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TUNING MORPHOLOGY OF MAGNETIC NANOPARTICLES-POLYMERIC MICROCAPSULES VIA ALTERING POLYETHYLENE GLYCOL (PEG) MOLECULAR WEIGHT

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ABSTRACT

Microcapsules are small particles with a size between 1 and 1000 µm comprising an active agent surrounded by natural or synthetic polymeric membrane materials which found remarkable advantages in engineering application such as environmental, catalysis, biomedical and sensing. One of the key benefits to realize microcapsules potential is through tuning porous structure which enable more active sites for reaction etc. Introduction of polymeric additive as pore former agent such as Polyethylene glycol (PEG) could be attractive option to enhance the diffusion capability of the microcapsules. Thus, this study embarks on the influence of different molecular weight of the PEG in tuning the morphology of the synthesized microcapsules. It is concluded that incorporation of different PEG molecular weight could tailor the morphology and pore structure of the resultant microcapsules.

Keywords: Nanoparticles; Microcapsule; tuning morphology; PEG molecular weight

INTRODUCTION

Microcapsules are small particles with a size between 1 and 1000 µm comprising an active agent surrounded by natural or synthetic polymeric membrane materials [1]. Microcapsule has remarkable advantages in engineering application for pollutants removal and biomedical field for transportation [2]. It has obviously drawn attention from the research community. Undeniably, it does have shortages but the key is to balance both the advantages and limitations to enhance microcapsule benefits. In environmental engineering application, microcapsules could serve as encapsulation agent of nanoparticles (NPs) to drastically reduce the risk associated to nano-toxicity

when it is indirect contact with surroundings [3]. In addition, this technique could improve the physical contact and promote catalytic degradations of pollutants while exhibit better recyclability without loss of activity after multiple catalytic degradation cycles [4], [5].

Earlier, our group had reported [3] Poly(vinylidene fluoride) (PVDF) is one of the promising polymer candidate of the main building block of the microencapsulation of the magnetic nanoparticles (MNP) for water remediation application using phase inversion mechanism. One of the PVDF distinct advantageous due to its of its desirable properties such as high hydrophobicity, excellent chemical and thermal resistances [6], [7]. One of the common issues of this system is the diffusion-limited which limits the penetration of the potential pollutants into microcapsules which could enhance the reaction rates of the pollutant degradation. In order to prepare high performance PVDF used as microcapsules, high porosity and suitable surface pore sizes and pore size distribution are essential to enhance the uptake rate [7], [8]. Therefore, as a commonly adopted approach, additives or pore formers are often used to balance or improve the uptake rate performance of the final microcapsules through adjusting the PVDF structure in the phase inversion process [9], [10]

Hence, this work primarily focuses on the tuning the morphology of the porous structure of the magnetic nanoparticles-PVDF microcapsules via using polyethylene glycol (PEG) as pore former. The influence of different molecular weight of PEG on the structures and morphologies of the microcapsules will be investigated. We anticipate PEG could induce or suppress the macrovoid expansion for PVDF microcapsules systems depending on its molecular weight Therefore, in this section the effects of PEG molecular weight will be presented to demonstrate its structural changes.

EXPERIMENTAL

Preparation of PVDF-PEG solution

PVDF (Poly(vinylidene fluoride)- Molecular weight 275, 000 g/mol) supplied by Sigma, Polyethylene glycol (PEG) with three different molecular weight (1,000 g/mol, 10,000 g/mol) and 35,000 g/mol) bought from Merck and DMF (N-Methylformamide) were prepared in the mass ratio of 1:0.5:9 (with 10 wt% of PVDF in the prepared polymeric solution). Initially, 10 g of PVDF powder and 5 g of PEG were added into a beaker containing 90 g of DMF solvent with the sensor tip of thermometer immersed into the solvent. After addition of mixture powders, it was sealed with parafilm instantaneously. In addition, the mixture was subjected to constant stirring at 180 rpm and stepwise heating from room temperature to 65 °C with a heating rate of 1−18 °C/minute simultaneously. This mixture was then being left under quiescence condition for 70 minutes after its temperature had reached 65 °C. Immediately after this step, the solution was cooled to 40 °C and left under constant stirring overnight.

Preparation of MNP-PVDF solution

The required amount of nanoparticles for synthesis of particles-polymeric microcapsule is 0.5 wt% of iron oxide MNPs-PVDF solution. Initially, 10 g of prepared PVDF solution was used to disperse the nanoparticles in a 20 mL glass vial under intensive sonication in order to ensure better dispersion of MNPs. In this case, direct addition of MNP powder into the PVDF solution should be avoided. This MNPs-PVDF solution was subsequently added into the remaining PVDF solution under intensive sonication.

