CHARACTERIZATION OF MICRO/NANO POROUS HOLLOW GLASS MICROSPHERES FABRICATED THROUGH VARIOUS CHEMICAL ETCHING PROCESSES FOR USE IN SMART COATINGS

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Abstract: Porous hollow glass microspheres have many uses, including encapsulation of active materials. In this paper a fast and facile method for fabricating porous hollow glass-microspheres was demonstrated by etching them using dilute hydrofluoric acid. Then, a highly reactive amine was infiltrated into the etched glass microspheres. Scanning electron microscopy was conducted for the hollow glass microspheres prior and post etching process. With regards to the porous hollow glass spherical sample, the spherical nature, morphology, pore diameter and the porosity were studied using scanning electron microscopy. Formation of the intact hollow glass microspheres with an open through wall porosities following phase separation and etching of the boron oxide rich phase was demonstrated using reciprocating shaker as the most suitable agitation method. The BET results indicated that the surface of the porous microspheres contained nano-pores. It is believed that the simplicity of the reported fabrication technique of micro/nano porous structure has the potential to scaling up for large scale production.

1. INTRODUCTION

In recent years various self-healing chemistries and material systems have been developed to address damaging issues in the field of materials science and engineering [1-6]. One of the most common strategies to provide self-healing ability is micro/nano capsules embedment [7, 8]. Recently the microencapsulation technology exhibited significant promise by providing "smart" functionality for applications such as self-healing composites and coatings [9-11].

Epoxy is one of the most widely used components of polymers in composites for diverse applications such as wind turbine blades, aircraft structures, sporting goods, and protective coatings. Most epoxy thermosets consist of a two-part system that when cured, creates a glassy polymer network with advantageous mechanical properties such as strength and stiffness [12]. When an epoxy composite or coating needs to be protected from micro cracking it seems that dual microcapsule system containing encapsulated epoxy and its hardener is very preferable. Various epoxy monomers have been easily encapsulated using several methods due to their good emulsivity in an aqueous environment [13-15]. However, Microencapsulation of hardener for epoxy has been attempted with only modest success [16-21]. This is mainly due to, the traditional amine-type curing agents for curing epoxy at room temperature are highly active, and hence, difficult to encapsulate in water or organic solvents [22-27].

Hollow glass microspheres are commercially available, finely dispersed, free-flowing powder consisting of thin walled (0.5-2.0μm) spherical glass particles having diameter, 10-200 μm [28, 29]. They are made from water resistant and chemically-stable soda-lime-borosilicate glass [30]. Hollow glass microsphere (HGM) has some unique properties, such as low density, low thermal conductivity and a low dielectric constant [31-33]. The hollow microspheres are used to reduce shrinkage, to adjust the rheological properties, to reduce part weight, and to lower cost [34]. These properties make them more suitable for application in areas such as fillers for polymeric materials, polymeric composites with special properties, syntactic foams, hydrogen storage and coatings [28]. These microspheres possessed two interconnected glass phases of different compositions; i.e. a silica rich and a boron oxide rich phases, within the thin microsphere walls as they were produced. This meant that leaching out the interconnected phase (boron oxide rich) would result in a porous microspheres wall structure formation

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with the potential of porosity tunability. Using this technique, it is possible to produce porous hollow glass microspheres (PHGM). The presence and tunability of these porosities would allow for materials filling [35].

Via a two-step method, first synthesized porous hollow glass microcapsules and then infiltrated them with reactive chemicals, it is possible to develop synthesis of mechanically robust, chemically and thermally stable micro-containers for using in self-healing systems [36].

In the present study, chemically and thermally stable micro containers have been synthesized to store DETA as a reactive agent for self-healing epoxy based coatings. The procedure was included the chemically etching commercially available hollow glass microspheres from 3MTM, with diluted hydrofluoric acid that resulted to produce porous HGMs and loading of the porous HGMs with DETA. In this procedure a rapid, facile, low cost, and high yield method was manipulated in order to produce porous hollow glass microspheres. The simplicity of the reported fabrication technique has the potential to be scaled up for large scale production. The product, porous hollow glass microspheres was characterized via scanning electronic microscope (SEM).

