J Mater Sci (2011) 46:3604–3610
DOI 10.1007/s10853-011-5276-3

Preparation and characterization of polystyrene/polycarbonate composite hollow microspheres by microencapsulation method

**Jie Li · Shujun Wang · Hongyan Liu ·
Sukai Wang · Long You**

Received: 4 November 2010 / Accepted: 12 January 2011 / Published online: 25 January 2011

Abstract Polystyrene/polycarbonate (PS/PC) composite hollow microspheres were successfully prepared via microencapsulation method. Fourier-transform infrared spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry, and thermogravimetric analysis were used for the characterization of the obtained hollow microspheres. SEM images showed that there were a big cavity and some small cavities inside the composite hollow microspheres, and the hollow microspheres prepared at 42 °C presented better morphology and smaller size distribution compared with that prepared at higher temperature of solvent evaporation. The tap density of the composite hollow microspheres increased from 0.28 g cm^{-3} at PS/PC composite concentration of 5 wt% in oil phase to 0.42 g cm^{-3} at concentration of 11.7 wt%. The mean diameter of the composite hollow microspheres ranged from 13 to 528 μm. It increased with an increase in the concentration of composite in oil phase and decreased with increasing the second rotating speed. Thermal analysis showed that the composite hollow had thermal stability below 358 °C.

Introduction

The synthesis of hollow microspheres in the nanometer to millimeter range, including organic hollow microspheres, inorganic hollow microspheres, and organic–inorganic composite microspheres, has received considerable attentions in recent years due to a wide variety of applications in composites encapsulation for controlled release systems and drug delivery, lightweight filler, confined nano- and meso-reaction vessels, catalytic carriers and so on [1–9]. As a kind of polymeric microspheres, polystyrene hollow microsphere with the characteristics of low density, optical scattering, high specific surface area and large useful inner space has been investigated by many researchers. Tsuji [10] prepared polystyrene hollow pellet for inertial confinement fusion experiments using emulsion technique. Mishra [11] fabricated polystyrene hollow microspheres as laser fusion targets by optimized density-matched emulsion technique. Following above studies, composite polystyrene hollow microspheres were further developed to improve the mechanical stability of the microspheres or endow the microspheres with new function. The composites usually incorporate a combination of metallic/organic and two types of organic particles. Zhang [12] synthesized uniform PS/α-Fe_2O_3 composite hollow microspheres with good photocatalytic activity, large surface area and a high remanent magnetization under hydrothermal conditions by hard template method. He et al. [13] prepared polystyrene/melamine–formaldehyde hollow microsphere composite by self-assembling of latex particles at emulsion droplet interface. However, these preparation methods of

J. Li · S. Wang (✉) · S. Wang · L. You
State Key Laboratory of Heavy Oil Processing,
China University of Petroleum, 102249 Beijing, China
e-mail: ivytea2008@hotmail.com

J. Li
e-mail: ivytea2008@sina.com

S. Wang
e-mail: yongyuanxiaotian@163.com

L. You
e-mail: youlong2004@126.com

H. Liu
College of Science, China University of Petroleum,
102249 Beijing, China
e-mail: lijie_3000@163.com

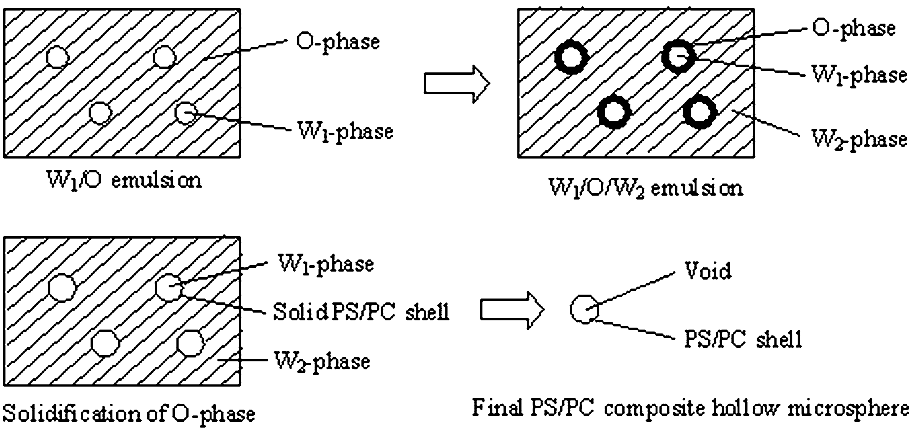

Fig. 1 Scheme illustration of the preparation of the composite hollow microspheres

composite hollow microspheres have inconvenient operation and high cost.

