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ORIGINAL CONTRIBUTION

Multihollow structured poly(methyl methacrylate)/silver nanocomposite microspheres prepared by suspension polymerization in the presence of dual dispersion agents

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Abstract Poly(methyl methacrylate) (PMMA)/silver nanocomposite microspheres with unique multihollow structures were prepared by suspension polymerization in the presence of dual dispersion agents. The addition of a lipophilic emulsifier, polyethylene glycol (30EO) dipolyhydroxystearate (Arlacel P135), not only stabilized water-in-oil (W/O) emulsion, but also converted silver nanoparticles from hydrophilic to lipophilic. When a suspension polymerization dispersion agent, poly(vinyl alcohol), was added to the above W/O emulsion system, a water-in-oil-in-water suspension was formed with silver nanoparticles dispersed in the oil phase. The suspension polymerization was carried out at low temperature with 2,2'-azobis(2,4-dimethylvaleronitrile) as the initiator. When modified silver nanoparticles were added, the rate of polymerization increased slightly. High monomer conversion (about 85%) was obtained in spite of low polymerization temperature of 30 °C. Under controlled conditions, PMMA/silver microspheres with various hollow structures were synthesized. The PMMA/silver microspheres with multihollow structure showed high antibacterial ability.

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Introduction

Recently, control of the morphology of particles has become an intensive area due to the important effects of particle morphology on the physical properties of the particles. The synthesis of core-shell, microdomain, interpenetrating network, and multihollow particles has been reported [1]. Multiple emulsions, or emulsions in emulsions, are complex systems in which small droplets are encapsulated by large droplets. These complicate emulsion systems are widely used to encapsulate active ingredients in myriad applications, including drug delivery [2, 3], foods [4, 5], cosmetics [6, 7], chemical separations [8], and syntheses of microspheres and microcapsules [9–13]. Many methods such as alkali swelling, dynamic swelling, and emulsion polymerization have been used to prepare hollow particles.

Among them, water-in-oil-in-water (W/O/W) double emulsion-based techniques are indeed attractive because the resulting double emulsions have two interfaces in the system: a small internal aqueous phase is dispersed in an oil phase, which, in turn, is dispersed in the second aqueous phase [14]. Okubo and co-workers [15–17] prepared submicrometer-sized multihollow particles via both alkali swelling and dynamic swelling methods. Omi et al. [18] produced hollow particles by two-stage suspension polymerization using a Shirasu porous glass membrane. Yang et al. [19] prepared micrometer-sized multihollow spheres of epoxy resin by a phase inversion technique. Several researcher prepared poly(methyl methacrylate) (PMMA) multihollow particles by W/O/W emulsion polymerization technique [20, 21].

The materials formed by embedding of inorganic particles into polymeric matrices represent a new class of polymeric materials that combine the properties of the inorganic particles (in terms of mechanical strength, modulus, and thermal stability) with the processability and the flexibility of organic polymer matrix. Of course, such materials can be obtained by simply mixing required organic and inorganic components [22]. However, in order to achieve the best dispersion of inorganic particles in polymer matrix and interfacial adhesion between the polymer and inorganic particle, the techniques for synthesizing composite particles made of inorganic particles encapsulated by polymers have been developed [23, 24] by using miniemulsion [25, 26], suspension [27], dispersion [28], and emulsion polymerization techniques [29, 30].

Poly(methyl methacrylate) is an important polymeric material with high light transmittance, colorlessness, chemical resistance, and weathering corrosion resistance. Due to these superior characteristics, PMMA has been widely used in coating, optical fiber, outdoor electrical applications, etc. [31–34].

Silver nanoparticles are widely used as photosensitive components [35], catalysts [36, 37], Raman spectroscopy enhancement additive [38], and chemical analysis [39]. Especially, silver is known to have a wide antibacterial spectrum [40]. Additionally, due to its comparatively high safety [41], many researchers have successfully developed antibacterial and disinfectant agents with silver composites using various carriers. In recent years, much effort has been devoted to the studies of the in situ synthesis of metal nanoparticles inside polymer matrix [42–44]. Zhu et al. [45] reported a method in that the reduction of silver ions and the polymerization of monomers occurred simultaneously by γ-irradiation.

