Journal of Alloys and Compounds 507 (2010) 302–308

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation of villus-like PMMA/silica hybrids via surface modification and wet grinding

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ARTICLE INFO

Article history:
Received 9 April 2010
Received in revised form 26 July 2010
Accepted 28 July 2010
Available online 4 August 2010

Keywords:
Polymethylmethacrylate (PMMA)
Silica
Microsphere
Vinyltriethoxysilane (VTEOS)
Wet grinding
Diffuser films

ABSTRACT

A novel method to prepare inorganic–organic hybrid with villus-like morphology comprising a layer of silica nanoparticles adsorbed on polymethylmethacrylate (PMMA) microsphere was presented in this article. At first, silica nanoparticles were surface treated with vinyltriethoxysilane (VTEOS), and then a wet grinding process with VTEOS as the dispersing agent was utilized to prevent the aggregation of nanoparticles. Zeta-potential measurements confirmed that the surface charge of these milled silica is negative. On the other hand, positively charged PMMA was prepared by adsorption of 2-(methacryloyloxy) ethyltrimethyl ammonium chloride (METMAC) on as-synthesized PMMA beads. Owing to the electrostatic interaction, the negatively charged silica particles were coated directly on the surface of positively charged PMMA microspheres. The hybrid is fully covered by a layer of silica and the silica content is 18.5%. From our results, it is evident that the villus silica layer adhered on the PMMA bead surfaces and it significantly enhanced the thermal stability of the hybrid microspheres. The characteristics and morphologies of the silica particles, PMMA beads and the resulting PMMA/silica hybrids were investigated by SEM, TEM, FESEM, EDS, FTIR, TGA, and aging analysis.

1. Introduction

Diffuser film is one of the basic elements of the backlight unit for liquid crystal displays (LCDs). The main function of diffuser films is to provide LCD a uniform luminance. Two types of diffusers, surface-relief and volumetric type, are commonly used. Surface-relief diffusers depend mainly on microstructures, such as microlenses and rough textures, on the surface to scatter light [1–4]. An easy way has been suggested to produce a rough surface on the optical film/plate, i.e., by coating the substrate with solutions containing TiO_2, SiO_2, polymethylmethacrylate (PMMA) or polystyrene (PS) particles [5]. On the other hand, volumetric diffusers depend mainly on transparent micro-beads or fillers including glass, polystyrene beads, and $CaCO_3$ particles located uniformly inside the plates to scatter light [6]. It is evident that desired light transmitting properties of diffuser films can be achieved by modifying both the volume and surface features of the film with the micro-beads. Generally, PMMA is a good optical material and can be used as diffuser beads because of its good light transmission and haze [6]. However, its thermal and mechanical properties have limited its applications. On the other hand, inorganic materials have the advantages of ultraviolet, heat, and weather resistance. However, the drawback is that inorganic particles aggregate seriously, resulting in light scattering and reduction in transparency. One possible solution to this dilemma is utilization of composite materials which combine the advantages of organic (polymer) and inorganic materials.

Conventional polymer composites are made of polymer resins and inorganic fillers. The incorporation of inorganic fillers significantly improves the physical properties, including the mechanical, optical, electrical, and thermal properties, of the polymer matrices [7,8]. However, the properties of these materials are often deteriorated by bad dispersion of inorganic fillers due to their high surface energy and easy agglomeration. Accordingly, several studies have been conducted on the preparation of composite particles consisting of cores covered with shells of different chemical compositions because the properties (magnetic, optical, electric, adsorptive, etc.) of such materials can be easily tuned by appropriate coating. The commonly described core–shell composite particle has the structure in which inorganic particles form the core and polymer forms the shell [9–11]. Recently, there has been increasing interest in the preparation of organic polymeric cores covered with inorganic shells which makes it possible to extend the use of the polymer particles in different areas

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doi:10.1016/j.jallcom.2010.07.187

of high technology [12–16]. Particularly, silica-coated polymer hybrid particles show their potential applicability in drug delivery, bio-materials, structural materials in aerospace, electronics, sensors, etc. [17–20]. Several methods such as in situ emulsion polymerization [21], Pickering or nanoparticle-stabilized emulsion polymerization [17,18], suspension polymerization [22], dispersion polymerization [23], miniemulsion polymerization [24], and soap-free emulsion polymerization [25] have been used to prepare silica-coated polystyrene hybrids. However, the report on the preparation of silica-coated PMMA hybrid is rare [19,26,27]. Depending on the interaction between silica and PMMA beads, hybrid microspheres with smooth silica shell [19] or raspberry-like hybrid microspheres could be obtained [26,27]. However, the low silica content (6.86%) in the former and the not fully covered PMMA surfaces in the latter might make these two PMMA/SiO_2 hybrids not good enough to use as diffuser beads in backlight unit for LCDs.