In this article, the authors report the preparation of PS/PC-composite hollow microspheres to further improve the mechanical stability of polystyrene hollow microspheres by microencapsulation method since in Lee' work the mechanical properties of the PS/PC composite were found to be enhanced than pure PS by adding PC that possesses high impact strength [14, 15]. Hollow microsphere preparation by microencapsulation method basically consists of four major steps [16]: (i) dissolution of PS and PC in an organic solvent (O) and emulsification of this oil phase with a aqueous phase (W_1), which forms W_1/O emulsion; (ii) emulsification of this W_1/O emulsion in a second aqueous phase, forming W_1/O/W_2 emulsion; (iii) removal of the solvent from the oil phase which is accompanied by solvent evaporation; (iv) harvesting and drying of the microspheres to remove the inner aqueous phase. The preparation procedure is shown in Fig. 1. The main advantages of microencapsulation method over other methods are the simple operation, low cost and "green process" in which the organic solvent and the second water phase can be reused. Thus, it is perfectly suitable for industrial fabrication of PS/PC composite hollow microspheres. The prepared PS/PC-composite hollow microspheres were characterized by FTIR, SEM, DSC, and TGA.

Experimental

Materials

Polycarbonate, high purity, was purchased from Engineering Plastics (Shanghai) Co., Ltd. Polystyrene was provided by Sinopec Beijing Yanshan petrochemical Co., Ltd. Gelatin was provided by Tianjin Fuchen Chemical Reagent Co., Ltd. Dichloromethane was obtained from Beijing Chemical Co., Ltd. Absolute ethanol, wt% >99.7%, was supplied by Beijing Chemical Co., Ltd. Sodium dodecylbenzene sulfonate was supplied by Tianjin Yingdaxigui Chemical Co., Ltd. All the chemicals were used as received without further purification.

Preparation of PC hollow microspheres

There are three different phases of solution adopted to prepare PS/PC hollow microspheres by microencapsulation method: W_1 phase: distilled water and sodium dodecylbenzene sulfonate; O phase: polycarbonate, polystyrene, compatiblizer, dichloromethane; W_2 phase: distilled water, gelatin, and sodium dodecylbenzene sulfonate.

The process of preparing PS/PC hollow microspheres is as follows: W_1 phase was placed into the O phase at room temperature, and the mixture was emulsified using a high shear dispersing and emulsifying machine (FM200). Then the prepared W_1/O emulsion was poured into W_2 phase and stirred by using an ordinary agitator. The formed W_1/O/W_2 multiple emulsions was placed into a three-neck round-bottomed flask and stirred at 300 rpm for 2 h, while the temperature was controlled between 42–45 °C. Then the temperature was elevated to 70–75 °C to solidify the PS/PC shell. The obtained PS/PC hollow microcapsules suspension was filtered and placed into absolute ethanol. After the encapsulated water was removed in drying oven for 48 h at 70 °C, PS/PC hollow microspheres were prepared.

Characterization of PS/PC hollow microspheres

FTIR was carried out on a Bruker Vector-22 FTIR spectrometer using a KBr pellet. Surface morphology of the fabricated PS/PC hollow microspheres was examined by scanning electron microscopy (Quanta 200F FEI, America) after vacuum sputtering the particles with gold. The particle size of PS/PC hollow microspheres was determined using SEM equipped with an image analysis software. The mean diameter of PS/PC hollow microspheres was obtained by calculating at least 250 hollow microspheres [17]. The tap density of the PS/PC hollow microspheres was determined by using a tap density tester (FZS4-4B). The thermal properties of PS and PS/PC composite hollow microspheres were analyzed by a differential scanning calorimeter (DSC 204 F4 Netzsch, Germany) under the protection of nitrogen flow. Heating rate was maintained at 10 °C min^{-1} in the temperature range of 20–800 °C.