2. EXPERIMENTAL

2. 1. Materials

The S22, K20 and K25 hollow glass microspheres (HGMs) were obtained from 3MTM Co. Table 1 presents some typical properties of these three products. Hydrofluoric

Table 1. Typical properties of S22, K20 and K25 glass microspheres

Product	90th% Size (μm)	Crush Strength (psi)	Density (gcm⁻³)
S22	65	400	0.22
K20	95	500	0.20
K25	90	750	0.25

acid (HF) and sodium hydroxide (NaOH) were purchased from Merck chemical company. Diethylenetriamine (DETA) as the epoxy hardener was ordered from Sigma Aldrich. All the chemicals were used as received from the suppliers.

2. 2. Etching of HGMs

Porous hollow glass microspheres were fabricated by etching commercially available hollow glass microspheres (K20, K25 and S22) with 2% diluted hydrofluoric acid (HF) solution. 3 g of HGM was mixed with 200 ml 2% HF acid in a well-sealed plastic vial and was constantly agitated for 5 minutes via four methods; first, using scientific ultrasonic cleaner (35 W), second, using mechanical stirrer (100 rpm), third using magnetic stirrer (100 rpm) with a Teflon coated magnetic stir bar and fourth using reciprocating shaker (100 rpm). After etching the spheres were vacuum filtered and rinsed with 200 ml of 2% NaOH then 500 ml of deionized water. The collected and washed spheres were soaked in deionized water to separate the HGM (which floated on the surface) from the PHGM (which sank to the bottom) (Fig. 1). The PHGMs were
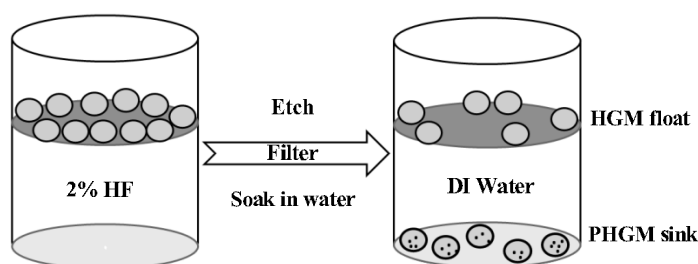

Fig. 1. Schematic of etching HGM to PHGM.

then dried at RT for 24 h as the target product.

2. 3. Scanning Electron Microscopy (SEM)

All scanning electron micrographs were obtained with a CAM SCAN MV 2300 SEM, that was utilized for observation of appearances of HGMs and PHGMs, their sizes, internal and external surface morphologies, wall thicknesses and sizes of holes in porous HGMs. Samples were sputtered with a thin layer of gold before SEM.

2. 4. Detection of Nano-Pores

Surface properties of the porous hollow glass microspheres were studied by the Brunauer-Emmett-Teller (BET) methods. N2 adsorption−desorption isotherms were measured using an automatic adsorption instrument (BELSORP-mini, Japan) for the determination of total pore volume. Prior to the measurement the samples were degassed at 120∘C for 3 h. The nitrogen adsorption–desorption data were recorded at liquid nitrogen temperature, i.e. 77 K. The pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method.

2. 5. Loading of the PHGMs with Amine

Glass walled microcapsules containing active amine (DETA) were produced by vacuum aided infiltration of the core chemical into the porous hollow glass microspheres. As the infiltration is done with the aid of vacuum, negative pressure is produced inside the capsules at the beginning. Encapsulation of DETA within the prepared microspheres by diffusion through wall porosity was done. With the infiltration of DETA the pressure difference between the capsules and outside environment gradually decreases to equilibrium. After full infiltration of amine solution into the cavity of the HGMs (passing about 1h), microspheres with amine solution inside were separated and collected as the target product as micro-containers for self-healing agents.

3. RESULT AND DISCUSSION

3. 1. Characterization of the HGMs

Figs.2, 3, 4 and 5 show scanning electron micrographs of the glass microspheres which are commercially available (S22, K20 and K25) after water-deposition to remove the debris.

Figs. 2a, b and c separately show the overview image of the original HGMs. Fig. 3 and 4 show the morphology of the outer surface of the microspheres. SEM images reveal that a lot of glass nano-particles adhere to the smooth outer surface of the original HGMs.

