Application of Square and Oblong Pore Shapes in Rotating Membrane Emulsification to Produce Novel Particulate Products

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Abstract

Rotating membrane emulsification (RMR) has been intensively developed and applied for producing emulsion as well as particulate products such as microcapsules. Polyurea microcapsules were generally prepared by interfacial polycondensation polymerisation with addition of modifier to produce more stable microcapsules. In this research, development of the RMR was applied for producing polymer particles stabilised by nanoparticle without any addition of surfactant or modifier. Two types of membrane pores, the square (Type-A) with hydraulic diameter (D_h) of 84 μm and oblong pores with an aspect ratio of 0.33 (Type-B) having D_h of 69 μm was investigated. For the membranes designed in this research, pore shape A membrane could produce good uniformity in both polyurea microcapsule and polymer particle. In the polymer stabilised particle, this membrane type obtained a narrower size distribution than the usage for o/w emulsification. Reasonable uniform particles at high membrane rotation speed could also be achieved with the use of Type-A membrane. The uniformity confirmed that there was only minor breakup of products during operation at high membrane rotation. This attractive feature was significant in the production of fragile or shear-sensitive particulate products since the delicate structure of these products is possibly easy to destroy at high membrane rotation speed.

Keywords: *polyurea microcapsules; particles stabilised nanoparticles; slotted pore*

INTRODUCTION

Membrane emulsification has been intensively applied to producing many particulate products (Spyropoulos *et al.*, 2004). Materials for membrane emulsification were selected such as ceramic, metals, shirasu porous glass (SPG), polymer and glass (Piacentini *et al.*, 2014). In addition, microfluidic device and microfabricated channel

arrays (Kobayashi *et al.*, 2011; Purwanti *et al.*, 2015) were also selected as membrane material in membrane emulsification. Several research have reported the progress of membrane emulsification (Vladisavljević, 2019; Yuan and Williams, 2014). Development of membrane emulsification by modifying the membrane tube to rotate namely Rotating Membrane Emulsification (RMR) was presented for production of precise emulsions (Aryanti *et al.*, 2009). An emulsion is one of commonly engineered in the form of liquid-based system, Other particulates in the form of semi solid-phase covers polymeric microspheres, gel microbeads, microcapsules, colloidosomes and solid in oil in water (s/o/w) emulsion.

Developments of membrane emulsification to generate other particulate products were also reported. Collins *et al.*, (2020) studied the formation of wax walled microcapsules via double emulsion using cross membrane emulsification. Double-emulsion-templated microspheres were produced premix membrane emulsification (Na *et al.*, 2019). In addition, hollow microspheres were prepared by Janus membrane emulsification (Chen *et al.*, 2019). Ohta *et al.* (2019) fabricated the PEG-coated PLGA microspheres via Shirasu Porous Glass (SPG) membrane emulsification. Furthermore, the RMR was successfully applied for production of agarose bed (Li *et al.*, 2015), food grade emulsion (Hancocks *et al.*, 2016), as well as pickering particle and emulsifer co-stabilised emulsions (Arkoumanis *et al.*, 2019)

This research emphasised production polyurea (PU) microcapsule and nanoparticle stabilised polymer particulate products via RMR. A microcapsule (MC) is a reservoir containing an active substance surrounded by a thin shell. Microcapsules are spherical or irregular particles in size between 50 nm to few hundred micrometres. Microencapsulation involves the embedding of at least one ingredient (active agent or core) into at least one other (shell material). In general, PU microcapsule prepares by interfacial polycondensation polymerisation (Hedaoo *et al.*, 2014; Scarfato *et al.*, 2007) with some modification process or adding a modifier. Difunctional and trifunctional isocyanate monomers were added in production of PU shell (Chang *et al.*, 2005). Isophorone Diisocyanate (IPDI) Trimer was added in PU microcapsule formation (Hedaoo *et al.*, 2014). In addition, El-Gibaly and Anwar (2004) used 4,4-diaminostilbene-2,2-disulfonic acid as co-monomer. A postmodification process of PU formation was studied using functional polyelectrolite (Fluorescein isothiocyanate) to investigate the chemistry on PU microcapsule surface and characterise the nucleophilic groups on the surface (Li *et al.*, 2011). Recently, Fu *et al.* (2019) prepared PU microcapsules by using chitosan oligomer as the wall material.

In this research, the RMR was applied for manufacturing polyurea microcapsules with no addition of surfactant or modifier. Moreover, surfactant-free polymer particles stabilised by nanoparticles via the RMR were investigated. Since research exploring particle stabilised emulsion using non-conventional emulsification process was not available, application of the RMR for producing polymer particle by nanoparticle was an attractive feature.