In our previous study, polymer/silver microspheres were prepared using suspension polymerization of monomer in the presence of hydrophilic silver nanoparticles [46–48]. However, the hydrophilic silver nanoparticles could not embed into polymer matrix uniformly but formed aggregates. In order to disperse the silver nanoparticles in polymer matrix, hydrophilic silver nanoparticles were modified by an oil-soluble surfactant, polyethylene glycol (30EO) dipolyhydroxystearate (Arlacel P135), which is commonly used for preparing W/O emulsion. Because of the low hydrophile–lyophile balance (HLB) number of Arlacel P135, the surface of the silver nanoparticles was converted from hydrophilic to hydrophobic by the adsorption of Arlacel P135, which resulted in a good dispersion of the silver nanoparticles in monomer droplets and polymer matrix. The effects of modified silver nanoparticles on the polymerization behaviors, morphology of PMMA microspheres, and antibacterial ability of the final particles are reported in this article. The control of hollow structure of PMMA in the presence of Ag nanoparticles is also studied.

Experimental

Materials

Methyl methacrylate purchased from Aldrich was sequentially washed with $NaHSO_3$ aqueous solution and water, and then dried with anhydrous $CaCl_2$, followed by distillation in a nitrogen atmosphere under reduced pressure [49]. The monomer-soluble initiator, ADMVN (Wako), was recrystallized twice in methanol before use. Poly(vinyl alcohol) (PVA) with number-average molecular weight of 127,000 and degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Arlacel P135 was used as an oil-soluble surfactant. Aqueous silver nanoparticle dispersion (AGS-WP001, 10,000 ppm) with diameters ca. 15–30 nm was purchased from Miji Tech., Korea. Deionized water was used for all the experiments.

Preparation of PMMA/silver nanocomposite microspheres

To prepare PMMA/silver nanocomposite microspheres, 0.06–0.54 g of Arlacel P135 was dissolved in 60 ml MMA monomer. After the surfactant Arlacel P135 was dissolved, 3.6 ml of silver nanoparticle in water suspension (10,000 ppm) and desired initiator (0.0001 mol/mol based on MMA) was mixed with 60 ml MMA monomer under ultrasonification for 5 min using Bandelin UW 3,100 equipment. Because Arlacel P135 is a low HLB surfactant, the silver nanoparticles were converted from hydrophilic to hydrophobic by adsorption of Arlacel P135, and transferred from aqueous phase to monomer phase. The mixture was then ultrasonificated at room temperatures for 5 min. Because a small amount of water was introduced into the monomer phase during the addition of silver nanoparticles, water in oil emulsion was formed in the presence of Arlacel P135. The above W/O emulsion was poured into a 250-ml round flask equipped with a two-bladed Teflon impeller and a condenser filled with 90 ml of 5% PVA–water solution. Due to the synergistic effects of oil-soluble surfactant Arlacel P135 and water soluble dispersing agent PVA, a W/O/W suspension was formed, and silver nanoparticles were dispersed in the monomer phase (confirmed by scanning electron microscope [SEM] picture of the final polymer particles, as shown later). The polymerization of MMA in the presence of aqueous silver nanoparticle dispersion was conducted at different temperatures under N_2. After predetermined times, the reaction mixture was

Table 1 Suspension polymerization conditions of MMA

Conditions	
Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.0001, 0.0005, 0.001 mol/mol of MMA
Suspending agent concentration	0.15, 0.5, 0.9 g/l of water
MMA/water	0.5, 1.0 l/l
Rpm	500
Temperature	30, 40, 50°C
Silver nanoparticles dispersion content	5, 10 wt% of MMA
Surfactant concentration	0.01, 0.03, 0.06, 0.09 wt% of MMA

cooled and kept for 1 day to separate the PMMA/silver spheres. The final PMMA/silver spheres were filtered and washed with warm water, and finally dried to remove monomer residue.

Conversion was calculated by measuring the weight of the final PMMA/silver microspheres. In the case of calculating of conversion, the weight of silver was ignored because the ratio of silver nanoparticles in the PMMA microsphere is less than 0.1%. Conversions were averages of three determinations. The detailed polymerization conditions are given in Table 1.

Characterizations

The molecular weights of PMMA were calculated using Eq. 1 [50].

$$[\eta] = 5.5 \times 10^{-5} [M_n]^{0.76} (\text{in benzene at } 25^{\circ}\text{C}) \qquad (1)$$

where $[\eta]$ is intrinsic viscosity. The number-average degree of polymerization (*Pn*) of PMMA was calculated from *Mn*. To precisely obtain the *Pn* of PMMA, in each case, the PMMA/silver spheres were purified by reprecipitation and centrifuged (20,000 rpm) from a benzene/hexane mixture, finally dried in a vacuum oven at 60 °C.