In this work, core–shell-like PMMA/silica hybrids having villus silica outerlayer were prepared via a three-step process. Firstly, nanosilica particles were modified with vinyltriethoxysilane (VTEOS), which contains a reactive vinyl functional group, to enhance the interaction between nanosilica particles and organic polymer beads. A wet grinding method was utilized to enhance the dispersion of these modified-silica nanoparticles. On the other hand, PMMA microspheres were prepared by alcoholic dispersion polymerization [8]. The PMMA beads were coated with a cationic additive that contains 2-(methacryloyloxy) ethyl-trimethyl ammonium chloride (METMAC) [15], which is positively charged. Since the silane-treated silica particles have a negative charge, they can be easily coated on the surface of positively charged PMMA microspheres by electrostatic attraction to form the PMMA/SiO_2 hybrid. The effect of wet grinding on colloidal stability of silica nanoparticles was also discussed. The products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectra (FTIR), thermal gravimetric analysis (TGA), and heat treatment process.

2. Experimental details

2.1. Materials

All of the chemicals used herein were of analytical grade. Silica particles (TS100), vinyltriethoxysilane (VTEOS) and 3-methacryloxy-propyl-trimethoxy silane (MPTMS) were purchased from Degussa Co. Ltd. Methyl methacrylate (MMA) (99%) was obtained from Acros. Lauroyl peroxide (LPO), 2-(methacryloyloxy) ethyltrimethyl ammonium chloride (METMAC) and poly(vinylpyrrolidon) (PVP, Mn: 40,000) were obtained from Aldrich. The primary size of silica particles is about 15–20 nm and the specific area is 125–175 m^2/g. Methacryloyloxy ethyl-trimethyl ammonium chloride aqueous solution (75 wt%) was used without further purification. The initiator, lauroyl peroxide (LPO), was used after recrystallization.

2.2. Preparation of modified-silica with VTEOS

A defined amount of VTEOS was added to 250 ml water/ethanol (10:1) solution under agitation. The resulting solution was stirred continuously at 60 °C for 2 h, during which time VTEOS was hydrolyzed. Silica particles were then added to the solution of hydrolyzed VTEOS and reacted at 60 °C for 2 h. The collected silica particles were washed with water and ethanol. The washed silica particles were then collected and dried at 50 °C for 12 h. Finally, an adsorbed layer of VTEOS was formed on the surface of silica particles.

2.3. Dispersion of modified-silica nanoparticles by a wet grinding process

Grinding is an important industrial operation that is used for the size reduction of materials and production of large surface area. However, the existence of a limit fineness is not unusual when the comminution process is performed by a dry grinding method. The importance of wet grinding mills increases steadily because of an increasing demand for fine and ultra-fine particles (less than 1 μm) [28]. Therefore, colloidal dispersions of silica particles were prepared by mixing various amounts of modified-silica particles in an aqueous solution with dispersant. The silane played several roles simultaneously in the present study such as a dispersion stabilizer, a dispersant for the silica solution, a modifier of silica particles, and the dispersion medium. To disaggregate the modified-silica powder in this medium a milling process with Y_2O_3 stabilized ZrO_2 beads was performed using a bead mill (Drais Perl Mill PML-H/V). The diameter of the mill ball is 0.2 mm and the filling percentage of grinding medium was 70%. The grinding medium was activated by the rotating agitator discs at a tip speed of 11.72 m/s (3200 rpm), which created a shearing force that dispersed the aggregated silica solution with dispersants. The temperature was controlled using cool water circulating in the double jacket of the grinding chamber. The particle size was controlled by the specific energy (the product of stress intensity and stress number) during the wet grinding process [29]. The bead mill stopped automatically when the preset specific energy was reached. Sedimentation tests were performed for the silica suspensions with various dispersants to measure the macroscopic stability of the silica dispersion. The secondary particle sizes in the silica dispersions were measured by dynamic light scattering spectroscopy with a particle analyzer.