MATERIALS AND METHOD
Materials

Polyurea was synthesized using polymerization reaction of isocyanate and amine. In this experiment, Desmodur N3300 (Bayer, Provided by WhitChem Limited, UK) was used as isocyanate source and dietylenetriamine (DETA, 98.5%, Acros Organics) was utilized as active hydrogen-containing component. N3300 is a mixture of Hexamethylene diisocyanate (HDI) oligomers. The oligomer distribution is consist as trimer (~50%), pentamer (> 20%) and heptamer + over (>30%). N330 with –NCO content 21.8% (w/w) was soluble in Toluene, having functionality value, viscosity and specific density of 3.5, 3000 and 1.16, respectively. DETA was soluble in water, having functionality value of 5 and a specific density of 0.95. A mixture of toluene as solvent and Desmodur N3300 (75% v/v) was employed as dispersed phase (oil phase) in order to produce droplets (microcapsules) within amine solution (1.5% v/v of DETA). Polyurea microcapsules were obtained using interfacial polymerization method. The chemical structure of trimer as a representative of N3300 and DETA are shown in Figure 1.

Oil in water emulsion was prepared with low viscosity paraffin wax (Fluka) with viscosity of 24 mPa.s as the dispersed phase. Tween 20 (polyoxyethylene sorbiton monolaurete) (Fisher Scientific, UK) was selected as emulsifier.
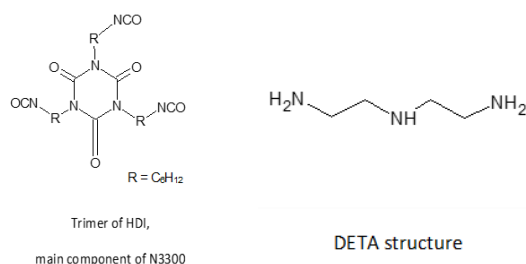

Figure 1. Structure of N3300 trimer and DETA

Rotating Membrane Emulsification (RMR)

The RMR emulsification apparatus comprised a tubular stainless steel membrane mounted on the shaft of a digital overhead stirrer (IKA Eurostar, No. 24820.00) to provide rotation of the membrane. The membrane was positioned vertically and centrally in a fixed measuring cylinder holding the continuous phase, Figure 2. The membrane rotation speed was varied from 700 - 1000 rpm, which corresponded to a shear rate range of
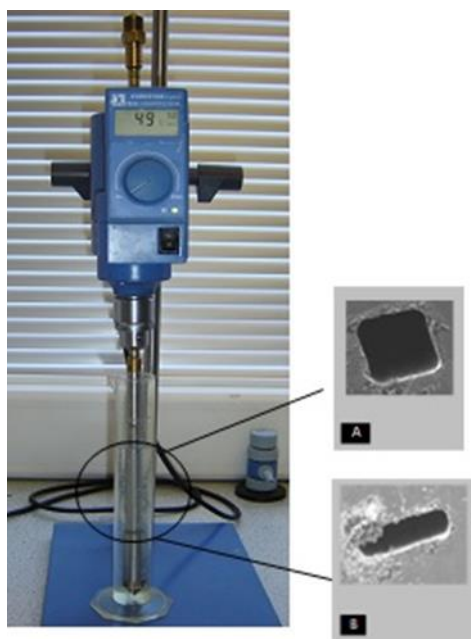
Figure 2. Batch rotating membrane reactor arrangement with stainless steel membrane positioned inside a measuring cylinder. Insert pictures are the SEM images of the drilled profile of Type-A and B membranes
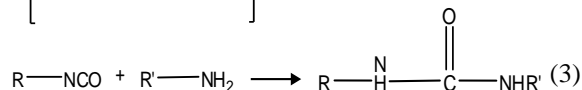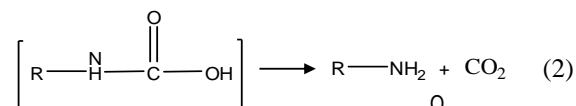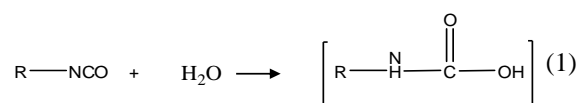
approximately 14 - 27/s. Flow rate of dispersed phase data were obtained using a stepwise flow syringe pump (Razel A99FMZ, Fisher Scientific) with a flow rate capacity up to 210 ml/h for dispersed phase injection (Aryanti et al., 2009). The syringe pump was connected with the membrane tube through a rotary transfer. The droplets formed were sampled on glass slides and analysed using microscopy. All the experiments were carried out at a constant ambient room temperature which was 23 °C. After each experiment, the membrane was carefully cleaned inside and rinsed thoroughly with distilled water to ensure that there was no cross-contamination between any two consecutive experimental runs.

The tubular membrane were fabricated consisting of round pores and pores with different pore aspect ratios. Membrane has square pores with an aspect ratio (L/W) of 1 was named as Type-A membrane and oblong pores with aspect ratio of 1:3 (0.33) was called as Type-B membrane. Pore length and pore width of the square membrane were 80 μm. For the oblong pores, the pore length was 46 μm and the pore width was 138 μm with pore hidraulic diameter (D_h) of 69 μm. The membrane pores were fabricated by Oxford Lasers Ltd. (Oxfordshire, UK) using trepanning technology.

