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Effect of Processing Conditions on the Properties of Nanocapsules for Self-Healing Materials

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A series of nanocapsules for self-healing materials were prepared by interfacial polymerization method using modified aliphatic amine (HB-1618) and urea formaldehyde resin as core material and shell material, respectively. The effect of processing conditions such as core/shell mass ratio, agitation rate and emulsifier on the properties of nanocapsules were investigated. Dispersion and surface morphology of nanocapsules were determined by optical microscope and scanning electron microscopy. The results showed that the optimum processing conditions were 0.7:1 for the core/shell mass ratio, 800 rpm for the agitation rate and 1 % for gum arabic content as the emulsifier. The results of SEM and osmosis performance evaluation showed nanocapsules were well encapsuled and the surface of the nanocapsule became rough, which is benefited for the use in the matrix materials.

Keywords: Curing agent, Nanocapsule, Interfacial polymerization process.

INTRODUCTION

In recent years, the development of self-healing materials is an area of great interest because of their self-healing capabilities in the case of a damage event[1-12]. Composite materials with self-healing capabilities require long term durability and reliability. It is a general approach to be encapsulated by the polymeric shell material. The curing agent is embedded into self-healing materials and as soon as the cracks destroy the capsules, the curing agent will be released to respond to the stimulation and achieve the purpose of reparation.

Numerous preparation technologies for encapsulation have been reported and *in situ* polymerization method is the most commonly used one. There is a shortcoming that the particle sizes of nanocapsules prepared by *in situ* polymerization method are relatively large (50-400 μm). The nanocapsules with larger particle size can only be applied in a thick coating and hardly form a continuous arrangement.

Compared with *in situ* polymerization method, interfacial polymerization technique is the easiest and best process for encapsulation. In this paper, nanocapsules with urea formaldehyde resin as shell material and modified aliphatic amine (HB-1618) as the core material were prepared by interfacial polymerization. The effects of processing conditions (such as core/shell mass ratio, agitation rate and different emulsifier) on the properties of the nanocapsules were studied.

EXPERIMENTAL

Modified aliphatic amine (HB-1618) was supplied by San Mu Group Corporation of Jiangsu, China. Sodium dodecyl sulfate, Sodium dodecylbenzenesulfonate, Op-10, SDBS, DBS and Arabic gum were supplied by Guangzhou Chemical Reagent, China and used as emulsifier. Triethanolamine, Sodium chloride, Hydrochloric acid, Acetone, resorcinol and *n*-octanol were supplied by Damao Chemical Reagent of Tianjin, China. Urea and 37 % formaldehyde used for the preparation of urea-formaldehyde prepolymer were supplied by Guangzhou Chemical Reagent, China. All commercial chemicals are used without further purification.

Preparation of nanocapsules

(1) U-F prepolymer preparation: Urea (U) and 37 wt. % formaldehyde (F) were mixed in a 250 mL three-necked round-bottomed flask and stirred at 70 °C for 90 min. The weight ratio between urea and formaldehyde was 1:2. After the urea was dissolved, the pH value of the mixed solution was kept about 8-9 by adding triethanolamine.

(2) Synthesis of nanocapsules: Curing agent (HB-1618) was dissolved into the solution of emulsifier and dispersed by ultrasonic equipment for 20 min and then stirred by mechanical stirred equipment for 20 min; the oil-in-water emulsion (O/W emulsion) was obtained. U-F prepolymer was added into the above O/W emulsion with 500 rpm continuous mechanical

agitation at 50 °C. Resorcinol (0.5 g) and NaCl solution (4 wt. %) were added into solution. After the solution was stirred for 20 min, the pH of solution was adjusted to 3 by adding 10 wt. % hydrochloric acid solution and then the solution was heated to 60 °C and kept at this temperature for 3 h. The nanocapsules were rinsed with deionized water and acetone, filtered and air-dried for 24 h.