2.4. Synthesis of PMMA microspheres

PMMA microspheres were synthesized via dispersion polymerization of methyl methacrylate using lauroyl peroxide and poly(N-vinylpyrrolidone) (PVP) as the initiator and the stabilizer, respectively, in a water/ethanol (1:1) solution at 80 °C for 6 h. The as-synthesized polymer was washed several times with ethanol/water solution in order to remove the unreacted monomers, and then the resulting microspheres were dried under vacuum at 50 °C for 24 h.

2.5. Preparation of nanosilica-coated PMMA microspheres

To prepare core–shell-like PMMA/silica particles, an electrostatic deposition method for anchoring silica onto the surface of PMMA microspheres was utilized. Firstly, the cationic precursors METMAC (1 wt%) and MPTMS (0.1 wt%) were dispersed in 100 ml deionized (DI) water and the mixture was heated to 70 °C under stirring. And then, the PMMA microspheres (4 wt%) were charged into the container and heated for 4 h, resulting in METMAC-modified PMMA particles. Finally, the wet milled silica (1 wt%) solution was added into the reactor under stirring. The reaction was continued overnight at 70 °C. After the reaction, the obtained precipitates were filtered and washed with water for several times. Then, the washed particles were collected and dried at 50 °C for 1 day in a vacuum oven. Fig. 1 displays a schematic illustration of the process to prepare the PMMA/silica hybrids.

2.6. Characterization

A grinding chamber (DRAIS Equipment Co., Ltd) was used in the dispersion stabilization and the batch milling of the silica solution was performed using a PML-H/V machine (Germany). The sizes of colloidal silica aggregates were characterized by dynamic light scattering (DLS, Zeta Plus, DelsaTM Nano Particle Analyzer Instruments) at a wavelength of 674 nm and an incident angle of 90°. The zeta-potential (Zeta Plus) of sterically stabilized colloidal silica was measured at varying pH values. Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer spectrometer with the KBr pellet method. The FTIR spectra were recorded in a wave number range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} and a scanning frequency of 20 Hz. Thermal gravimetric analysis (TGA) was performed using a Perkin Elmer Pyris TGA. Transmission electron microscope (TEM) images were captured using a Hitachi TEM, operated at 25 kV. Scanning electron microscopic images were obtained using a JEOL JSM-6400 on the sample that had been plasma-coated using a Filgen Osmium Plasma Coater. The composites were characterized using a field emission scanning electron microscope (FESEM, JSM-6340F, and JEOL). A built-in energy dispersive X-ray spectrometer (EDX) in JSM-6340F was adopted to analyze the chemical composition of the particles.

3. Results and discussion

3.1. FTIR spectra of the VTEOS-modified-silica nanoparticles

The FTIR spectra of the unmodified-silica, neat VTEOS and VTEOS-modified-silica are shown in Fig. 2. From the spectrum of VTEOS-modified-silica, a very pronounced band at 950–1200 cm^{-1}, together with two less pronounced bands at 2961 and 2873 cm^{-1}, corresponding to vibration absorption of the C–H group, are found. In addition to Si–O–Si vibration bands at 1101, 945, 798, and 464 cm^{-1}, a peak at 1634 cm^{-1} was attributed to vinylic C=C vibrations [30]. The presence of $Si–CH=CH_2$ stretching bonds of VTEOS at 1410 and 2930 cm^{-1} confirms the existence of silane on the surface of silica particles (Fig. 2). However, the FTIR spectrum of silane derivatives attached to the silica surface has distinctive changes as compared with that of free silane molecule, indicating that VTEOS does interact with silica particle surfaces. A possible mechanism representing the surface modification of silica nanoparticles by VTEOS is displayed in Fig. 3.