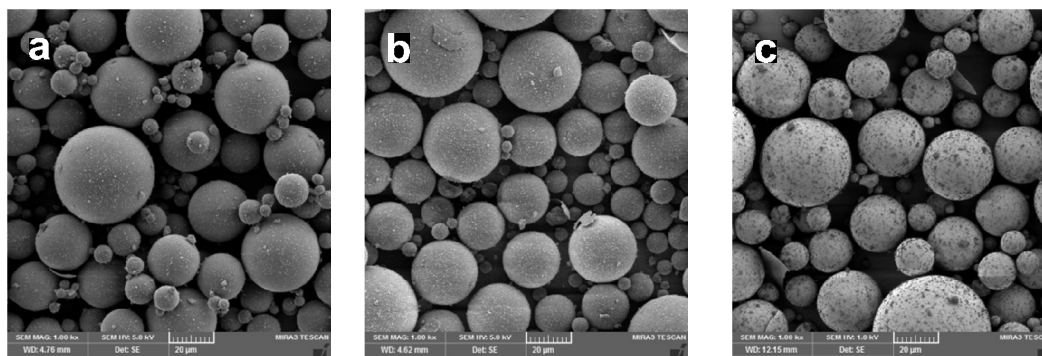Fig. 5a, b and c show the shell thickness of original HGMs. The average measured shell thickness is 0.3 μm.

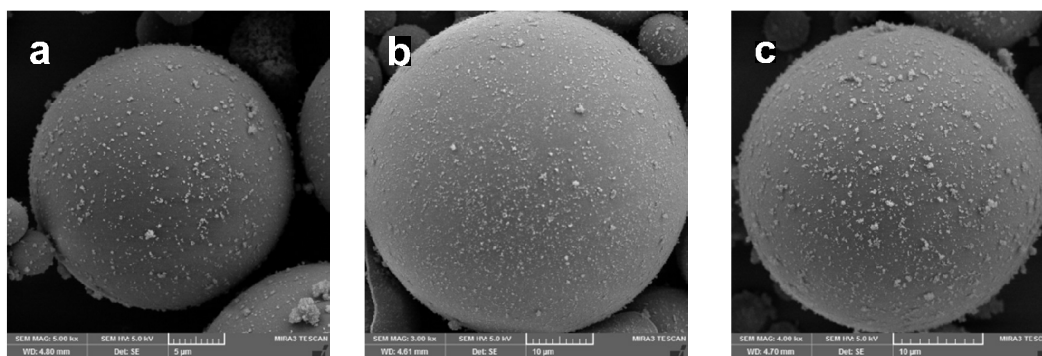**Fig. 2.** Overview of original HGMs, a: S22, b: K20, c: K25.

Fig. 3. Single original HGMs, a: S22, b: K20, c: K25.
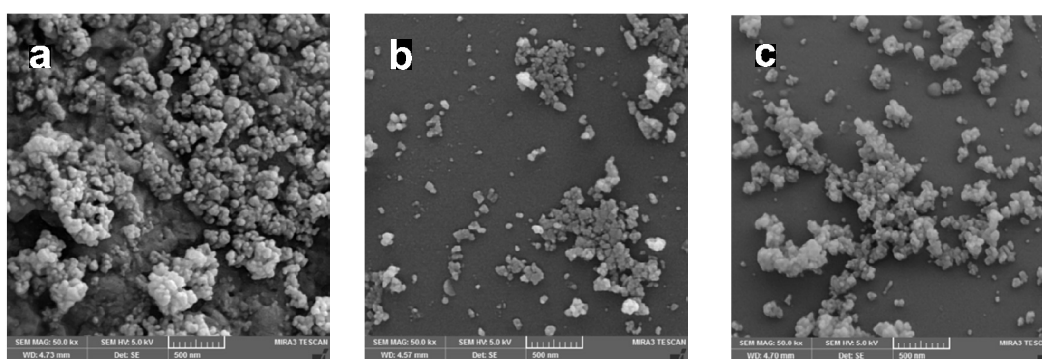

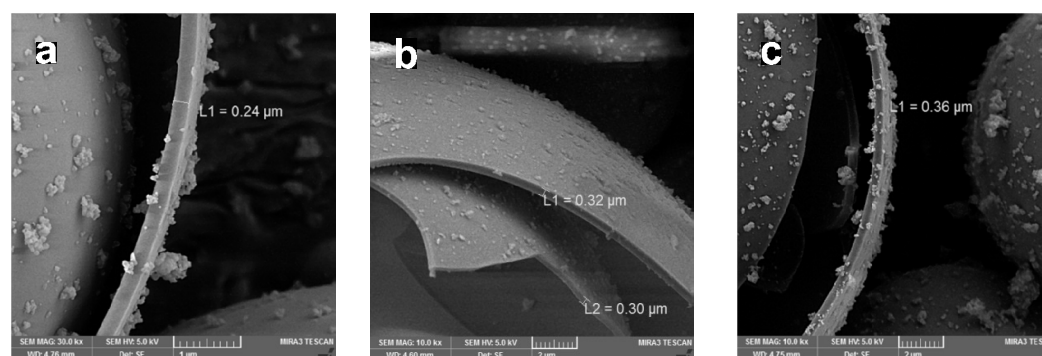**Fig. 4.** Surface morphology of original HGMs, a: S22, b: K20, c: K25.