The surface morphology of the PMMA/silver microspheres was examined using a Hitachi S-570 scanning electron microscope (SEM). To confirm the successful incorporation of silver nanoparticles into PMMA microspheres, wide-angle X-ray diffraction (XRD) measurements were performed at room temperature with a Rigaku (D/Max IIIB) X-ray diffractometer using Ni-filtered CuKα radiation. The antibacterial performance was investigated to examine the biological function of PMMA/silver nanoparticle microspheres by KSM 0146 (shake flask method) using ATCC 6538 (*Staphylococcus aureus*) and ATCC 25922 (*Escherichia coli*).

Results and discussion

Suspension polymerization behavior of PMMA/silver microspheres

In the current study, ADMVN was used to prepare PMMA/silver nanocomposite microspheres at room temperature. Figure 1a presents the conversion–time relationship at different polymerization temperatures with an initiator concentration of 0.0001 mol/mol of MMA in the presence of modified silver nanoparticles. Although a low initiator concentration was used, the conversion increased steadily with the reaction time at a reaction temperature of 30–50 °C until ca. 85–95% of conversion. The high conversion suggests that the chain transfer and termination reactions

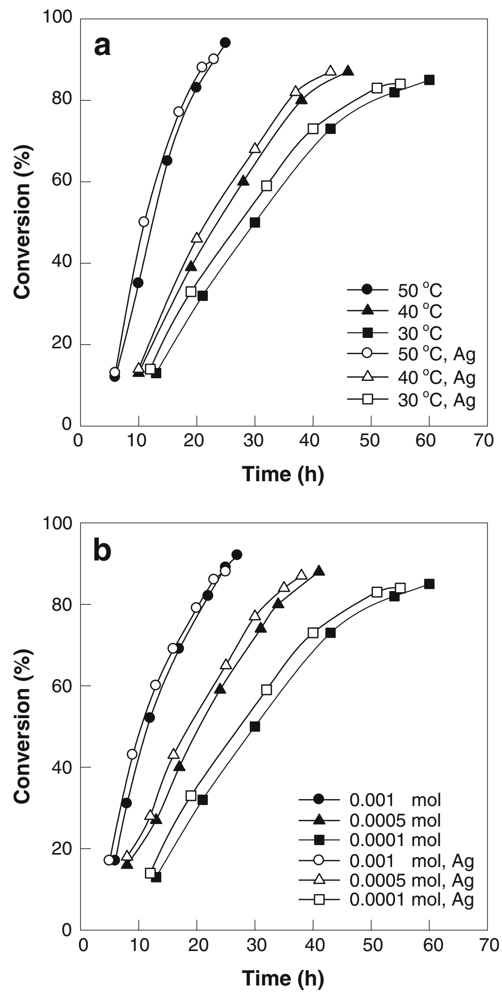

Fig. 1 Conversion of MMA into PMMA/silver suspension polymerization (**a**) with different polymerization temperatures (**b**) with different ADMVN concentrations at 40 °C. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.15 g/l of water; surfactant concentration: 0.09 wt% of MMA; silver nanoparticles dispersion content: 10 wt% of MMA)

Table 2 Molecular weights of pure PMMA and PMMA/silver

Sample	P_n
Pure PMMA	3.56×10^{-4}
PMMA/silver 5%	3.27×10^{-4}

were not significant under the conditions used in this study. The molecular weights of pure PMMA and PMMA/silver microspheres are given in Table 2. Pure PMMA and PMMA/silver nanocomposite microspheres used for calculating molecular weight were prepared in the same conditions. As shown in Table 2, the molecular weight of PMMA/silver 5% nanocomposite microspheres is similar to that of pure PMMA. Conversions at different initiator concentrations with or without modified aqueous silver nanoparticles at 40 °C are shown in Fig. 1b. The polymerization rate was increased with increasing the initiator concentration, which coincided well with the theoretical predictions [51].

In our previous study [47], the rates of polymerization with hydrophilic silver nanoparticles dispersed in water are slightly lower than those without silver nanoparticles, while all cases in this study, the rates of polymerization with modified silver nanoparticles are slightly higher than these without silver nanoparticles. The actual reason for the increase in the polymerization rate when the silver nanoparticles were dispersed in the water phase, but the decrease in the polymerization rate when the silver nanoparticles were dispersed in monomer phase is not clear and more work is needed.