Production of Polyurea Microcapsules

Polyurea were obtained from the reaction of amino-functionalized monomers of polyamine with isocyanate. The reaction is a part of the moisture-curing process for isocyanates, with react with water

to afford moisture-cured polyurea coatings. The reactions for the moisture-curing process are described in the following (Ni *et al.*, 2002):

$$R-NCO \ + \ H_2O \longrightarrow \left[R-\underset{H}{N}-\underset{\underset{O}{\|}}{C}-OH \right] \quad (1)$$

$$\left[R-\underset{H}{N}-\underset{\underset{O}{\|}}{C}-OH \right] \longrightarrow R-NH_2 \ + \ CO_2 \quad (2)$$

$$R-NCO \ + \ R'-NH_2 \longrightarrow R-\underset{H}{N}-\underset{\underset{O}{\|}}{C}-NHR' \quad (3)$$

In reaction (1), isocyanate group reacts with water forming a carbamic acid intermediate. This carbamic is unstable and will spontaneously decarboxylate into an amine and carbon dioxide as illustrated in reaction (1). Amine further reacts with another isocyanate groups to produce a urea crosslink (reaction (3)).

Production of polymer via an emulsion precursor stabilised by nanoparticles

A polymer solution containing bisphenol type polyester resin (20% wt) of ethyl acetate was used as dispersed phase and silica nanoparticle (Nalco 1060, 100 nm) was used by stabiliser. An aqueous solution containing 15% wt% of Nalco solution was prepared as the continuous phase. The polymer solution has viscosity of 8.7 mPas at shear stress of 1.5 Pa and 20 °C while the aqueous phase has viscosity of 1.7 mPas. The disperse phase was introduced into the centre of the membrane tube by a pipette and permeated through the membrane pores under the driving force of the hydrostatic head into the continuous phase (Yuan et al., 2014).

Particle and Membrane Analysis

Offline particle analysis was used to characterize the emulsions and novel particulate products. The droplets/particulates formed were taken from continuous phase container using pipette and were sampled on a glass slide without coverslip. Droplet sizes were analysed by a digital microscope (Nikon model SMZ800) based on fields of view from the sample using magnification from 10 to 63 times. For each experiment, several emulsion samplings (more than 5) were taken. Each sampling could produce about 3-5 fields of view. Every field of view consisted of numerous droplets depending on their sises (Aryanti et al., 2009).

The images were recorded by digital camera (Spot Insight QE Model 4.2) and controlled by SPOT Advanced software. The droplet diameter was then measured from image analysis and data were calculated from more than two hundred measurements using an ImageJ software. The software allowed to

measure and to count automatically the droplets being present in selected fields of view. In some cases (e.g. for close contact droplets), manual measurements were required in order to provide a precise droplet size (Aryanti et al., 2009).

The droplet size was represented by average diameter and number-based size distribution. The uniformity of the droplets was evaluated in the terms of coefficient of variations (CV) which is defined as:

$$CV = \frac{S_d}{D_{avg}} x100 \qquad (1)$$

$$D_{avg} = \frac{\sum N_i D_i}{\sum N_i} \qquad (2)$$

$$S_d = \sqrt{\frac{\sum N_i (D_i - D_{avg})^2}{\sum N_i}} \qquad (3)$$

Pores of the new membrane designs were characterised using both a digital microscope (Nikon model SMZ800) and a scanning electronic microscope (SEM, Philips XL-30ESEM). The membrane was sat on an aluminium stud through a conductive tape and then placed in the vacuum chamber directly without any surface treatment. Each membrane was imaged for 10-15 pores at a magnification of 250 times for examining the pore morphology and dimension.
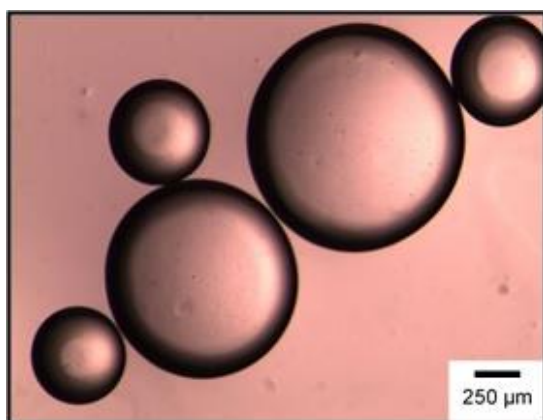

Figure 3. Photomicrograph of polyurea microcapsule using round pores membrane at membrane rotation speed of 700 rpm, dispersed phase flow rate of 0.026 m³/m².hr

RESULTS AND DISCUSSION
Uniformity of Urea Microcapsules
The photomicrograph of polyurea microcapsule is presented in Figure 3. The figure shows that the microcapsule shape was spherical although the uniformity was poor. The spherical shape of microcapsule confirmed that amount of isocyanate was enough to react both with water and amine. Microcapsules having average diameter of 576 μm

with coefficient of variations (CV) of 37% were obtained. The capsules were much larger in size (some exceeding 800 μm) than the o/w emulsion produced with the same membrane rotation speed and dispersed phase flux. Using round pores membrane with 100 μm in diameter, the ratio of the capsule to droplet diameter was 5.7. The poor uniformity of microcapsule was caused by high interfacial tension of dispersed-continuous phase resulting from the absence of surfactant.