Fig. 5. Shell thickness of original HGMs, a: S22, b: K20, c: K25.

3. 2. Characterization of the PHGMs

3. 2. 1. SEM Results

Figs. 6, 7, 8 and 8 show SEM images of etched GMs with diluted hydrofluoric acid (HF) using different techniques (ultrasonic waves, mechanical stirrer, magnetic stirrer and reciprocating shaker) for using them as micro-containers containing self-healing active agents, DETA.

Figs. 6a, b and c show etched GMs using ultrasonic waves, (S22, K20 and K25). It can be seen that the etched GMs can be totally broken
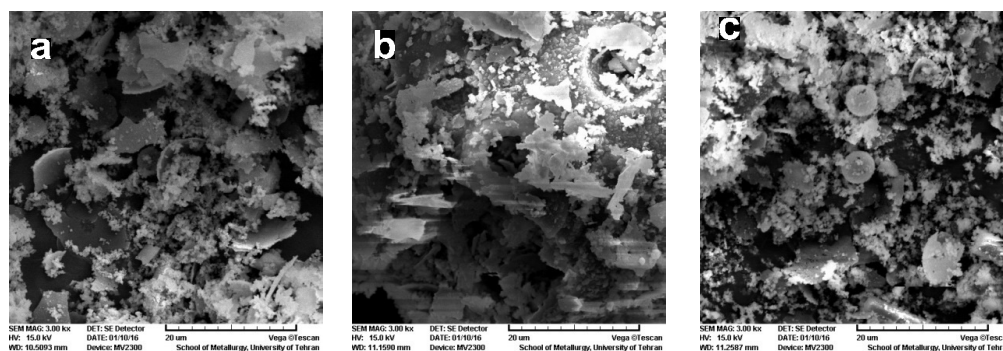
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Fig. 6. Etched GMs using ultrasonic process, a: S22, b: K20, c: K25.

and destroyed by the ultrasonic waves, although it is not possible to detect GMs as separate spheres. It shows that the energy that comes from this method is much more than that of required.

Figs. 7a, b and c show etched GMs using mechanical stirrer (S22, K20 and K25). Surprisingly, a new structure of GMs was obtained. Their morphology has changed from spherical shape to porous pill shape. This kind of morphology had not been reported in any other reports. It may be explained by breaking and rejoining of microspheres' broken walls. It can be distinguished that the circular perimeter of spheres has changed to semi-hexagonal shape.

Figs. 7a, b and c show etched GMs using magnetic stirrer (S22, K20 and K25). Following etching probably due to mechanical weakening of the spheres wall, they can be partially broken. However, this structure is not suitable for storing of chemical liquid, neither.

Figs. 9a, b and c show etched GMs using reciprocating shaker (S22, K20 and K25). Compared with the original microspheres, the etched ones show rough surfaces with very few through-holes at several microns that can be found at every etched HGM. The quality of new rough surface might bring about another advantage that enhances interfacial bonding strength when used in a polymeric matrix.

Formation of intact hollow glass microspheres with an open through wall porosity following phase separation and etching of the boron oxide rich phase was demonstrated using reciprocating shaker as the best agitation method.