Morphology of PMMA/silver nanocomposite microspheres

Scanning electron microscope photographs of PMMA and PMMA/silver microspheres with 10 wt% silver nanoparticles and 0.5 g/l PVA (based on water phase) are presented in Fig. 2. As expected, the surface of pure PMMA microspheres shown in Fig. 2a is smooth and clean. In Fig. 2b, the surface of PMMA/silver nanocomposite microspheres reveal the round form shadings appeared by inner hollow structures. To further study the hollow structure in the PMMA/silver nanocomposite microspheres, the cross-section and inner surface of the PMMA/silver nanocomposite microspheres were investigated. As shown in Fig. 3, pure PMMA microspheres have smooth and clean cross-section, while PMMA/silver nanocomposite microspheres have multihollow structures and silver nanoparticles were well-dispersed in the matrix of PMMA without any aggregation. The hollow structure of the PMMA microspheres indicates the presence of W/O/W emulsion during the polymerization. It is believed that the synergic effect of hydrophobic surfactant Arlacel P135 and monomer dispersion agent PVA played an important role in the formation of W/O/W emulsion. In other words, the low

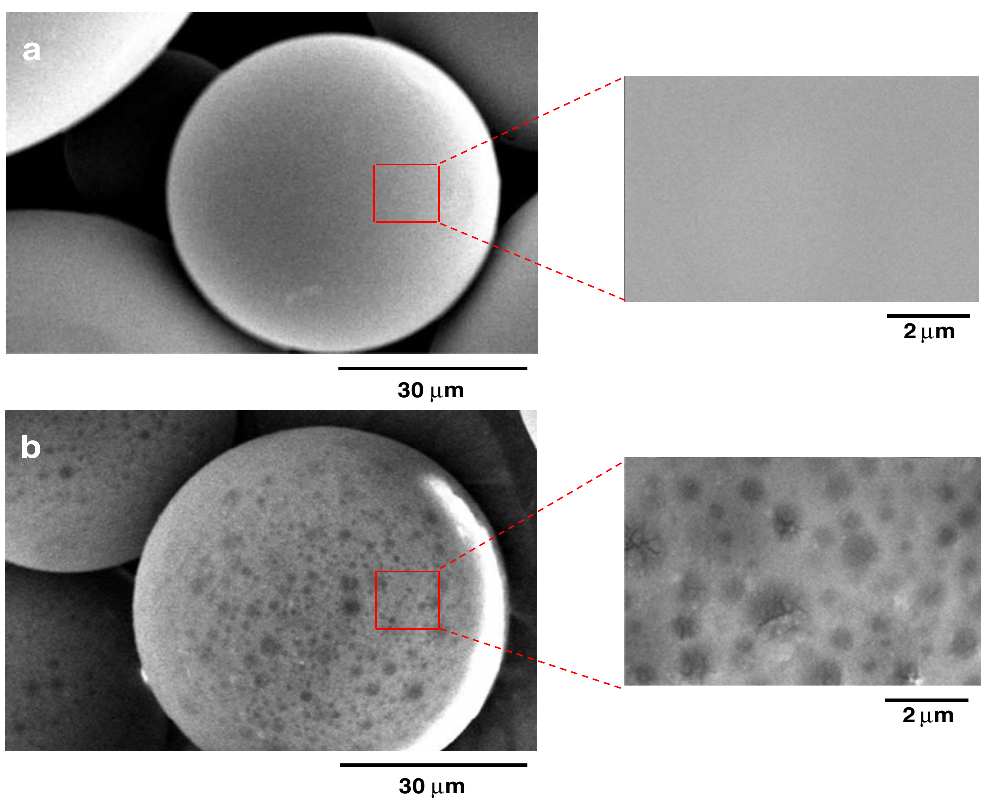

Fig. 2 **a** SEM photographs of pure PMMA microspheres and (**b**) PMMA/silver nanocomposite microspheres with silver nanoparticles concentration of 10 wt%. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.5 g/l of water; surfactant concentration: 0.09 wt% of MMA)