Results and discussion

FTIR of PS/PC composite hollow microspheres

FTIR spectra were recorded in the transmittance mode. The FTIR spectra of pure PS, pure PC and PS/PC composite hollow microspheres are shown in Fig. 2, respectively. For PS, the peaks at 695 and 754 cm^{-1} can be attributed to C–H bonds of mono-substituted benzene ring. The peaks formed at 1451 and 1492 cm^{-1} represent C–H bonds. A peak at 1600 cm^{-1} represents C=C bonds of benzene ring, while the peak at 2920 cm^{-1} is saturated CH and $\mathrm{CH_2}$ bonds. The band at 3025 cm^{-1} represents C–H bonds that connected directly to C=C bonds of benzene ring. The absorption bands as obtained from the pristine PC spectrum are identified as 768 cm^{-1}: out of phase skeletal vibration of C–H deformation; 829 cm^{-1}: $\mathrm{C(CH_3)}$ stretching vibration, 1227 cm^{-1}: C–O stretching vibration; 1506, 1600 cm^{-1}: C=C phenyl ring stretching vibration; 1774 cm^{-1}: C=O stretching vibration; 2484 cm^{-1}: hydroxyl stretching bond; 2966 cm^{-1}: $\mathrm{CH_3}$ stretching vibrations; 3060 cm^{-1}: CH stretching vibration of aromatic compounds. All the above band assignments for PS and PC are identical to that for PS and PC reported in literatures [18, 19].

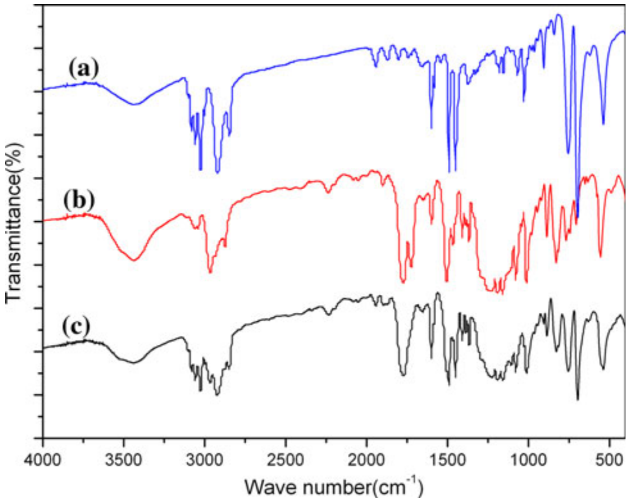

Fig. 2 FTIR spectra of pure PS (*a*), pure PC (*b*), and PS/PC hollow microspheres (*c*)

All the characteristic peaks of pure PS at 695, 754, 1492, 1451, 1600 cm^{-1} and the peaks of pure PC at 829, 1227, 1506, and 1774 cm^{-1} appear in the spectrum of PS/PC-composite hollow microspheres. In view of the above, it can be established that the microsphere is composed of PS and PC.

SEM of PS/PC composite hollow microspheres

The morphology of the PS/PC-composite hollow microspheres is shown in Fig. 3. Figure 3a shows that PS/PC-composite hollow microspheres present spherical shape and the surface is smooth and nonporous. However, Crotts [20] prepared various porous hollow microspheres composed of poly(D, L-lactic-co-glycolic acid) using the water/oil/water (W/O/W) multiple emulsion solvent evaporation technique. The pores are attributed to the fact that the internal water droplets in the low polymer concentration solution tend to coalesce together more easily. Thus, the nonporous PS/PC composite hollow microspheres prepared in this study may be ascribed to the suitable composite concentration (5–15 wt%). To indicate the hollow structure, the PS/PC composite hollow microspheres were incised. SEM images of the incised composite hollow microspheres are shown in Fig. 3b, c. It can be observed that a big cavity and some small cavities around the big one are inside the microspheres. According to Gao's work [21], there was only a single cavity inside the microspheres. The emulsion droplets with more than one inner micro-droplet evolve toward honeycomb structure depending on the formulation conditions [22]. The resulted small cavities in this study can be attributed to the fact that the stirring rate for the secondary emulsification is much smaller (200–600 rpm) than that of the primary emulsification (10000–20000 rpm) and therefore the diameter of the inner microdroplets is much smaller than that of the emulsion droplet [23], leading to the honeycomb structure.