Determination of for encapsulation rate of nanocapsules: Encapsulation rate of nanocapsule was established by the method of extraction and acetone was used as an extraction solvent. The samples were crushed and washed with acetone several times and then dried at room temperature for 24 h.

$$\text{Encapsulation rate} = (m_1\text{-}m_2)/mL \times 100\ \%$$

where m_1 and m_2 are the initial mass of the complete nanocapsules and the mass of the remained wall material, respectively.

Properties test of nanocapsule: Average diameter analysis was carried out with a nanoparticle size analyzer (ZS90). Dispersion and surface morphology of nanocapsules were determined by optical microscope (OM) and scanning electron microscopy (SEM).

Osmosis performance evaluation of nanocapsule: A certain amount of nanocapsules were dispersed in anhydrous alcohol at room temperature for a certain time and then the nanocapsules were filtered, dried and weighed. The above operation was repeated until the total amount of dispersion time reached 24 h. The relationship between the mass of nanocapsule and dispersion time was obtained.

RESULTS AND DISCUSSION

Effect of core/shell mass ratio on the formation of nanocapsules: According to the research[13], the core/shell mass ratio is the most influencing factor for the encapsulation rate, morphology, particle size and distribution of the nanocapsule. In order to estimate the effect of different core/shell mass ratio on the encapsulation rate, adhesion, particle size and distribution, the results of encapsulation rate, average diameter and optical microscope images with different core/shell mass ratio were showed in Table-1 and Fig. 1.

The results of Table-1 and Fig. 1 showed that when the core/shell mass ratio was 0.5:1, the encapsulation rate and the average diameter of the nanocapsules were 32.3 % and 993.2 nm, respectively. The main reason was that the size of core droplet was smaller when the core/shell mass ratio was low and the adhesion among the nanocapsules occured because of the excess shell materials which was disadvantage for the dispersion property of the nanocapsules. Raising the core/shell mass ratio to 0.7:1, the encapsulation rate and the average diameter of the nanocapsules were 70.1 % and 523.2 nm, respectively and the nanocapsules showed better dispersion property which was beneficial for the dispersion the of nanocapsules into the epoxy resin matrix. When the core/shell mass ratio reached 0.8:1, the encapsulation rate and the average diameter of the nanocapsules were 51.4 % and 633.6 nm, respectively and the adhesion occurred again. When the core/shell mass ratio was raised to 1:1, no nanocapsules was formed. The main reason of the unencapsulated shell materials was that the core materials was so adequate and the shell materials could not encapsulate the core materials. So considering the encapsulation rate, average diameter and the adhesion of the nanocapsules, the optimum core/shell mass ratio was 0.7:1.

Effect of agitation rate on the formation of nanocapsules: The effect of the agitation rate on the encapsulation rate, average diameter and adhesion were investigated and the results were showed in Table-2 and Fig. 2 at different agitation rate on the processing condition of 0.7:1 for the core/shell mass ratio.