These circular pores may be caused as a result of the individual spherical particles of one phase being embedded in a matrix of the second phase. The mechanism that governs the formation of these phases is nucleation and growth that occurs during the processing of HGM. One phase is
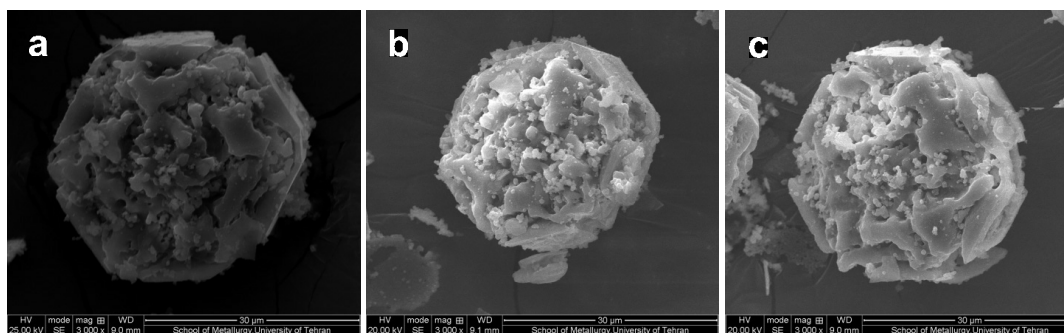

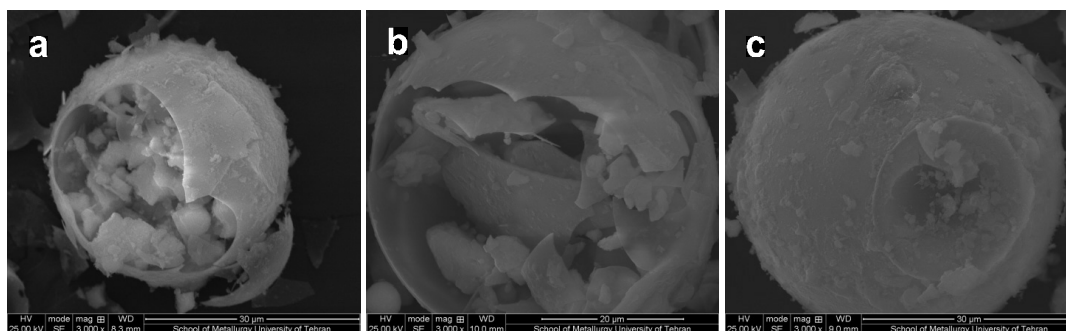**Fig. 7.** Etched GMs using mechanical stirrer, a: S22, b: K20, c: K25.

Fig. 8. Etched GMs using magnetic stirrer, a: S22, b: K20, c: K25.

more soluble in hydrofluoric acid than the other. The uneven surface morphology observed on borosilicate HGM could be explained based on phase separation that occurs due to spinodal decomposition. These two phases show some amount of continuity and interconnectivity. It is possible that the type of large hole porosity seen in the etched HGMs is a result of droplet nucleation that occurred during the formation and cooling of the microsphere during the fabrication process [37].

The different pore structure of etched S22, K20 and K25 hollow glass microspheres may be due to different chemical compositions of HGM S22, HGM K20 and HGM K25 during manufacturing. 3MTM reports that the spheres are all made of soda–lime–borosilicate glass, but the widely differing physical properties (Table 1) indicate differences in composition.

Overall, it is clear that K25 etched spheres were of good quality judging by the images obtained and therefore were selected for the filling experiment with DETA.

3. 2. 2. BET Results

Nitrogen adsorption-desorption measurements were performed to examine the inner architectures of the K25 etched spheres. Fig. 9 shows the detailed pore structure of the PHGMs analyzed using nitrogen adsorption-desorption isotherms at 77 K. The isotherms exhibit type IV adsorption-desorption isotherm with an obvious hysteresis loop at pressure of 0.6–0.9, responding to the presence of mesopores.

The mesoporous pore size distribution calculated using BJH model and is shown in Fig. 10. The pore size distribution indicates that the material has an average pore size of 10 nm. These results indicate that the surface of the porous
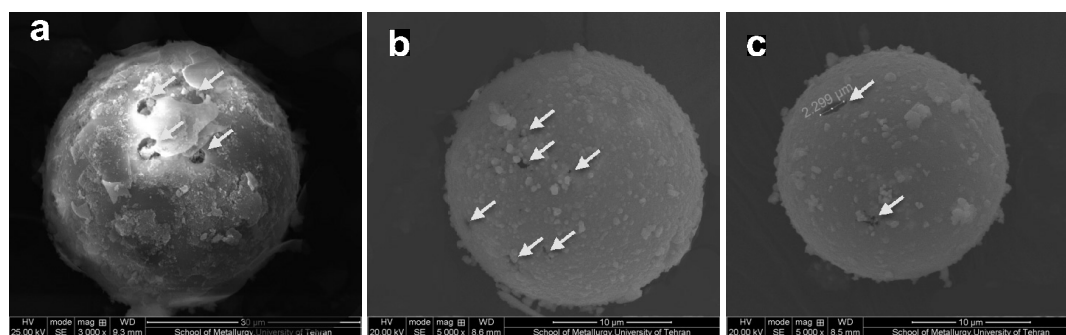