Synthesis of MNP-PVDF Microcapsules

PVDF solution was channeled through a 0.05 cm end-point diameter of micropipette tip by Watson Marlow Peristaltic Pump (0.5 mL/minute) followed by the drop wise addition of this polymer solution into a coagulation bath for microcapsules formation. The distance between the micropipette tip and surface coagulation was ~35 cm. The position of coagulation bath was adjusted manually to avoid the accumulation of microcapsules formed in one single area. Having too many polymeric microcapsules undergoing phase inversion process in one region will promote the fusion of multiple microcapsules to form doublet, triplet or even a clump of large polymeric clusters. The prepared polymeric solution was pumped through a tube and dropped into a coagulation bath consisting water and 5% SDS (Sodium Dedocyl sulfate). Phase inversion is occurred once after the droplet of polymeric solution dropped into coagulation bath.

Table 1: Experimental matrix of the prepared MNP-PVDF microcapsules with various PEG molecular weights (MW) as fillers

Sample number	PVDF (10 wt%)	PEG MW (0.5wt%)	MNP (0.5wt%)	BET surface area (cm^2/g)
A	Yes	-	Yes	4.341×10^3
B	Yes	1,000 g/mol	Yes	6.277×10^3
C	Yes	10,000 g/mol	Yes	7.158×10^3
D	Yes	35,000g/mol	Yes	5.892×10^3

Characterization of the MNP-PVDF microcapsules

In order to evaluate the morphologies of MNP-PVDF microcapsules in cross sectional view were inspected on field emission scanning electron microscopes (FESEM) (Carl Zeiss Leo Supra 50 VP Field emission, Netherlands). The microcapsules were fractured in liquid nitrogen using razor blade and coated with gold under vacuum before test. The surface area of the sample microcapsules synthesized were determined by N_2 sorption using a porosimetry analyzer (ASAP 2020, Micromeritics, USA) with a Brunauer−Emmett−Teller (BET) model. Samples were degassed before measurement at 105 °C for 8 hours.

RESULT AND DISCUSSION

The morphology of the cross sectional views of the microcapsules were studied with FESEM. In Figure 1, the cross sectional view of microcapsules with different magnification (100X, 1000X and 5000X) are shown for PEG additives with different molecular weight (A1- A3 for no PEG; B1-B3 for PEG 1000 g/mol; C1-C3 for PEG 10, 000 g/mol and D1-D3 for PEG 35,000 g/mol). The overall diameter of the microcapsules were measured on average of 300 samples were 1.4 mm±0.2 mm and consistent for all samples. PEG with different molecular weight exerted an obvious effect on pore structure of the inner diameter of the microcapsules. Overall morphology of the microcapsules without addition of the PEG as polymer additives revealed dense surfaces at the inner part of the microcapsules compared to outer surface as shown in Figure 1A. This could be due to interaction between polymer (PVDF) and solvent used (DMF) during the phase inversion [11]. On the other hand, as the molecular weight of PEG increased, there is an evolution of distinct macrovoids at the inner diameter of the microcapsules whereas at the outer diameter of the microcapsules finger like pore structure diminished into sponge like structure (figure 1B-D). This evolution could be resulted from the interaction of between more hydrophilic PEG mismatch in thermodynamics potentials with the PVDF and DMF in ternary phase diagram system [12], [13]. Furthermore, the interconnected porous structure networking from finger like structure suppressed to sponge like structure could be attributed by possible role of PEG molecular weight chain which induce delayed mixing behavior [7]. Furthermore, from the Nitrogen sorption analysis, it were revealed that BET surface area (as shown in Table 1) of the microcapsules increased up to 10, 000 g/mol before suppressed when higher molecular weight of PEG been used (35, 000 g/mol). BET surface area could be an indicator of the accessible porous structure available for reaction. This analysis can be corroborated with SEM data to understand further the morphology changes of the microcapsules structure with respect to variation of PEG molecular weight. It could be deduced from the above analysis that PEG acted as a pore- forming agent when it had a lower molecular weight, whereas PEG could suppress the growth of finger-like macrovoids with the further molecular weight increasing [6].