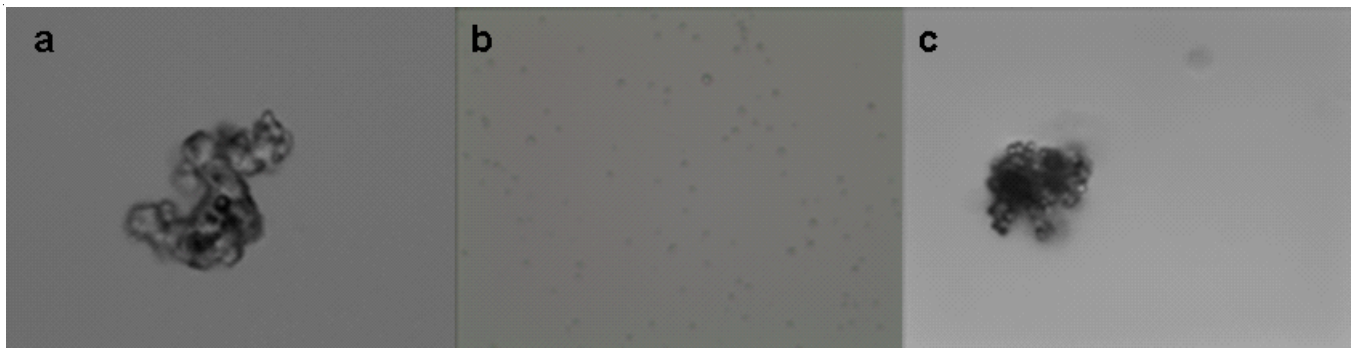

Fig. 1. Optical microscope images of nanocapsules with different core/shell mass ratio (a-0.5:1; b-0.7:1; c-0.8:1)

TABLE-1
EFFECT OF CORE/SHELL MASS RATIO ON THE ENCAPSULATION RATE AND AVERAGE DIAMETER

Core/shell mass ratio	0.5:1	0.7:1	0.8:1	1:1
Encapsulation rate (%)	32.3	70.1	51.4	None
Average diameter (nm)	993.2	523.2	633.6	None

TABLE-2
EFFECT OF AGITATION RATE ON THE ENCAPSULATION RATE AND AVERAGE DIAMETER

Agitation rate (rpm)	500	800	1000	1200
Encapsulation rate (%)	51.8	75.6	52.3	42.6
Average diameter (nm)	612.7	541.5	324.2	556.3