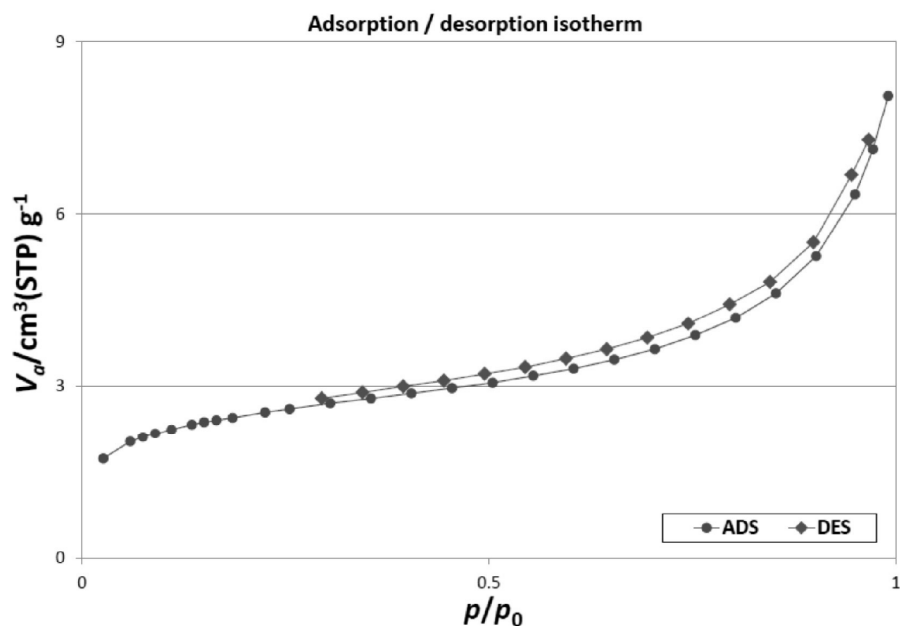**Fig. 9.** Etched GMs using reciprocating shaker, a: S22, b: K20, c: K25.

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Fig. 10. Nitrogen absorption and desorption isotherms of PHGMs.
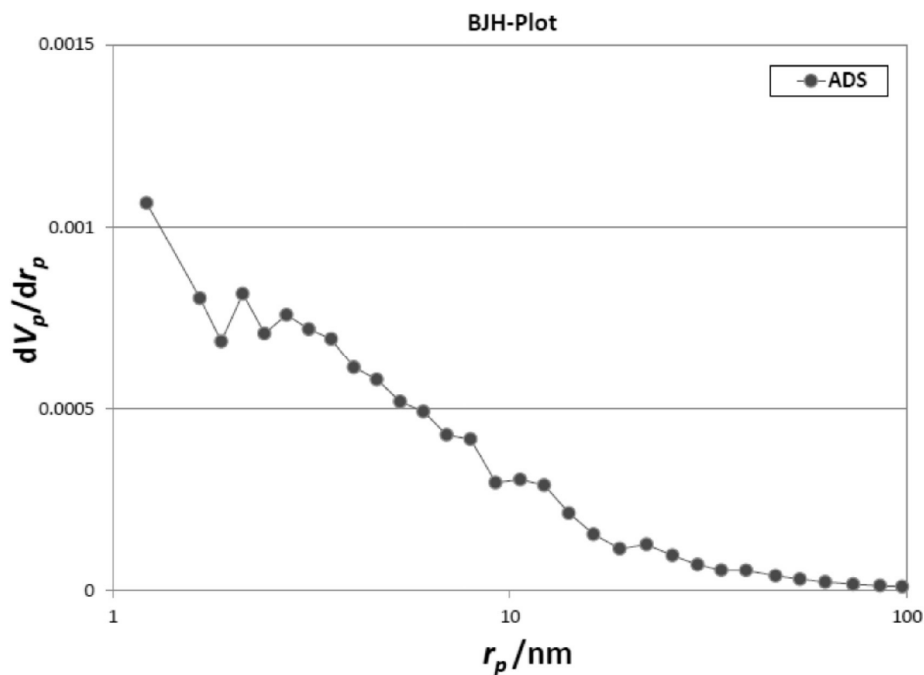
Fig 11. Pore size distribution of PHGMs calculated by BJH method.

microspheres contained nano pores. So, the final product would be micro/nano porous structure.

