using field emission-scanning electron microscopy (FE-SEM)

Figure-4 shows the FE-SEM micrographs of PDMS microspheres at 180 × of magnification. The PDMS microspheres were observed using Secondary Electron Image (SEI) mode. PDMS microspheres were characterized with smooth surfaces. Although the size of microspheres obtained were non-consistent with high level of variability, but this method produce relatively small size of microspheres down to tenths of micrometer. The suspension polymerization technique can produce large quantity of microspheres in simple fabrication setup. Unlike the microfluidic technique, suspension technique does not require the preparation of microfluidic device, electronic infusion system to control the flow rate of continuous phase and syringe pump to control the different flow rate of dispersion phase [13].

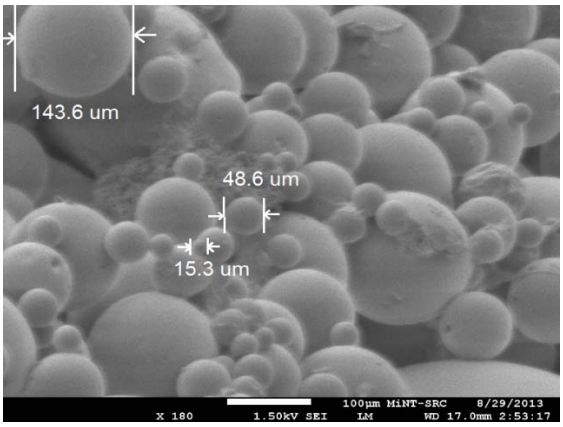

Figure-4. The size of microspheres (Scale bar: 100µm).

CONCLUSIONS

Bulk PDMS microspheres had been fabricated using simple suspension polymerization technique. The PDMS microspheres are highly adhesive in aggregates. However, the speed of stirring was influence the diameter of the microspheres. The result of spectrum indicates that the microspheres were successfully stained using Toluene. The PDMS microspheres have the potential to be applied as a sensor based on optical changes.

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