Temperature of solvent evaporation

It is known from published work that the temperature of solvent evaporation is a key parameter influencing the preparation of the hollow microspheres because the rate of volatile solvent removal from the solidifying microspheres is controlled by the temperature [24, 25]. Higher temperatures will facilitate the evaporation of the solvent while lower temperatures will prolong the preparation process. The morphology of the composite hollow microspheres prepared at temperatures of 42, 43, and 44 °C was examined while other preparation conditions were fixed. Figure 4 shows that the size distribution of composite hollow microspheres prepared at higher temperatures (43 and 44 °C) shifts toward the larger size compared to the

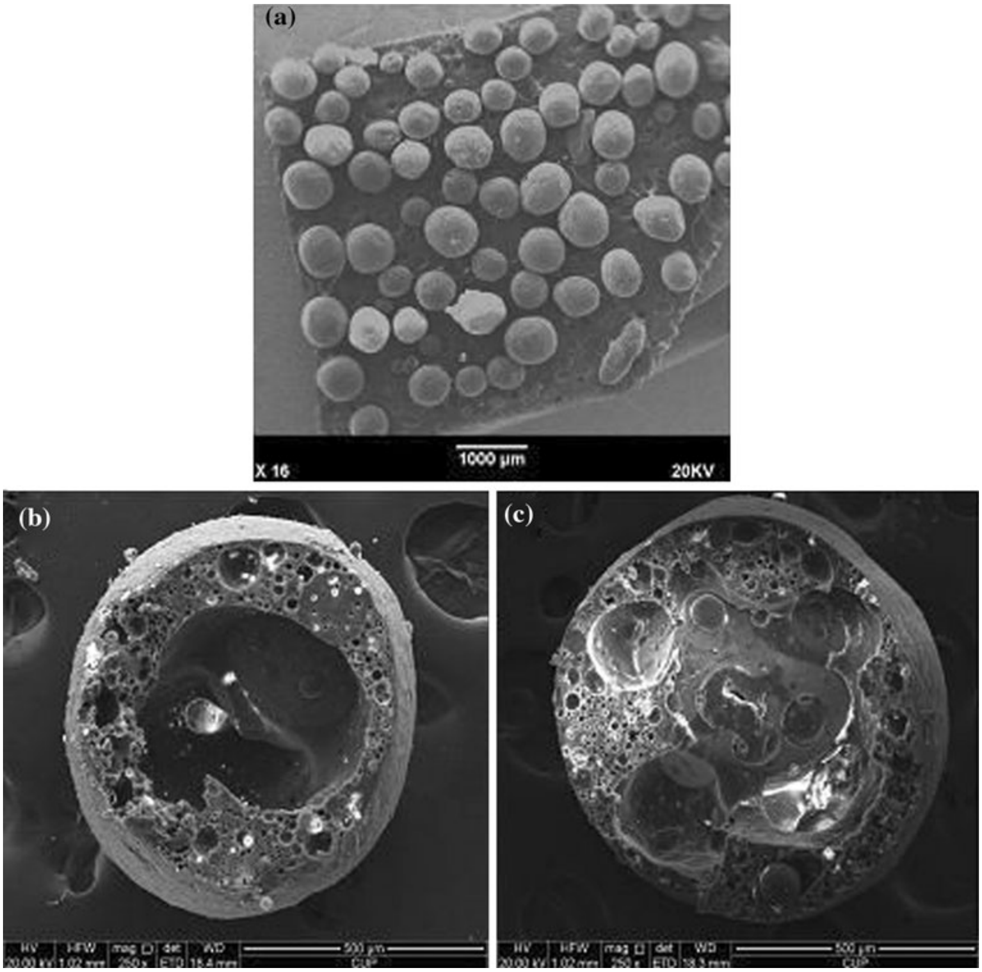

Fig. 3 SEM images of the hollow microspheres (**a**) and the incised hollow microspheres (**b**, **c**)

microspheres prepared at 42 °C, and some broken fragments can be observed. The resultant larger microspheres are due to very rapid microsphere solidification with insufficient mixing time to reduce droplet size. The generated fragments can be explained by following reason. Previous study showed that after a thin polymer film was precipitated at the interface, the remaining volatile solvent evaporation may be hindered by this physical barrier [26]. Thus, when the temperature was too high, the pressure applied on the polymer film was increased too much, which would result in rupture of the freshly formed polymer wall.

Tap density of PS/PC composite hollow microspheres

Tap density is the apparent density of a volume of powder obtained when its receptacle is tapped. The tap density of a material can be used to predict its floatability and compressibility. The influence of the concentration of composite in oil phase on the tap density of hollow microspheres was studied when the composite was composed by 50 wt% PS and 50 wt% PC, and W_1 and W_2 phases were kept invariant. Figure 5 shows that the tap density of the composite hollow microspheres increased with increasing the concentration of composite in oil phase from 0.28 g cm^{-3} at concentration of 5 wt% to 0.42 g cm^{-3} at concentration of 11.7 wt%. This can be explained by the fact that with increasing the concentration of composite in oil phase, the volume fraction of the internal aqueous phase in the primary W_1/O emulsion was decreased, resulting in composite hollow microspheres with small hollow cavities and higher tap density. The tap density of the prepared composite microspheres is much lower than the density of raw PS (1.05 g cm^{-3}) and PC (1.21 g cm^{-3}), which suggests the hollow structure of the composite microspheres.