In conventional emulsification process, observations showed that capsule membrane fragments were present (Ni *et al*., 1995). Figure 3 suggests that there was no evidence of fragmentation of the capsules. Such fragmentation would have indicated that the initial capsules had non-uniform strength, leading to the possibility of breakage of some capsules in the population. The initial capsule membrane was formed due to the polymerisation reaction between monomer at each dispersed and continuous phase. The monomer at each phase diffuses into oil-water interface and reacts to form a polymer surrounding the droplet (the initial membrane). When the initial membrane is formed, the water-soluble monomer has to diffuse across the membrane into the oil phase reacting with the oil-soluble monomer to thicken and to strengthen the membrane (Korshak and Vasnev, 1989). With the type of result obtained in Figure 3, it can be seen that the RMR system appears feasible for producing polyurea microcapsules.

Figure 4 shows a comparison of particle size distribution between basic o/w emulsion and polyurea microcapsule using 100 μm round pore.
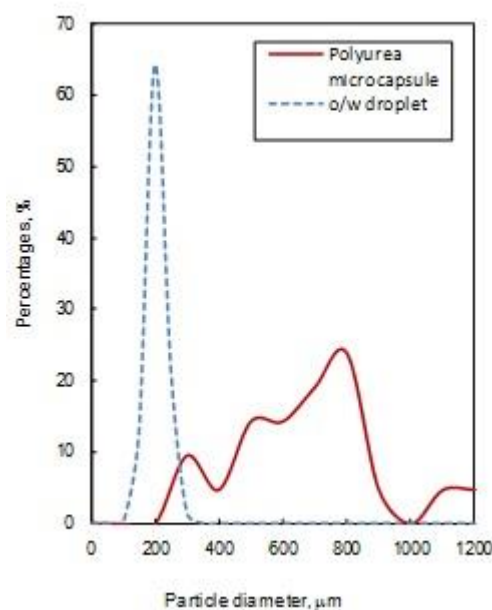

Figure 4. Droplet size distribution of o/w emulsion and the final polyurea microcapsule at membrane rotation speed of 700 rpm, for dispersed phase flow rate of 0.026 m³/m².hr

The size distribution of polyurea microcapsules was wider, bimodal and generated non-uniform microcapsules compared to the size distribution of o/w emulsion. This is because the stabilisation process in the polyurea microcapsule was mainly based on interfacial tension itself without adding any surfactant or modifier in the continuous phase. Some studies in polyurea microcapsule used different modifier in order to prevent agglomeration and increase capsule uniformity. Surfactants such as Tween 20, Tween 40, Tween 80 and PVA or carboxy metyl cellulose (Hashemi and Zandi, 2001) and Span 80 (Hongbing, *et al.*, 2008) were addedd to continuous phase to improve capsule characteristics. In addition, modifications composed difunctional and trifunctional isocyanate monomers (Chang *et al.*, 2005), Isophorone Diisocyanate (IPDI) Trimer (Hedaoo *et al.*, 2014), 4,4-diaminostilbene-2,2-disulfonic acid as co-monomer (El-Gibaly and Anwar, 2004) were studied. In addition, a postmodification process of PU formation by using functional polyelectrolite (Fluorescein isothiocyanate) was reported (Li *et al.*, 2011).

Figure 4 also shows that the average droplet size for o/w emulsion is 182 μm. This gave droplet size/ pore size ratio of only 1.8 which is smaller than droplet size/pore size ratio for polyurea, 5.7. Droplet production rate for o/w emulsion was about 6 droplets per second. In contrast for polyurea microcapsules, droplet production rate was poor which was only 1 droplet per second. Low droplet production rate is reasonable since in polyurea microcapsule the dispersed phase has high viscosity. For polyurea microcapsule formulation, the dispersed phase is a mixture of hexamethylene diamine (HDI) and toluene which has higher viscosity compared to paraffin oil in o/w emulsification. The high viscosity of dispersed phase leads to less detaching force of the droplets from membrane pores. In addition, for polyurea microcapsule formulation the absence of surfactant in the continuous phase caused high interfacial tension.