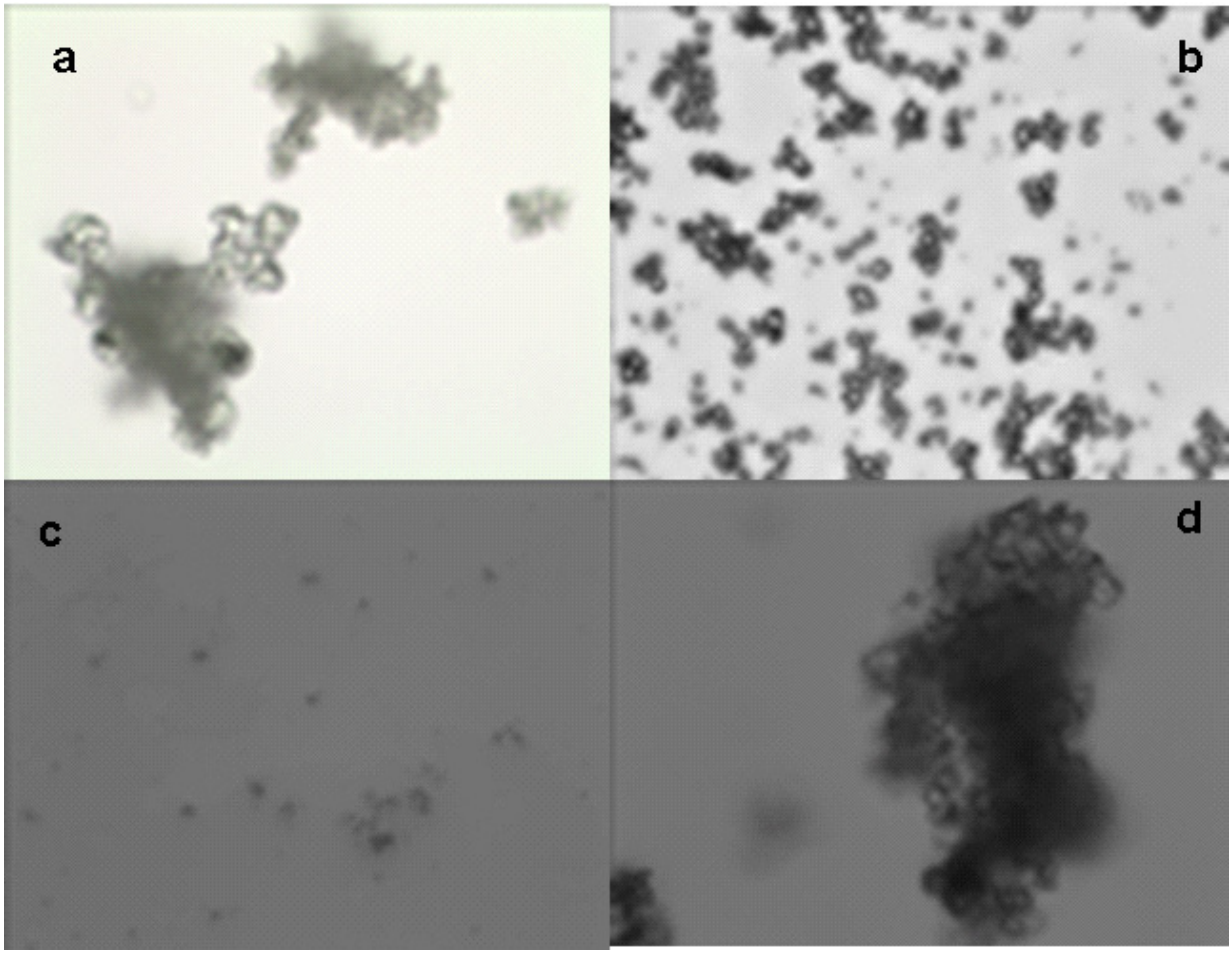

Fig. 2. Optical microscope images of nanocapsules with different agitation rate (a-500 rpm; b-800 rpm; c-1000 rpm; d-1200 rpm)

Table-2 and Fig. 2 showed that the agitation rate was 500 rpm, the encapsulation rate was 51.8 % and the average diameter was 612.7 nm. When the agitation rate was increased to 800 rpm, the encapsulation rate was increased to 75.6 % and the average diameter was decreased to 541.5 nm and the dispersion of the nanocapsules became better. Continuously raising the agitation rate to 1000 rpm and 1200 rpm, the encapsulation rate was decreased and adhesion occurred. The main reason was that as the agitation rate increased, many smaller size droplet existed in emulsion due to the larger shear stress, so the encapsulation rate decreased. Therefore considering the encapsulation rate, average diameter and the adhesion of the nanocapsules, the optimum agitation rate was 800 rpm.

Effect of different emulsifiers on the formation of nanocapsules: The effect of different emulsifiers on the encapsulation rate, average diameter and adhesion of the nanocapsules were investigated and the results were showed in Table-3 and Fig. 3 at different agitation rate on the processing condition of 0.7:1 for the core/shell mass ratio and 800 rpm for agitation rate.

In the process of preparing nanocapsules, the emulsifier plays an important role. The formation of core material droplets not only depend on the external agitation, but also on the emulsification of emulsifier. In this section, the effect of anionic surfactant (SDBS, DBS) and non-ionic surface active agents (Arabic gum, Op-10) was investigated. The results of different emulsifiers on the nanocapsules encapsulation rate, particle size and distribution were showed in Table-3 and Fig. 3.

Hydrophilic-lipophilic balance value (HLB) is an important constant for helping match the oils used with appropriate emulsifiers. In this section, HLB values of Op-10, SDBS, DBS and Arabic gum were 14.5, 13, 10.6 and 8, respectively. Table-3 indicated that with a decrease in HLB, the encapsulation rate and the average diameter increased. When two emulsifiers DBS and Arabic gum were mixed used, the encapsulation rate decreased and adhesion occurred. The highest encapsulation rate of the nanocapsule was up to 75.4 % using Arabic gum as emulsifier. Fig. 3 showed the better dispersion of the nanocapsules prepared with Arabic gum as emulsifier, which was