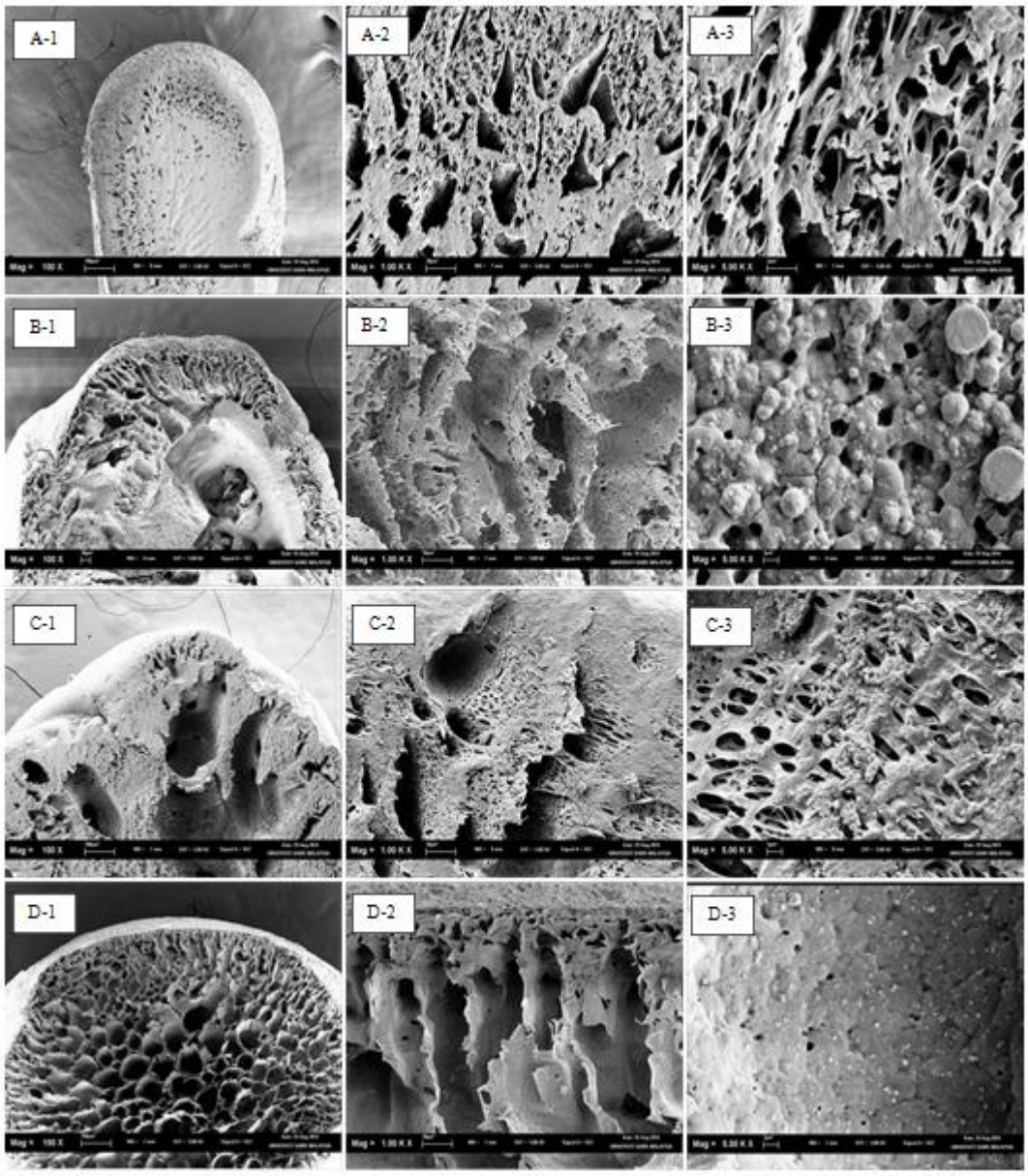

Figure 1: overall SEM morphology of the microcapsules without PEG as for forming agent (A1-A3) and variation of PEG molecular weight (B1-B3 (1000g/mol); C1-C3 (10,000 g/mol); D1-D3 (35,000 g/mol))

CONCLUSION

The results of the present work suggested that the addition of PEG with different molecular weight could change the PVDF membrane structure and properties.

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REFERENCES

[1] I. M. Martins, M. F. Barreiro, M. Coelho, and A. E. Rodrigues, *Chem. Eng. J.*, **245** 191–200 (2014)
[2] M. S. Osman, L. Kong, N. Ahmad, and J. Lim, *Advanced Materials Research* **1113** 566-570 (2015)
[3] L. Kong, X. Gan, A. L. Bin Ahmad, B. H. Hamed, E. R. Evarts, B. Ooi, and J. Lim, *Chem. Eng. J.*, **197** 350–358 (2012)
[4] M. G. Buonomenna, A. Figoli, I. Spezzano, R. Morelli, and E. Drioli, *J. Phys. Chem. B*, **112** (36) 11264–11269 (2008)
[5] M. G. Buonomenna, A. Figoli, I. Spezzano, M. Davoli, and E. Drioli, *Appl. Catal. B Environ.*, 80 185– 194 (2008)
[6] D. Zuo, Y. Xu, W. Xu, and H. Zou, *Chinese J. Polym. Sci.*, **26** (4) 405 (2008)
[7] S. Wongchitphimon, R. Wang, R. Jiraratananon, L. Shi, and C. H. Loh, *J. Memb. Sci.*, **369** (1–2) 329–338 (2011)
[8] H.-C. Kang, Y. Chen, E. E. Arthur, and H. Kim, *Int. J. Hydrogen Energy*, **39** (28) 15656–15664 (2014)
[9] F. Liu, N. A. Hashim, Y. Liu, M. R. M. Abed, and K. Li, *J. Memb. Sci.*, **375**1–27 (2011)
[10] G. Kang and Y. Cao, *J. Memb. Sci.*, **463** 145–165 (2014)
[11] M. G. Buonomenna, A. Figoli, I. Spezzano, R. Morelli, and E. Drioli, *J. Phys. Chem. B*, **112** (36) 11264–11269 (2008)
[12] A. Perazzo, V. Preziosi, and S. Guido, *Advances in Colloid and Interface Science*, **222** 581-599 (2015)
[13] A. K. Hołda and I. F. J. Vankelecom, *J. Appl. Polym. Sci.* **132** 42130 (2015)