This results in high capilary force which is the major force of holding droplets. Both less detaching force and high holding force yielded capsules with large sizes. As the large droplet had long time to detach, the droplet production rate of polyurea microcapsule was significantly smaller than droplet production rate of o/w emulsion.

Polyurea microcapsule using a membrane Type-A produces more uniform microcapsules (Figure 5). The examination of Type-A membrane for o/w emulsions confirmed that the pore shape could produce reasonably uniform o/w droplets. The figure presents improved polyurea capsules and better uniformity compared to Figure 3. The capsules have 464 μm in size with CV about 12.5%. This size is 20% smaller than capsules produced with round 100 μm membrane. The CV of capsules confirmed better uniformity, a decrease from 37% to 12.5%.

Figure 6 depicts comparison of particle size distribution between the o/w emulsion and polyurea microcapsule using Type-A membrane at the same operational condition (membrane rotation speed of 700 rpm and dispersed phase flow rate of 0.096 m^3/m^2.hr).

The figure illustrates the improvement of uniformity of the polyurea microcapsule formed. The capsule size distribution was narrower and showing unimodal distribution. This result confirmed that polyurea microcapsule with uniform size could be produced through RMR using Type-A membrane without adding any surfactant in the continuous phase.
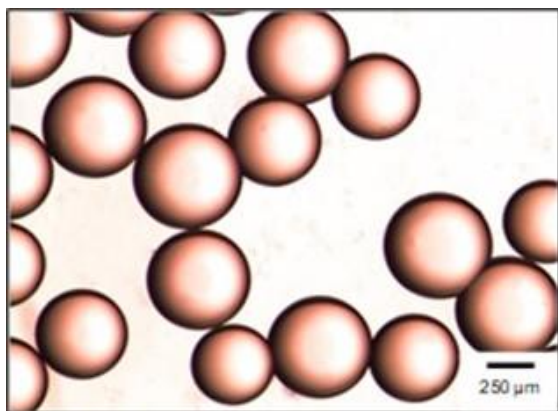

Figure 5. Photomicrograph of polyurea microcapsule using Type-A membrane at membrane rotation speed of 700 rpm, for dispersed phase flow rate of 0.096 m^3/m^2.hr
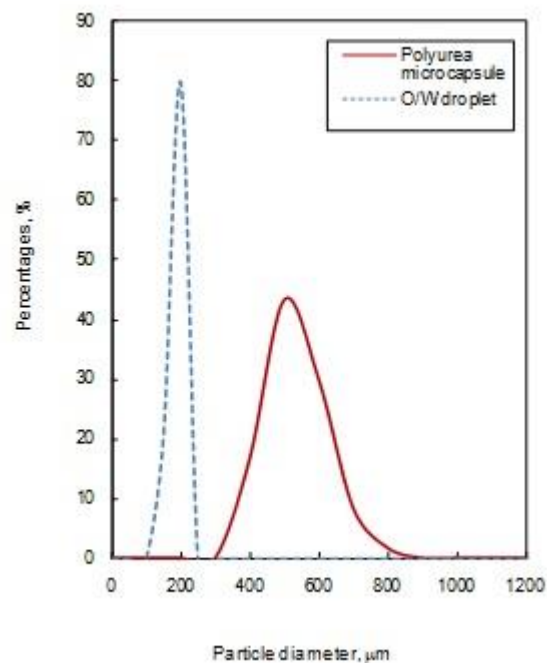

Figure 6. Size distribution of the o/w droplet and polyurea microcapsule using Type-A membrane at rotation speed of 700 rpm, for dispersed phase flow rate of 0.096 m^3/m^2.hr

Moreover, it was a significant result since the capsules could be stabilised only by interfacial polymerisation. Another point to consider that membrane pore shape also plays an important role in maintaining capsule stabilisation since it can produce more uniform capsules. In this case, the size distribution of the capsules is evidently uniform (cf. Figure 4) confirming the absence of significant capsule breakage or coalescence.

Type-A membrane was able to produce droplets at similar size continuously. For o/w emulsion at 700 rpm the Type-A membrane produced about 20 droplets per second while for polyurea microcapsule the membrane generates just 2 droplets per second. Although the droplet production rate for polyurea microcapsules was not as great as droplet production rate for o/w emulsion, the use of Type-A membrane for polyurea microcapsule formulation slightly enhanced the droplet production rate from 1 droplet per second using round pore to 2 droplets per second. The low droplet production rate was caused by high viscosity of dispersed phase and high interfacial tension of continuous phase as described before.