TABLE-3
EFFECT OF EMULSIFIER ON THE ENCAPSULATION RATE AND AVERAGE DIAMETER

Emulsifier	Op-10	SDBS	DBS	Arabic gum	0.5 % DBS to 1.5 % Arabic gum	1.5 % DBS to 0.5 % Arabic gum
Hydrophilic-lipophilic balance value (HLB)	14.5	13.0	10.6	8.0	8.65	9.95
Encapsulation rate	51.3 %	56.9 %	62.5 %	75.4 %	51.3 %	49.2 %
Average diameter (nm)	224.5	258.2	256.5	526.3	975.0	452.1

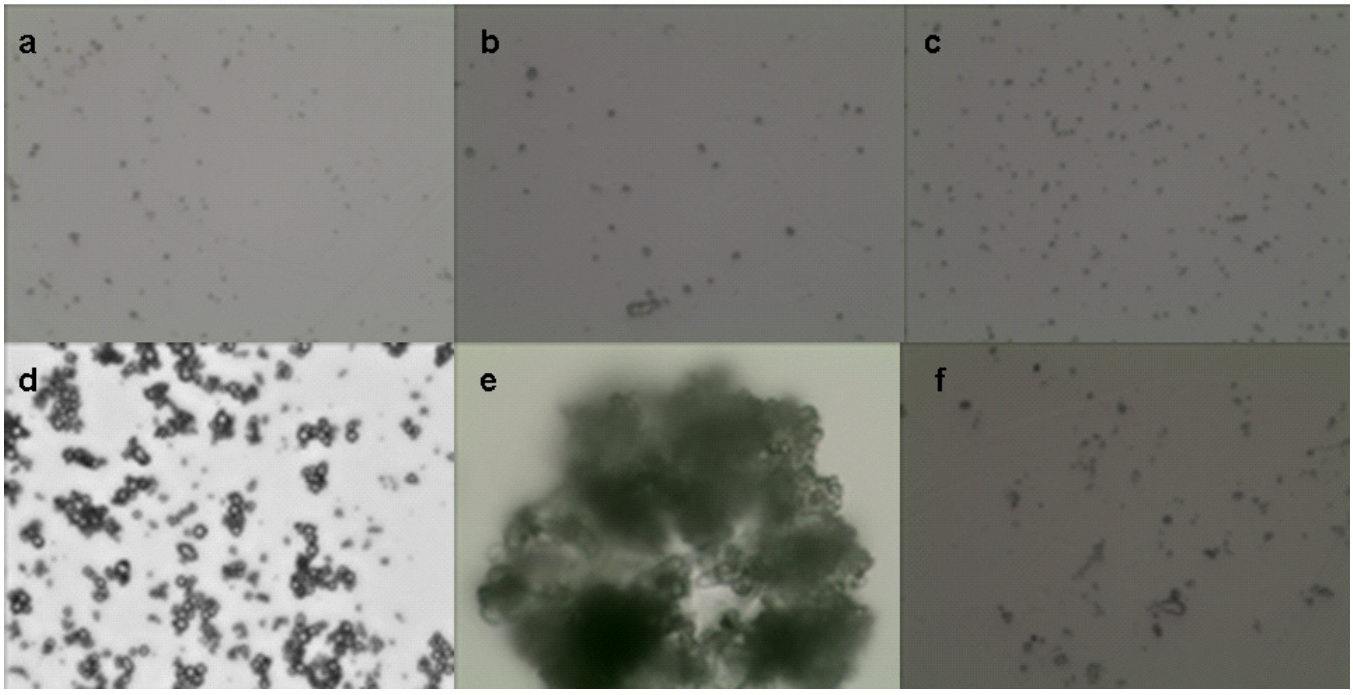

Fig. 3. Optical microscope images of nanocapsules with different emulsifiers (a-Op-10; b-SDBS; c-DBS; d-Arabic gum; e-0.5 % DBS to 1.5 % Arabic gum; f-1.5 % DBS to 0.5 % Arabic gum)

favorable for the application in self-healing materials. Therefore, Arabic gum was used as optimal emulsifier in this paper.