Micro-pores of various sizes have been observed previously in the SEM images. This micro/nano porous structure of PHGMs is favorable to efficient improve the hardener

absorbing properties for using in micro/nano capsule based self-healing coatings.

4. CONCLUSION

In this paper, the fabrication of microcapsules containing reactive amine using PHGMs that successfully developed by etching HGMs, has been reported. As a result of using different agitation techniques, different morphologies were obtained. Accordingly, the mechanical/magnetic stirring and sonicating mixing techniques did not have the desired result in comparison to that of the reciprocating shaker. In this process, the HGMs achieved the small through-holes in the shell that was suitable for infiltration of amines in them. According to the BET results, the structure of PHMs' surface contained nano pores, too. This work offers a facile path to obtain PHGM, which can be used as a suitable container for encapsulating active materials in self-healing smart coating systems.

REFERENCES

1. Vander Zwaag, S., "Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science", Springer, Verlag, 2007.
2. Wu, D. Y., Meure, S. and Solomon, D., "Self-healing polymeric materials: a review of recent developments", Progress in Polymer Science, 33, 2008, 479–522.
3. Wool, R. P., "Self-healing materials: a review", Soft Matter, 4, 2008, 400–418.
4. Ghosh, S., "Self-healing materials: fundamentals", design strategies, and applications, Wiley-VCH, 2009.
5. Syrett, J., Becer, C., Haddleton, D., "Self-healing and self-mendable polymers", Polymer Chemistry, 1, 2010, 978–987.
6. Blaiszik, B. J., Kramer, S. L. B., Olugebefola, S. C., Moore, J. S., Sottos, N. R. and White, S. R., "Self-healing polymers and composites", Annual Review of Materials Research, 40, 2010, 179–211.
7. Yin, X., Liu, Z., Wang, D., Pei, X., Yu, B. and Zhou, F., "Bioinspired Self-Healing Organic Materials: Chemical Mechanisms and Fabrications", Journal of Bionic Engineering, 12, 2015, 1–16.
8. Ghosh, S. K., "Functional Coatings", Wiley-VCH, 2006.
9. Benita, S., "Microencapsulation Methods and Industrial Applications", 2nd ed., Taylor & Francis, CRC Press, Philadelphia, 2006.
10. Park, B. D., Lee, S. M., Roh, J. K., "Effects of formaldehyde/urea mole ratio and melamine content on the hydrolytic stability of cured urea-melamine-formaldehyde resin", European J. Wood Products, 67, 2009, 121-123.
11. Samadzadeh, M., Hatami Boura, S., Peikari, M., Kasiriha, S. M. and Ashrafi, A., "A review on self-healing coatings based on micro/nanocapsules", Progress in Organic Coatings, 68, 2010, 159–164.
12. Petrie, E. M., "Epoxy Adhesive Formulations", McGraw-Hill, New York, 2006.
13. Yin, T., Rong, M. Z., Zhang, M. Q. and Yang, G. C., "Self-healing epoxy composites— preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent", Composites Science and Technology, 67, 2007, 201–212.
14. Xiao, D. S., Rong, M. Z. and Zhang, M. Q., "A novel method for preparing epoxy-containing microcapsules via UV irradiation-induced interfacial copolymerization in emulsions", Polymer, 48, 2007, 4765–4776.
15. Zhang, H. and Yang, J., "Development of self-healing polymers via amine–epoxy chemistry: I. Properties of healing agent carriers and the modelling of a two-part self-healing system", Smart Materials and Structures, 23, 2014, 065003 (11pp).
16. Yuan, Y. C., Rong, M. Z., Zhang, M. Q., Chen, J., Yang, G. C. and Li, X. M., "Self-healing polymeric materials using epoxy/mercaptan as the healant", Macromolecules, 41, 2008, 5197–5202.
17. Xiao, D. S., Yuan, Y. C., Rong, M. Z. and Zhang, M. Q., "Self-healing epoxy based on cationic chain polymerization", Polymer, 50, 2009, 2967–2975.
18. Yuan, Y. C., Rong, M. Z., Zhang, M. Q., "Preparation and characterization of microencapsulated polythiol", Polymer, 49, 2008, 2531-2541.
19. Xiao, D. S., Yuan, Y. C., Rong, M. Z. and

Zhang, M. Q., "Hollow polymeric microcapsules: preparation", characterization and application in holding boron trifluoride diethyl etherate, Polymer, 50, 2008, 560–568.