Stability and Structure Assessment

In order to test the stability of produced microcapsules, an assessment was conducted by examining the capsule sizes after a couple of days. The microcapsule stability is demonstrated in Figure 7. The figure illustrates that there is no significant difference in capsule diameter after 24 hours, 48 hours and 1 week assessment. The capsules have reasonably uniform diameters at about 670 μm. The result confirms that the capsule has good stability in terms of its size.
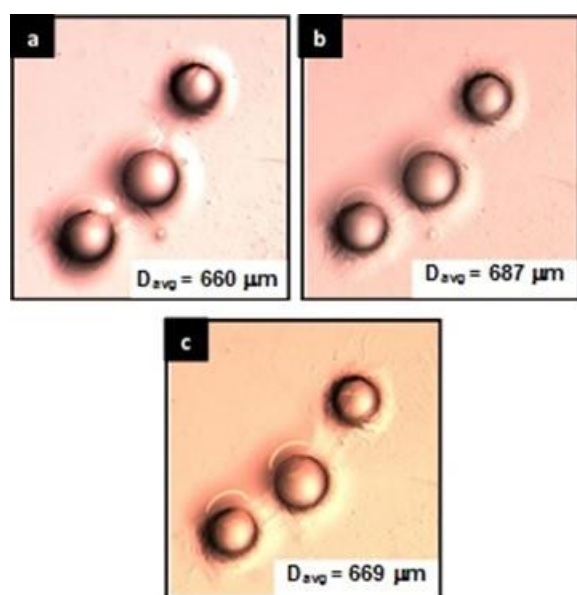

Figure 7. Photomicrograph of coarse polyurea microcapsules showing microcapsule stability at : (a) 24 hours, (b) 48 hours and (c) 1 week
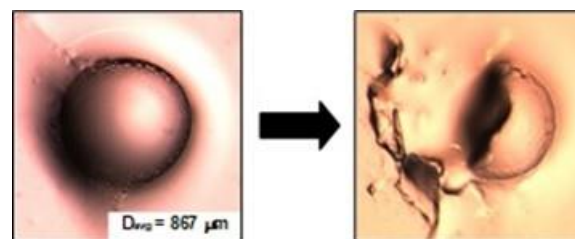

Figure 8. Microscopic images of a coarse polyurea microcapsule produced using RMR round pore 100 μm at 700 rpm and oil phase efflux of 2.6×10^{-2} $m^3/m^2.hr$ showing inside the structure of the microcapsule

Further, an assessment to verify the microcapsule structure was performed by breaking the coarse microcapsule. The result is shown in Figure 8. The broken capsule shows its core-shell and spherical structure. An examination of polyurea microcapsules using toluene diisocyanate (TDI) as isocyanate source showed that the capsules were not always reported to be completely spherical and had thick walls (Hong and Park, 2000).

In addition, the capsules with spherical and clear surface were also reported when the mixture of TDI and isophorone diisocyanate (IPDI) was used. Difference morphology of polyurea microcapsule (shape, roughness and thickness) certainly affected the release behaviour of the microcapsule. However, the result of stability and structure assessment demonstrated that the hexamethylene diamine (HDI) was a good isocyanate source since acceptable polyurea morphology could be obtained. In conclusion, the key outcome is that RMR is a feasible process for the production of stable core-shell structured microcapsules.

In the polyurea microcapsule system, toluene and isocyanate are an encapsulated material and amine-isocyanate acting as the wall material and the microcapsule formation is based on interfacial polycondensation method. With this method, the capsule shell is formed at the interface of two immiscible phases (droplet/liquid) containing complementary monomer. One monomer (amine) is present in the continuous phase and the other monomer isocyanate is present in the dispersed phase. When those two monomers meet at the interface, a polycondensation reaction is taking place and the core material is surrounded by a polymeric layer. Since amine is insoluble in droplet phase, the polycondensation results in the formation of reservoir microcapsule. The schematic structure of a core-shell polyurea microcapsule is illustrated in Figure 9.

Nanoparticle-stabilised Polymer

Emulsion can also be stabilised by solid nanoparticles. Particle-stabilised emulsions have advantages compared to the usage of surfactant in
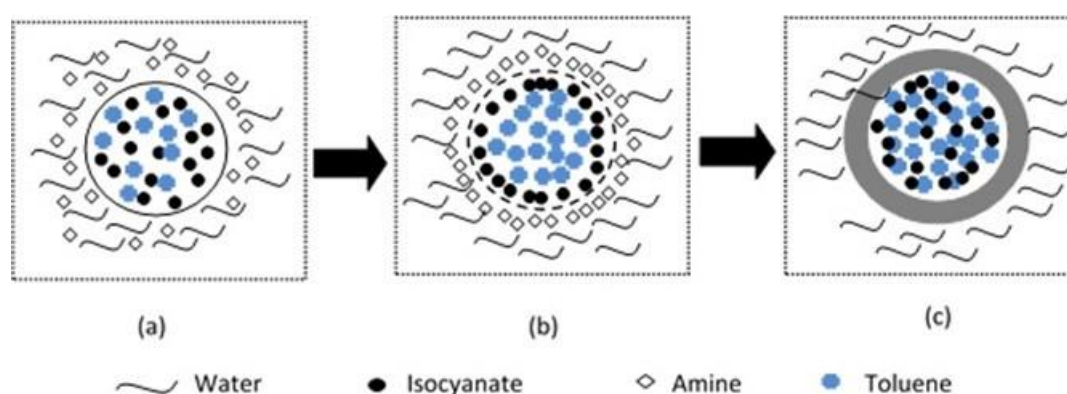
Figure 9. A schematic illustration of polyurea core-shell microcapsule formation

terms of stability enhancement to prevent coalescence and elimination of adverse effect of surfactants. Compared to the surfactant system, particles do not assemble into aggregates in the same way that surfactant molecules form micelles and hence there is no solubilisation phenomenon in the use of particles (Aveyard *et al.*, 2003). In addition, particle-stabilised emulsions which are close to inversion point tend to be the most stable.