Particle size of PS/PC composite hollow microspheres

The relationship of the mean particle size of the composite hollow microspheres and the concentration of composite in

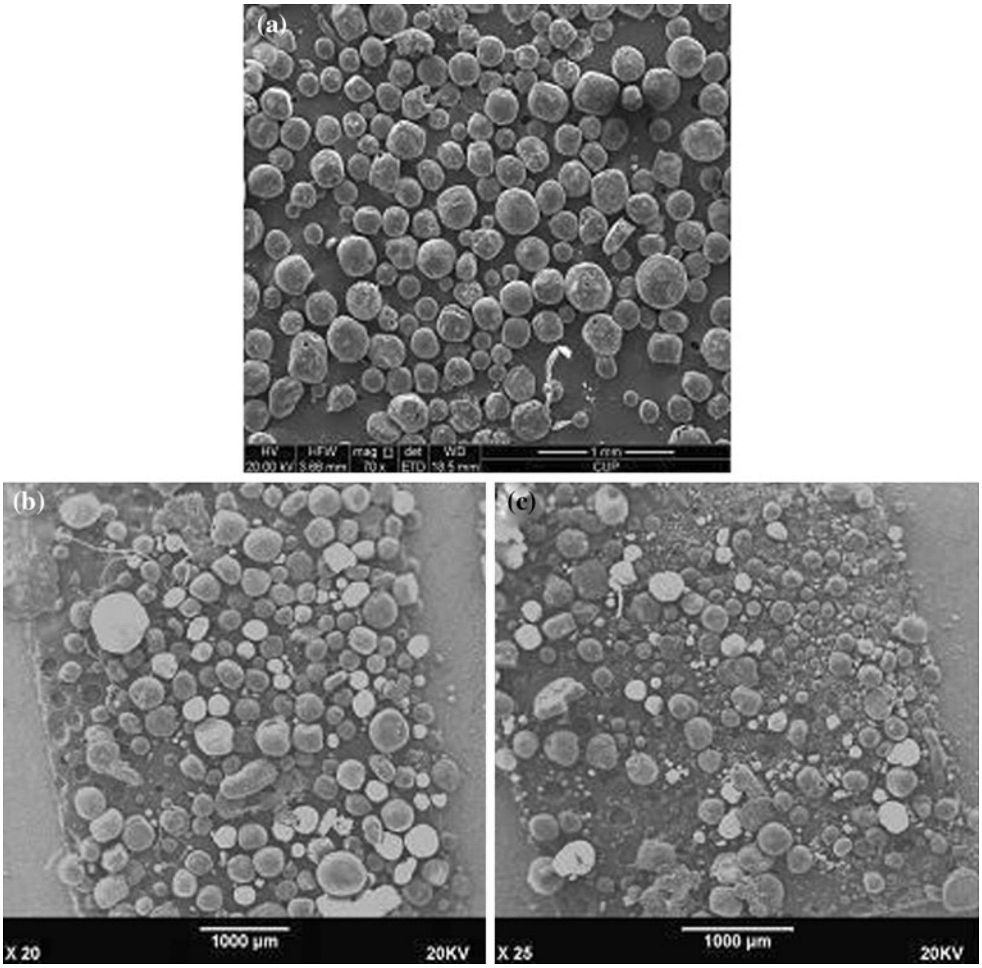

Fig. 4 SEM images of hollow microspheres prepared at temperature of 42(**a**), 43(**b**), and 44 °C(**c**)