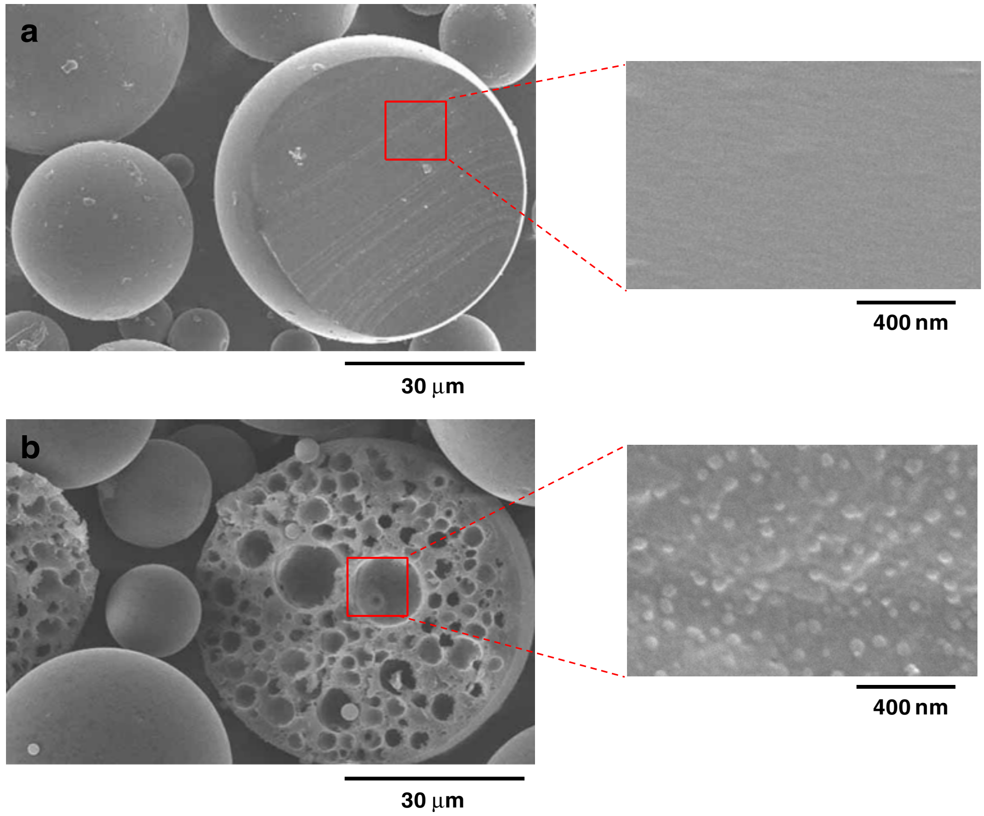

Fig. 3 SEM photographs of cross-section and inner surfaces of **a** pure PMMA microspheres and **b** PMMA/silver nanocomposite microspheres with silver nanoparticles concentration of 10 wt%. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.5 g/l of water; surfactant concentration: 0.09 wt% of MMA)

HBL surfactant Arlacel P135 functions as both W/O emulsifier and silver nanoparticle modification agent, and PVA functions as an O/W emulsifier. As a result, a W/O/W suspension was formed.

Various hollow structures of PMMA/silver nanocomposite microspheres are shown in Fig. 4. The structure of the pores inside the PMMA microspheres is dependent on the concentration of surfactant Arlacel P135. This result