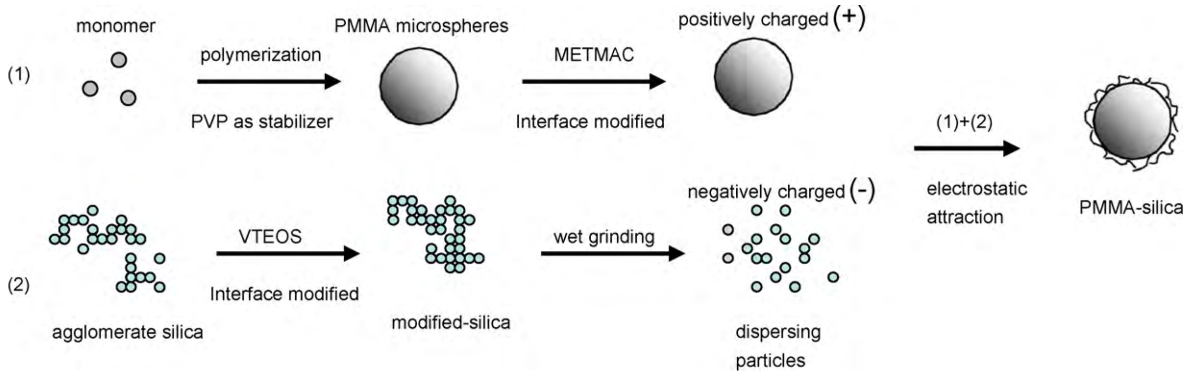

Fig. 1. The schematic illustration of the assembly of modified-silica on the PMMA microspheres to form villus layer core–shell-like particles.

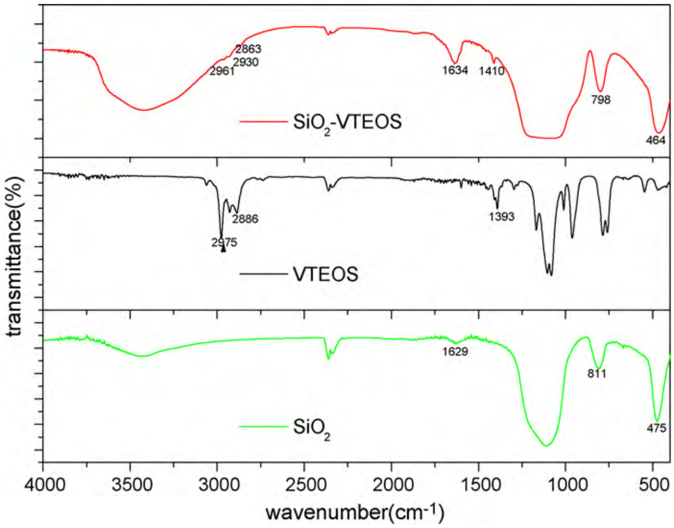

Fig. 2. FTIR spectra of silica, modified-silica particles, and VTEOS.

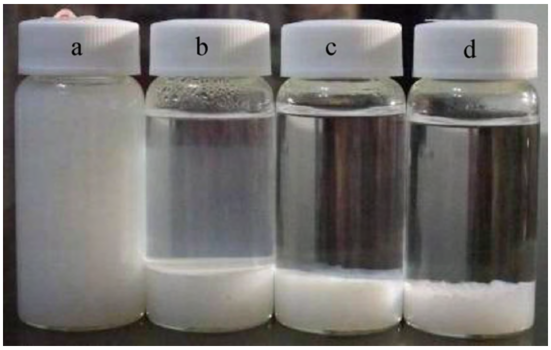

Fig. 4. Photographs of solubility measurements after 30 days: (a) modified-VTEOS–silica dispersion by wet grinding, (b) modified-VTEOS–silica dispersion, (c) modified-MPTMS silica dispersion by wet grinding, and (d) unmodified-silica.

3.2. The effects of wet grinding and dispersants on the dispersion of silica

As shown in Fig. 4, untreated and VTEOS-modified-silica nanoparticles aggregated easily and precipitated rapidly in aqueous solution during the sedimentation test, indicating that they had insufficient dispersion capacity. To disaggregate the silica nanoparticle in aqueous solution the milling process with ZrO_2 beads was performed using VTEOS or MPTMS as dispersants. In order to investigate the stability of the suspensions received after the dispersing process, sedimentation tests were performed to measure the macroscopic stability of the silica dispersion with various dispersants. The images of silica suspensions after standing for 30 days at room temperature are shown in Fig. 4. It is clear from Fig. 4 that wet grinding can effectively disperse the silica in aqueous solution when VTEOS was used as a dispersant. However, wet-ground MPTMS-stabilized silica nanoparticles in aqueous solution began to flocculate after standing for 30 days. Based on the results from sedimentation test, one can conclude that the stability of the suspensions strongly depends on the choice of the dispersant and VTEOS is a more effective dispersant than MPTMS for preparing stable colloidal silica solution. The greater stability of the VTEOS can be attributed to the fact that the silanol group generated from hydrol-