20. McIlroy, D. A., Blaiszik, B. J., Caruso, M. M., White, S. R., Moore, J. S. and Sottos, N. R., "Microencapsulation of a reactive liquid-phase amine for self-healing epoxy composites", Macromolecules, 43, 2010, 1855-1859.

21. Jin, H. H., Mangun, C. L., Stradley, D. S., Moore, J. S., Sottos, N. R. and White, S. R., "Self-healing thermoset using encapsulated epoxy-amine healing chemistry", Polymer, 53, 2012, 581- 587.

22. Belbekhouche, S., Ali, G., Dulong, V., Picton, L. and Cerf, D. L., "Synthesis and characterization of thermosensitive and PH-sensitive block copolymers based on polyetheramine and pullulan with different length", Carbohydrate Polymers, 86, 2011, 304–312.

23. Yu, J. and Yang, Q., X., "Magnetization improvement of Fe-pillared clay with application of polyetheramine", Applied Clay Science, 48, 2010, 185–190.

24. Tan, S., Walus, S., Gustafsson, T. and Brandell, D., "3-D Microbattery electrolyte by selfassembly of oligomers", Solid State Ionics, 198, 2011, 26–31.

25. Guan, N. N., Xu, J., Wang, L. Y. and Sun, D. J., "One-step synthesis of amine-functionalized thermo-responsive magnetite nanoparticles and single-crystal hollow structures", Colloids and Surfaces A, 346, 2009, 221–228.

26. Kondyurin, A., Komar, L. A. and Svistkov, A. L., "Combinatory model of curing process in epoxy composite", Composites:B, 43, 2012, 616–620.

27. Li, Q., Mishra, A. K., Kim, N. H., Kuila, T., Lau, K. and Lee, J. H., "Effects of processing conditions of poly(methylmethacrylate) encapsulated liquid curing agent on the properties of self-healing composites", Composites:B, 49, 2013, 6–15.

28. Dalai, S., Vijayalakshmi, S. and Sharma, P., "Preparation of Hollow Glass Microspheres (HGMs) from amber coloured and borosilicate glass frits", Advanced Materials Research, 678, 2013, 37-41.

29. Budov, V. V., "Hollow glass microspheres". Use, properties and technology (Review), Glass and Ceramics, 51, 1994, 7-8.

30. FN Mutua, P Lin, JK Koech, Y Wang, Surface Modification of Hollow Glass Microspheres, Materials Sciences and Applications, 2012, 3, 856-860.

31. Li, J., Luo, X. and Lin, X., "Preparation and characterization of hollow glass microsphere reinforced poly(butylene succinate) composites", Materials and Design, 46, 2013, 902–909.

32. Tagliavia, G., Porfiri, M., Gupta, N., "Analysis of flexural properties of hollowparticle filled composites", Composites B: Engineering, 41, 2010, 86–93.

33. Dimchev, M., Caeti, R., Gupta, N., "Effect of carbon nanofibers on tensile and compressive characteristics of hollow particle filled composites", Materials & Design, 31, 2010, 1332–1337.

34. Aruniit, A., Kers, J., Majak, J., Krumme, A. and Tall, K., "Influence of hollow glass microspheres on the mechanical and physical properties and cost of particle reinforced polymer composites", Proceedings of the Estonian Academy of Sciences, 61, 2012, 160–165.

35. Mohtadi, R., Matsunaga, T., Heung, K., Schumacher, R., Wicks, G., "Hollow Glass Microspheres as Micro Media for Complex Metal Hydrides Hydrogen Storage Compounds", Journal of the South Carolina Academy of Science, 9, 2011, 1-4.

36. Zhang, H. and Yang, J., "Etched glass bubbles as robust micro-containers for selfhealing materials", Materials Chemistry A, 1, 2013, 12715-12720.

37. Newell, J. D., Patankar, S. N. and Edwards, D. B., "Porous microspheres as additives in lead–acid batteries", Journal of Power Sources, 188, 2009, 292–295.