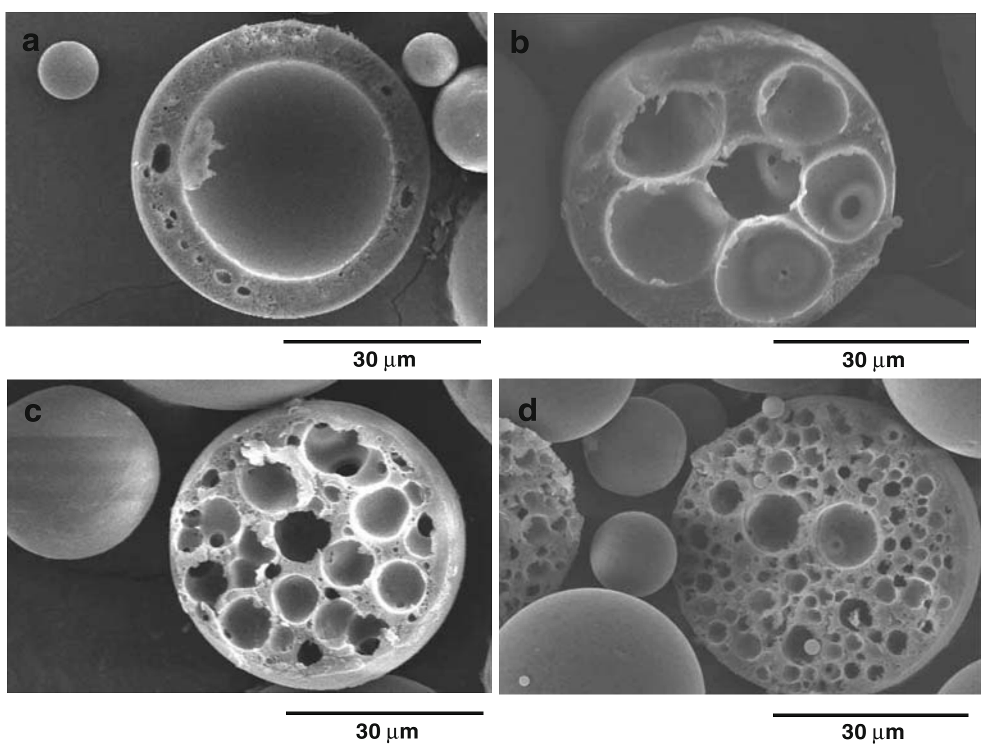

Fig. 4 Various hollow structures of PMMA/silver nanocomposite microspheres with **a** 0.01 wt%, **b** 0.03 wt%, **c** 0.06 wt%, and **d** 0.09 wt% surfactant concentration of MMA. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.5 g/l of water; silver nanoparticles dispersion content: 10 wt% of MMA)

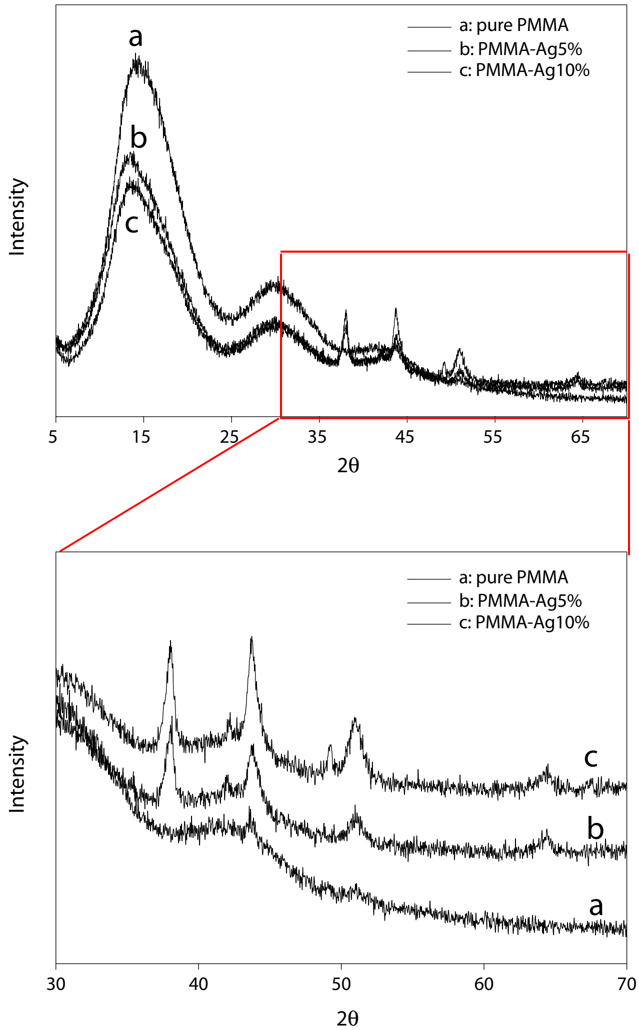

Fig. 5 XRD patterns of pure PMMA microspheres and PMMA silver nanocomposite microspheres; **a** pure PMMA, **b** PMMA/silver with 5 wt% silver nanoparticles, and **c** PMMA silver with 10 wt% silver nanoparticles. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.5 g/l of water; surfactant concentration: 0.09 wt% of MMA)

indicates the hollow structured PMMA microspheres, either with or without silver nanoparticles, could be synthesized and controlled by an in situ suspension polymerization method as reported in this study. For example, the inner morphology of PMMA/silver nanocomposite microspheres could be changed from single hollow to multi-hollow by increasing of Arlacel P135 concentration. It is well-known that the size of liquid droplets in an oil phase is dependent on the surfactant concentration.

Therefore, it is reasonable to believe that at low Arlacel P135 concentration, one large water droplet was formed inside the monomer suspension, resulting in a large and single hollow polymeric microspheres, as shown in Fig. 4a. However, as Arlacel P135 concentration was increased, many small water droplets were formed and encapsulated inside the oil droplet, resulting in the formation of multi-hollow morphology as shown in Fig. 4b–d. It was also noted that the size of the hollow microspheres decreased as the surfactant concentration increased, which agrees well with the general theory [52–55].