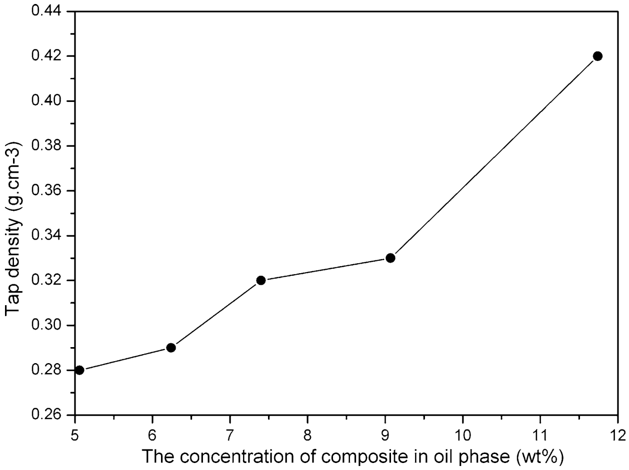

Fig. 5 Relationship between the concentration of composite in oil phase and the tap density

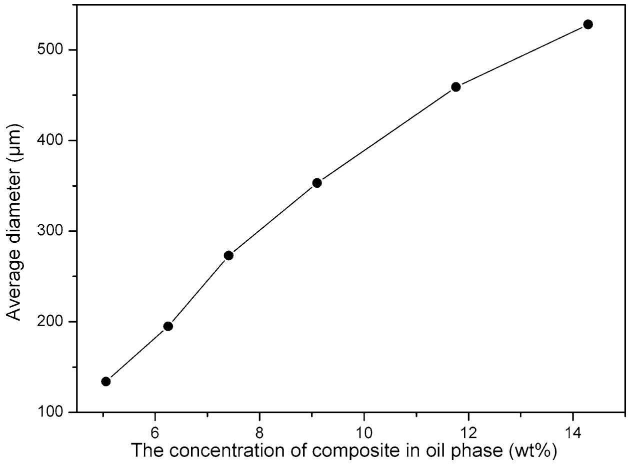

Fig. 6 The effect of the concentration of composite in oil phase on the average diameter

oil phase is exhibited in Fig. 6. The concentration of composite in oil phase was varied between 5 and 14.3 wt% to study its effect upon the particle size, while the composite was composed by 50 wt% PS and 50 wt% PC, and other reaction conditions were fixed. It reveals that the mean diameter of composite hollow microspheres gradually increased from 135 to 528 μm as the concentration of composite in oil phase increased from 5 to 14.3 wt%. The increase in size of the hollow microspheres with increasing composite concentration arised from the higher viscosity of oil phase, inhibiting emulsifying process when oil phase was emulsified into W_2 phase with homogenization.

To indentify the effect of the stirring rate for the secondary emulsification on the mean diameter of the composite hollow microspheres, the composite concentration was fixed at 7 wt% while the stirring rate was varied between 225 and 600 rpm. The effect of increasing the stirring rate on the particle size is shown in Fig. 7. It shows that the mean diameter of the composite hollow microspheres decreased with increasing the stirring rate from 470 μm at 225 rpm to 13 μm at 600 rpm. This can be explained by the fact that faster second emulsifying rotating speed dispersed W_1/O droplets of smaller size into W_2, resulting in $W_1/O/W_2$ emulsion droplets with small size and accordingly smaller hollow microspheres were formed. This result is also confirmed by Yang's work that high stirring speed can reduce microsphere size [27]. However, when the stirring rate was increased to 675 rpm, the hollow microspheres could not be formed nearly. The image of the product fabricated at 675 rpm is shown in Fig. 8. It can be observed that there are few spherical microspheres but many fragments. As a consequence of the immediate solvent extraction, the polymer precipitation occurs instantaneously upon emulsification and a thin film builds up at the interface. Thus, if the stirring rate is too fast, it may break the thin formed polymer film before total solidification. This is likely to be the reason for the broken hollow microspheres.

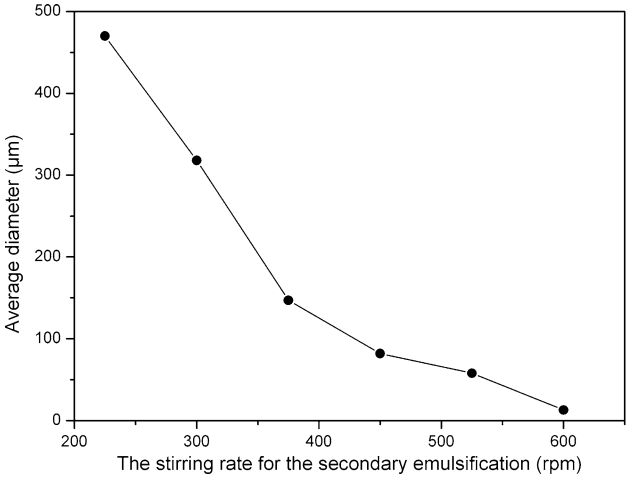

Fig. 7 The effect of the stirring rate for the secondary emulsification on the mean diameter