As conventional emulsion works at high mechanical shear which is possible to break up the nanoparticle aggregates, it is difficult to fabricate structure with uniform layer thickness and pore size especially those with large pore size (Xu *et. al.*, 2005). With the use of emulsification process such as membrane emulsification, microfluidic or microchannel, uniform and monodispersed droplets could be achieved and hence it is possible to produce highly emulsion structure. To date, only limited research exploring particle stabilised emulsion using non conventional emulsification process is available. Xu *et al.* (2005) described the preparation of o/w emulsion stabilised solely by completely hydrophilic silica particle using microchannel emulsification. The results show that the microchannel emulsification process is suitable for preparing o/w emulsion stabilised solely by hydrophilic silica particle. In addition, using the microchannel emulsification the thickness of the adsorbed layer was bigger in size and no breakup took place during emulsification.

In view of the fact that the new membrane design of the RMR was a promising method to produce a uniform and monodispersed droplet. Further study was carried out using nanoparticles to stabilise the emulsion precursor to polymer particle manufacture. Two different types of pores, namely Type-A and Type-B membranes were examined and polymer particles uniformity were characterised based on droplet size, coefficient of variation (CV) and particle size distribution.

Figure 10 shows the quite uniform polymer particle stabilised by nanoparticles using Type-A and Type-B membrane. For Type-A membrane, the polymer particles have 182 µm in average size with CV about 10.3 % and have particle/pore aspect ratio of 2.2. As comparison, the Type-A membrane at 1000 rpm produces o/w droplet with average diameter of 140 µm and CV of 13.5%. By using Type-B membrane, the average polymer particles size was 282 µm with CV about 16% and particle/pore aspect ratio of 4.3. In contrast for o/w emulsification using Type-B membrane, the average droplet size was 124 µm with CV of 13% and particle/pore aspect ratio of 1.9. Polymer particles prepared using Type-B membrane had a larger average diameter compared to particles prepared using Type-A membrane. This was caused by higher capillary pressure of Type-B membrane and more pore fluid velocity of this type membrane compared to those of Type-A membrane. Based on the result obtained in Figure 10, the polymer particles have average diameters larger than the o/w emulsion droplet. The large diameter was presumably caused by different viscosity of the dispersed phase between the paraffin oil in o/w emulsification and polymer particle. The dispersed phase for o/w emulsification was low viscosity paraffin oil which had the viscosity of 24 mPas, while the dispersed phase viscosity for polymer particle production was 8.7 mPas. The low viscosity of disperse phase gives result to a small capillary number compared with the higher viscosity of dispersed phase. As the capillary number was smaller, the viscous force was less dominant than the interfacial tension force. This would slow down the particle detachment from the pores and result on larger particle diameter.

In addition, the results obtained in Figure 10 illustrates that the size distribution of the polymer particle membrane was slightly narrower than size distribution of o/w emulsion when the Type-A membrane was used. This confirms that the size distribution of polymer particle was more uniform than the o/w emulsion. In addition, it can also be evidence that Type-A membrane had worked well for producing nanoparticle-stabilised particle polymer.
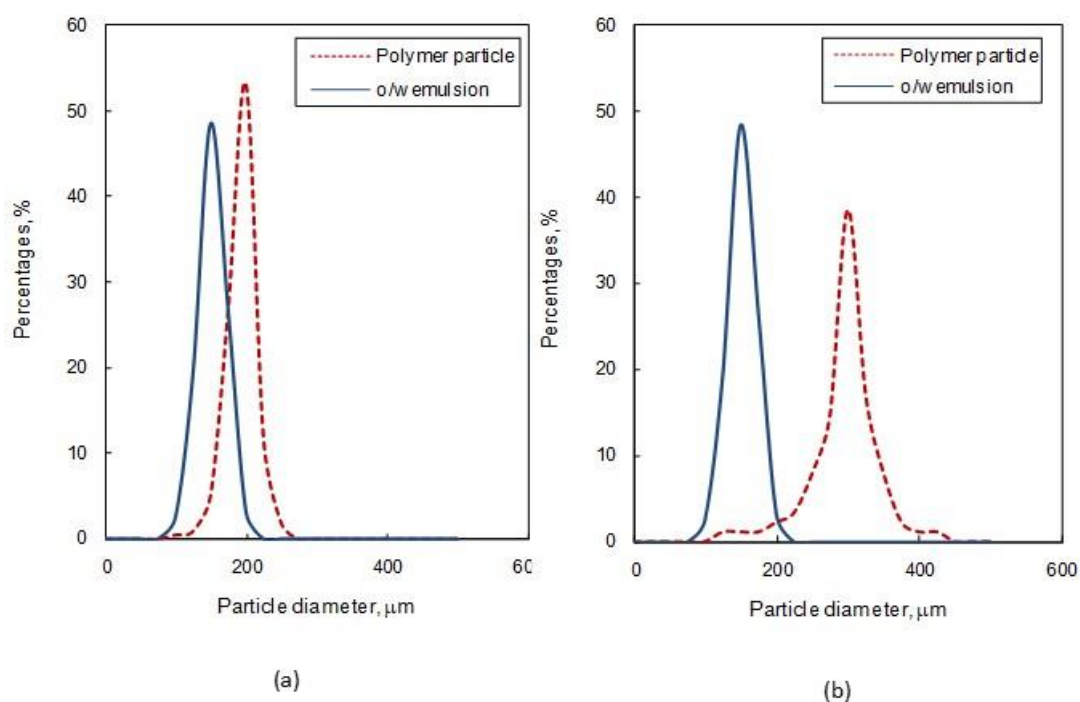
(a)