The PMMA microspheres and PMMA/silver nanocomposite microspheres with silver nanoparticle contents of 5 and 10 wt% were characterized by XRD, and the results are shown in Fig. 5. The XRD pattern of PMMA/silver nanocomposite microspheres shows diffraction peaks at 2θ of ca. 38.2°, 44.6°, 64.1°, and 77.5°, respectively. Because PMMA is a typical amorphous polymer, the diffraction peaks in the XRD pattern should be ascribed to the crystal structure of silver. The XRD pattern clearly indicates that PMMA/silver nanocomposite microspheres were successfully prepared with modified silver nanoparticles. According to the results of reference [56], these peaks are corresponding to the 111, 200, 220, and 311 planes of the silver nanocrystals with cubic symmetry.

In order to evaluate the biological function in the PMMA/silver nanocomposite microspheres, the antibacterial test was conducted and the results are shown in Fig. 6. In the absence of silver nanoparticles (PMMA microspheres), the number of bacteria remained constant. However, by adding silver nanoparticles to the PMMA microspheres, the number of bacteria decreased dramatically. Moreover, as the concentration of silver nanoparticles increased, the number of bacteria decreased more sharply. Within 1 week, most of the initially inoculated bacteria disappeared. From this result, it is evidenced that the PMMA/silver nanocomposite microspheres have powerful antibacterial ability. Even though the silver nanoparticles were entrapped in the internal voids of the microspheres,

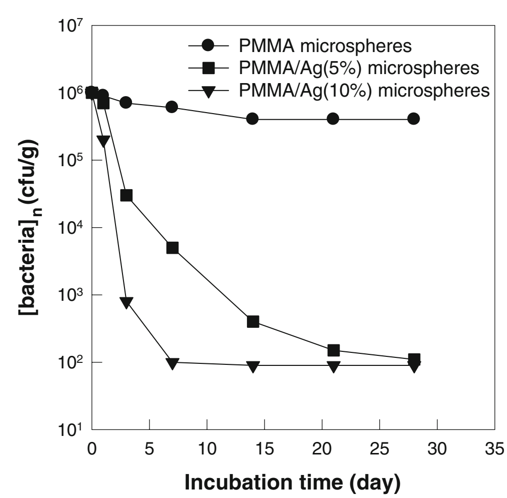

Fig. 6 Preservation performance of PMMA/silver nanocomposite microspheres. (ADMVN concentration: 0.0001 mol/mol of MMA; concentration of suspension agent PVA: 0.5 g/l of water; surfactant concentration: 0.09 wt% of MMA)

the ionization of silver metals seems to happen effectively through the nanosized pore channels of the polymer wall [21]. Hereby, it is verified that a high antibacterial ability of silver nanoparticles can be achieved by immobilizing the silver nanoparticle in a polymer matrix.

Conclusions

In this work, PMMA/silver nanocomposite microspheres with multihollow morphology were successfully prepared by suspension polymerization of MMA in the presence of modified silver nanoparticles and a low HBL surfactant. High conversion of the polymerization (85%) was achieved when low temperature initiator (ADMVN) was used. The hollow structure can be controlled by the concentration of Arlacel P135, and the suspension particle size is affected by silver nanoparticle addition. In the case of using the modified silver nanoparticles, the rate of polymerization increased slightly. Preservation test indicates the PMMA/silver nanocomposite microspheres with multihollow structure showed a powerful antibacterial ability.