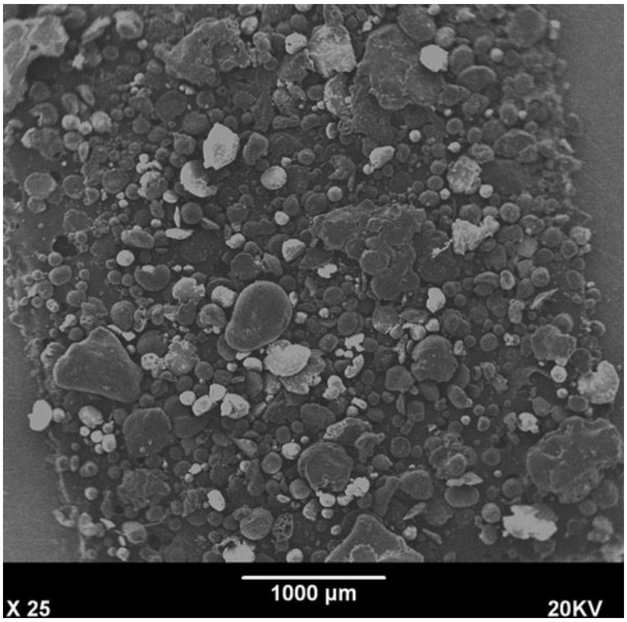

Fig. 8 SEM image of the hollow microspheres prepared at 675 rpm

Thermal analysis of PS/PC composite hollow microspheres

Figure 9 shows the DSC results of both pure PS hollow microspheres and PS/PC-composite hollow microspheres. For pure PS-hollow microspheres, the heat absorption peak at about 363 °C is due to the decomposition of PS and the strong heat absorption peak at 409 °C corresponds to further decomposition of PS. For PS/PC-composite hollow microspheres, the heat peak at 403 °C is attributed to the decomposition of PS and PC.

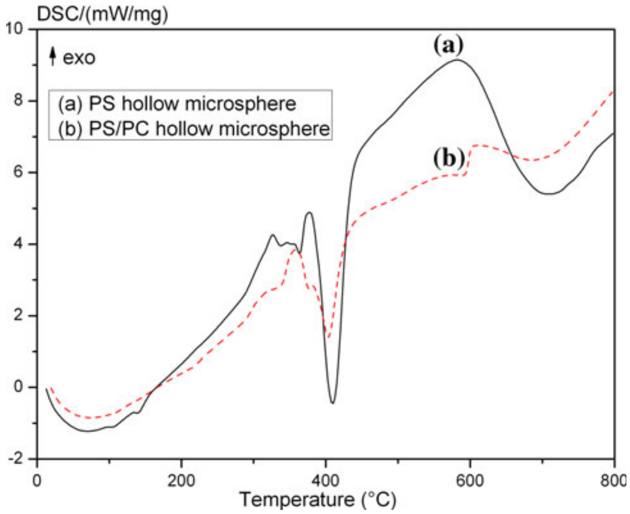

Fig. 9 DSC thermograms of PS (*a*) and PS/PC hollow microspheres (*b*)

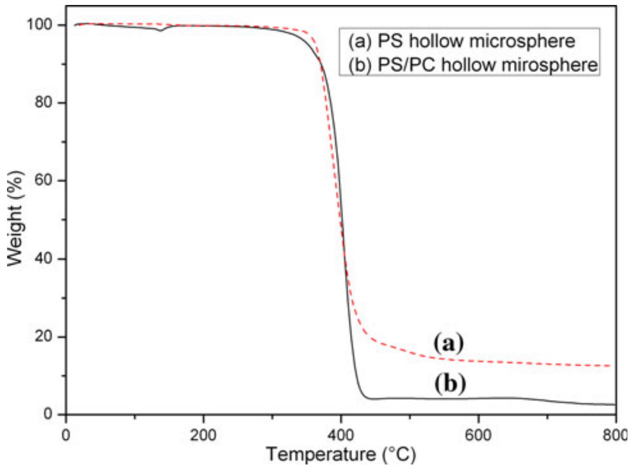

Fig. 10 TG thermograms of PS (*a*) and PS/PC composite hollow microspheres (*b*)

The thermal decomposition behavior of both pure PS hollow microspheres and PS/PC-composite hollow microsphere is shown in Fig. 10. The composite hollow microsphere is composed by 50 wt% PS and 50 wt% PC. Figure 10 shows that about 95 wt% of the total weight of PS-hollow microspheres loss occurs between 358 and 435 °C owning to the fast thermal decomposition of PS while 79 wt% the total weight of composite hollow microspheres loss occurs in the same temperature range. The results indicate that in the composite, the pyrolysis of partial PC occurs, except the decomposition of most PS. This may be due to an interaction between PS and PC in the temperature range of 358–435 °C since there is no noticeable weight loss for PC below 450 °C [28].