(b)

Figure 10. Droplet distribution of polymer particle at membrane rotation speed of 1000 rpm (a) Type-A membrane and (b) Type-B membrane
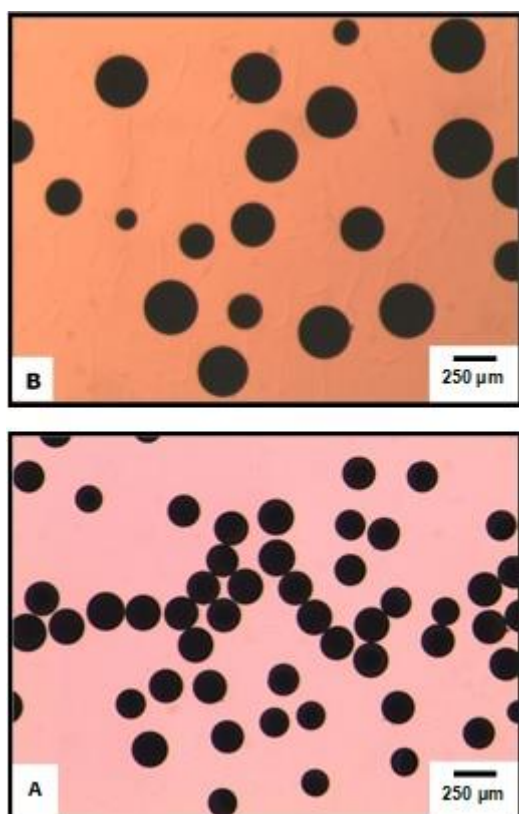

Figure 11. Photomicrograph of polymer particles stabilised with nanoparticles at the membrane rotation speed of 1000 rpm using (A) Type-A and (B) Type-B membrane

Figure 11 shows the photomicrograph of polymer particles stabilised with nanoparticle prepared using Type-A and Type-B membranes. According to the figure, the black colour in photomicrograph images was caused by the adsorption of nanoparticles at the oil-water interface. In a particle stabilised emulsion, the mechanism of stabilisation can be achieved by adsorption of particle at the oil-water interface and remain there to form a dense (monolayer or multilayer) around the droplets to reduce coalescence. Further additional stabilisation also possibly takes place when there are particle-particle interactions forming a three-dimensional network of particles in the continuous phase surrounding the drops. It was reported that once adsorbed, particles would be strongly held at oil-water interface (Binks and Lumsdon, 2002). With this fact, it was also assumed that there was no desorption of adsorbed nanoparticle from the droplet surface.

CONCLUSION

The application of rotating membrane emulsification for producing functional particulate products have been investigated using polyurea formulation and polymer particle stabilised by nanoparticles. Square pores (Type-A membrane) and oblong pores with an aspect ratio of 0.33 (Type-B membrane) were also examined for polymer particle production in order to observe their performance.

Polyurea microcapsules produced using the RMR showed good uniformity especially with the Type-A membrane. Time stability assessment

demonstrated that the microcapsule was stable in the term of size. Structure assessment illustrated that a core shell structure could be obtained. Moreover, good achievement could be demonstrated because acceptable uniformity capsules and narrow particle size distribution were produced with the absence of surfactant.

NOTATION

CV   : Coefficient of Variation, %
D_{avg} : Average droplet diameter, μm
D_h : Hydraulic diameter, μm
N_i : Number of particles counted at the mean fraction size D_i.
S_d : Standard deviation of droplet diameter

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