Effect of emulsifier content on the formation of nanocapsules: Arabic gum was used as the emulsifier for the preparation of nanocapsules. The effect of emulsifier content (0.5, 1 and 1.5 %) on the encapsulation rate, average diameter and optical microscope were investigated. Table-4 showed that when the Arabic gum content was 1 %, the encapsulation rate of the nanocapsules was the highest (79.9 %). Fig. 4 showed that when the Arabic gum content were 0.5 or 1 %, adhesion occurred. When the Arabic gum content was 1 %, the nanocapsule size increased and dispersion was uniform. Therefore, the optimal Arabic gum content was 1 %.

TABLE-4
EFFECT OF CONTENT OF EMULSIFIER ON THE ENCAPSULATION RATE AND AVERAGE DIAMETER

Content of emulsifier	0.5 %	1.0 %	1.5 %
Encapsulation rate	48.8 %	79.9 %	65.5 %
Average diameter (nm)	423.5	562.3	442.9

Scanning electron microscope (SEM): The optimal processing conditions for the preparation of nanocapsules were 0.7:1 for the core/shell mass ratio, 800 rpm for agitation rate and 1 % for gum content as emulsifier. The morphology of the nanocapsules was characterized by SEM and the results were showed in Fig. 5. Fig. 5 (a) showed that the nanocapsules existed uniform distribution. Fig. 5 (b) showed the surface of the nanocapsule became rough, which was beneficial for the interfacial join between nanocapsule and matrix.

Osmosis performance evaluation of nanocapsule: Fig. 6 showed osmosis performance evaluation of nanocapsule. As can be seen in Fig. 6, there is large mass change from 2 g to 1.74 g in the first hour because of that part of core material was not well covered and directly dissolved in ethanol. In the next 23 h, the mass of microcapsules was decreased from 1.74 to 1.67 g which was not largely changed. So the nanocapsules were well encapsuled and slowly osmosed.

Conclusions

• Nanocapsules with urea formaldehyde resin as shell material and modified aliphatic amine (HB-1618) as core material were prepared by interfacial polymerization process. The effect of core/shell mass ratio, agitation rate and emulsifierst on the encapsulation rate, average diameter and dispersion of nanocapsules were investigated. The results showed

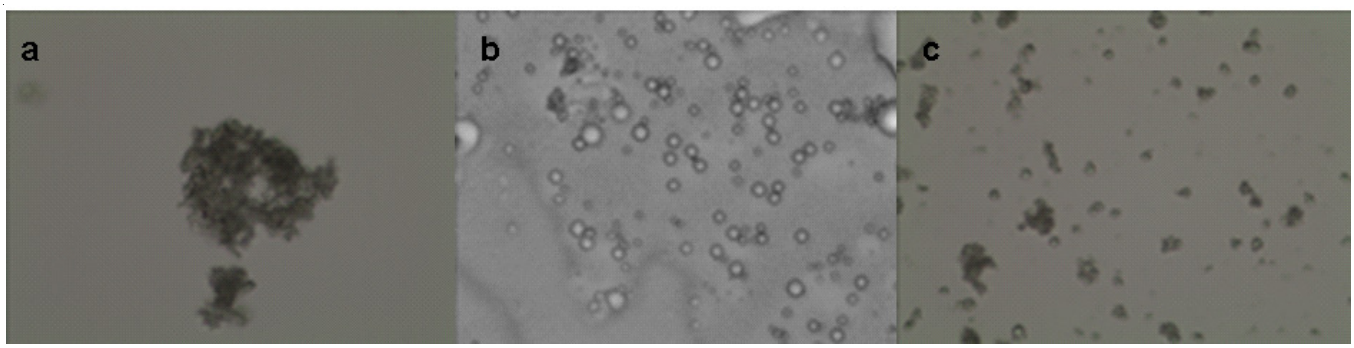

Fig. 4. Optical microscope images of nanocapsules with different content of emulsifiers (a-0.5 %; b-1.0 %; c-1.5 %)