Conclusions

Nonporous polystyrene/polycarbonate (PS/PC)-composite hollow microspheres were successfully fabricated by microencapsulation method. SEM analysis showed that there were a big cavity and some small cavities inside the composite hollow microspheres. The hollow microspheres prepared at 42 °C presented better morphology and smaller size distribution compared with that prepared at higher temperature of solvent evaporation. The tap density of the composite hollow microspheres increased from 0.28 g cm^{-3} at composite concentration of 5 wt% in oil phase to 0.42 g cm^{-3} at concentration of 11.7 wt%. The mean diameter of the composite hollow microspheres increased with an increase in the concentration of composite in oil phase and decreased with increasing the second rotating speed. Thermal analysis showed that the composite hollow microspheres were stable below 358 °C.

Acknowledgements The authors gratefully acknowledge China University of Petroleum (Beijing) for giving them the opportunity to do this research and for their financial support.

References

1. Ansermet JP, Baeriswyl E (1994) J Mater Sci 29:2841. doi:10.1007/BF01117591
2. Verweij H, With G, Veeneman D (1985) J Mater Sci 20:1069. doi:10.1007/BF00585751
3. Joseph NJ, Lakshmi S, Jayakrishnan A (2002) J Control Release 79:71
4. Xu XL, Sanford AA (2004) J Am Chem Soc 9:7940
5. Naskar MK, Chatterjee M, Lakshmi NS (2002) J Mater Sci 37:343. doi:10.1023/A:1013656413578
6. Guan G, Zhang Z, Wang Z, Liu B, Gao D, Xie C (2007) Adv mater 19:2370
7. Li SY, Nguyen Lynsa, Xiong HR (2010) Nanomedicine 6:127
8. Kato T, Ushijima H, Katsumata M, Hyodo T, Shimizu Y (2002) J Mater Sci 37:2317. doi:10.1023/A:1015381603159
9. Wang XX, Ji HF, Zhang X, Zhang H, Yang XL (2010) J Mater Sci 45:3981. doi:10.1007/s10853-010-4470-z
10. Tsuji R, Ogushi Y (1997) Fusion Eng Des 34–35:811
11. Mishra KK, Khardekar RK, Singh R, Pan HC (2002) Pramana-J Phys 59:113
12. Zhang YP, Chu Y, Dong LH (2007) Nanotechnology 18:435608
13. He XD, Ge XWW, Wang MZ, Zhang ZC (2005) Polymer 46:7598
14. Lee WJ, Dong CL (2000) Polymer 41:1749
15. Sai S, Adam DM, Mary CB (2007) Int J Solids Struct 44:2381
16. Freitas S, Merkle HP, Gander B (2004) J Control Release 102:313
17. Yuan L, Gu AJ, Liang GZ (2008) Mater Chem Phys 110:417
18. Tan WT, Radhi MM, Rahman MZA, Kassim AB (2010) J Appl Sci 10:139
19. Bok NJ, Charles AW (2005) Thermochim Acta 426:73
20. Crotts G, Park TG (1995) J Control Release 35:91
21. Gao F, Su ZG, Wang P, Ma GH (2009) Langmuir 25:3832
22. Yang YY, Chung TS, Ng NP (2001) Biomaterials 22:231
23. Iosif DR, Fumio W, Motohiro U (2004) J Control Release 99:271
24. Yang YY, Chung TS, Bai XL, Chan WK (2000) Chem Eng Sci 55:2223
25. Yang YY, Chia HH, Chung TS (2000) J Control Release 69:81
26. Li M, Olivier R, Denis P (2008) Int J Pharm 363:26
27. Yang YY, Chung TS, Ng NP (2001) Biomaterials 22:231
28. Bok NJ, Charles AW (2004) Polym Degrad Stabil 86:419