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References

1. Hong Z, Jun Z, Guangsu H (2006) Colloid Polym Sci 284:1031
2. Nakano M (2000) Adv Drug Deliv Rev 45:1
3. Vasiljevic D, Parojcic J, Primorac M, Vuleta G (2006) Int J Pharm 309:171
4. Weiss J, Scherze I, Muschiolik G (2005) Food Hydrocoll 19:605
5. Lobato-Calleros C, Rodriguez E, Sandoval-Castilla O, Vernon-Carter EJ, Alvarez-Ramirez (2006) Food Res Int 39:678
6. Yoshida K, Sekine T, Matsuzaki F, Yanaki T, Yamaguchi M (1999) J Am Oil Chem Soc 76:195
7. Lee MH, Oh SG, Moon SK, Bae SY (2001) J Colloid Interface Sci 240:83
8. Chakraborty M, Ivanova-Mitseva P, Bart HJ (2006) Sep Sci Technol 41:3539
9. Utada AS, Lorenceau E, Link DR, Kaplan PD, Stone HA, Weitz DA (2005) Science 308:537
10. Nie ZH, Xu SQ, Seo M, Lewis PC, Kumacheva E (2005) J Am Chem Soc 127:8058
11. Zoldesi CI, Imhof A (2005) Adv Mater 17:924
12. Koo HY, Chang ST, Choi WS, Park JH, Kim DY, Velev OD (2006) Chem Mater 18:3308
13. Chu LY, Utada AS, Shah RK, Kim JW, Weitz DA (2007) Angew Chem Int Ed 46:8970
14. Koo BM, Jung JE, Han JH, Kim JW, Han SH, Chung DJ, Suh KD (2008) Macromol Rapid Commun 29:498
15. Okubo M, Ito A, Hashiba A (1996) Colloid Polym Sci 274:428
16. Okubo M, Mori H (1997) Colloid Polym Sci 27:634
17. Okubo M, Minami H (1997) Colloid Polym Sci 275:992
18. Omi S, Ma GH, Nagai M (2000) Macromol Symp 151:319
19. Yang Z, Zhao D, Xu M (2000) Macromol Rapid Commun 21:574
20. Kim JW, Joe YG, Suh KD (1999) Colloid Polym Sci 277:252
21. Lee JE, Kim JW, Jun JB, Ryu JH, Kang HH, Oh SG, Suh KD (2004) Colloid Polym Sci 282:295
22. Wu W, He T, Chen JF (2006) Mater Lett 60:2410
23. Lee CF, Chiu WY (1993) Polym Int 30:475
24. Wu W, Chen JF, Shao L, Lu SC (2002) J Univ Sci Technol Beijing 9:426
25. Tiarks F, Landfester K, Antonietti M (2001) Langmuir 17:5775
26. Erdem B, Sudol ED (2000) J Polym Sci A: Polym Chem 38:4419
27. Duguet E, Abboud M, Morvan F (2000) Macromol Symp 151:365
28. Stejskal J, Kratochvil P, Armes SP (1996) Macromolecules 29:6814
29. Haga Y, Watanabe T, Yosomiya R (1991) Angew Makromol Chem 189:23
30. Hergeth WD, Steinau UJ, Bittrich HJ (1989) Polymer 30:254
31. Coover HW, McIntyre JM Jr (1985) In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI (eds) Encyclopedia of polymer science and engineering,. vol. 1. Wiley, New York, p 234
32. Nuyken O, Lettermann G (1992) In: Kricheldorf HR (ed) Handbook of polymer synthesis, Part A. Marcel Dekker, New York, p 223
33. Kim KH, Jo WH, Jho JY, Lee MS (2003) Fiber Polym 4:97
34. Cho JW, Lee SH, So JH, Jaung JY (2004) Fiber Polym 5:239
35. Hailstone RK (1995) J Phys Chem 99:4414
36. Sun T, Seff K (1994) Chem Rev 94:857
37. Tada H, Teranishi K, Inubushi Y, Ito S (2000) Langmuir 16:3304
38. Nickel U, zu Castell A, Poppl K, Schneider S (2000) Langmuir 16:9087
39. Pal T (1994) J Chem Educ 71:679
40. Iwata Y (1996) Zeolite News Lett 13:8
41. Oya A (1996) Journal of Antibacterial Antifungal Agents Japan 24:429
42. Hatchett DW, Josowicz M, Janata J (1999) Chem Mater 11:2989
43. Huang CJ, Yen CC, Chang TC (1991) J Appl Polym Sci 42:2237
44. Gotoh Y, Igarashi R, Ohkoshi Y, Nagura M (2000) J Mater Chem 10:2548
45. Zhu YJ, Qian YT, Li XJ, Zhang MW (1998) Nanostruct Mater 10:673
46. Yeum JH, Sun Q, Deng Y (2005) Macromol Mater Eng 290:78
47. Yeum JH, Deng Y (2005) Colloid Polym Sci 283:1172
48. Yeum JH, Ghim HD, Deng Y (2005) Fiber Polym 6:277
49. Polacco G, Palla M, Semino D (1999) Polym Int 48:392
50. Kurata M, Tsunashima Y (1989) In: Brandrup J, Immergut EH (eds) Polymer handbook. 3rd edn. Wiley, New York, p VII/13
51. Cox BG (1994) Modern liquid phase kinetics. Oxford University Press, Oxford
52. Landfester K, Bechthold N, Tiarks F, Antonietti M (1999) Macromolecules 32:5222
53. Jeong HG, Ji SJ, Lee SJ (2002) Polymer (Korea) 26:759
54. Van Zyl A, Wet-Roos D, Sanderson R, Klumperman B (2004) Eur Polym J 40:2717
55. Lian S, Wang E, Gao L, Wu D, Song Y, Xu L (2006) Mater Res Bull 41:1192
56. Dong AG, Wang YJ, Tang Y (2002) Chem Commun 4:350