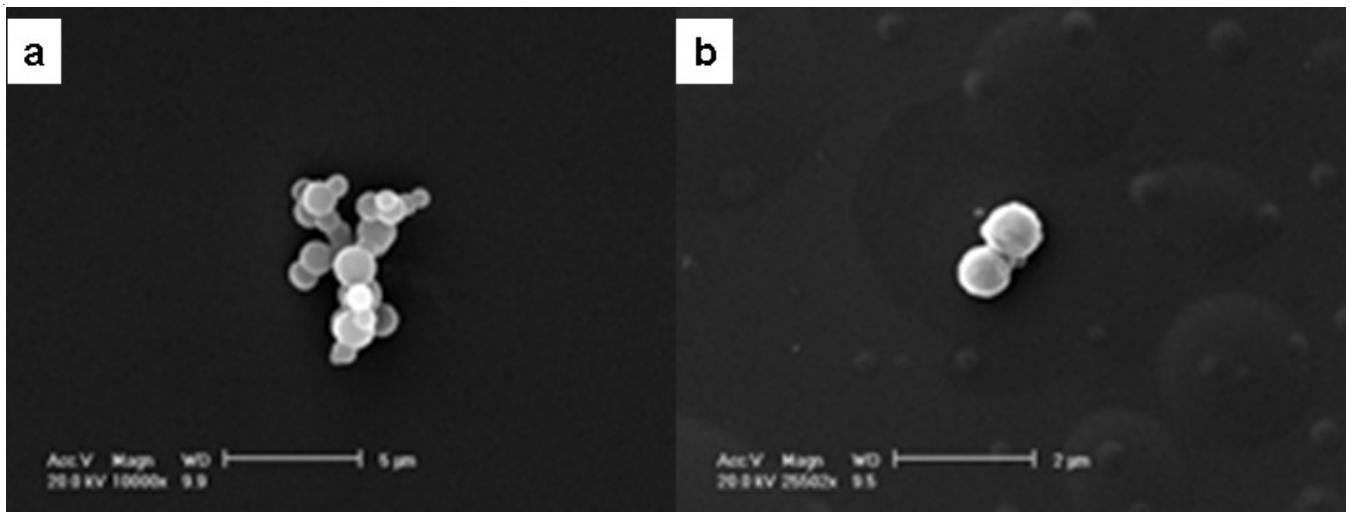

Fig. 5. SEM of epoxy resin nanocapsule (a) and (b) single

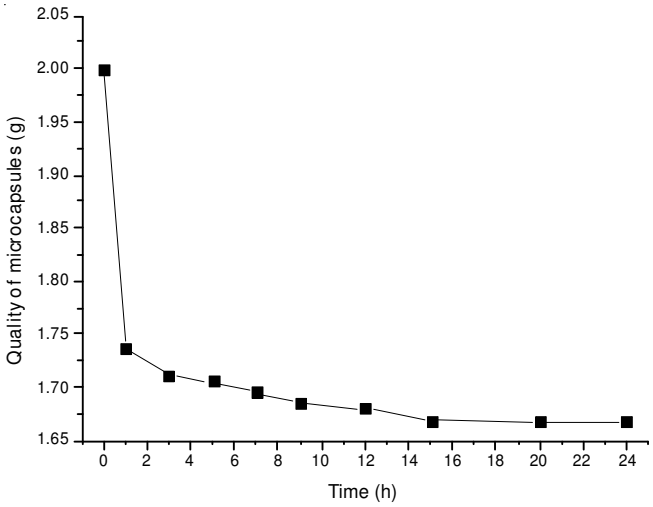

Fig. 6. Osmosis performance evaluation of nanocapsules

the optimum processing conditions were 0.7:1 for the core/shell mass ratio, 800 rpm for agitation rate and 1 % for gum content as emulsifier.

• The results of SEM and osmosis performance evaluation showed nanocapsules were well encapsuled and the surface of the nanocapsule became rough, which was beneficial for the use in the matrix materials.

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