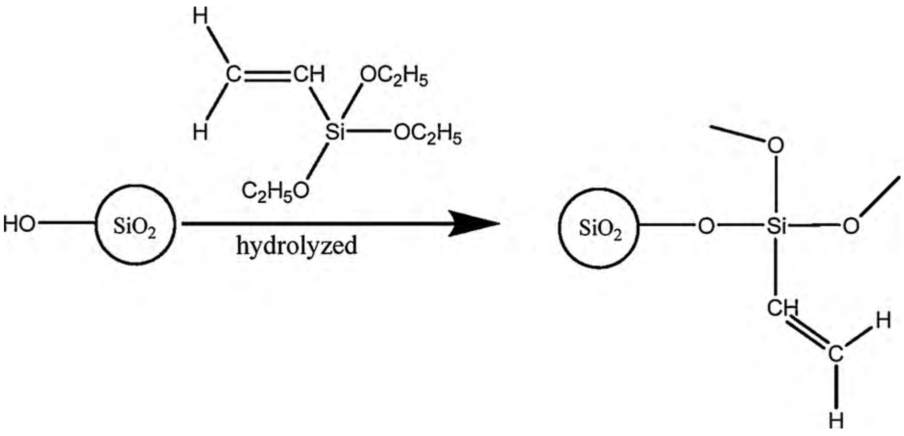

Fig. 3. A possible mechanism representing the surface modification of silica nanoparticles by VTEOS.

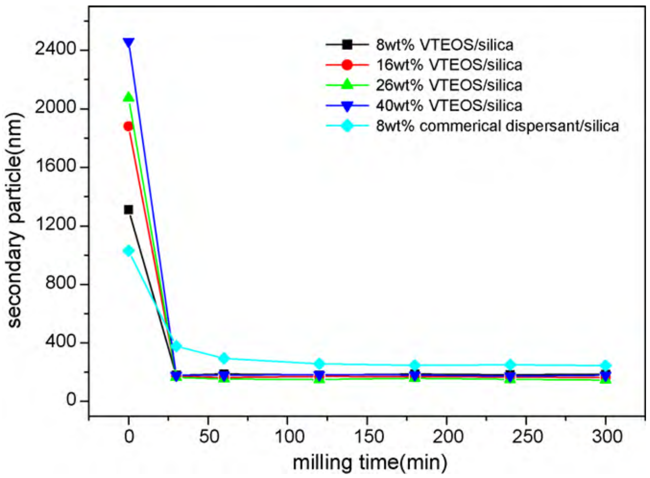

Fig. 5. The change of secondary particle size of colloidal silica dispersion with milling time for various VTEOS/silica ratios.

ysis will form very stable siloxane in the subsequent condensation reaction. On the other hand, the trimethoxysilyl groups in MPTMS can undergo hydrolysis/polycondensation reactions, resulting in cross-linking of silica to produce agglomeration [31].

The sizes of secondary silica particles with various dispersants and milling time are displayed in Fig. 5. Regardless of the VTEOS concentration, the secondary particle size of silica decreased to the range of 160–170 nm after milling for 30 min when VTEOS was used as a dispersant. When a commercial surfactant (HA540ES/760) (1:1) was used as a dispersant the secondary particle size of the milled silica dispersion was larger than that of the silica colloid dispersed with VTEOS. It indicates that VTEOS is a more effective dispersant than HA540ES/760 (1:1). Moreover, the secondary particle size increased only slightly within 30 days for the VTEOS-stabilized silica dispersion (Fig. 6), indicating that the secondary particle size remained roughly constant and the VTEOS-stabilized silica dispersions are very stable. During the milling process, the dispersant will be adsorbed on the surface of silica nanoparticles, resulting in the change of the surface charge and the steric hindrance capability of the silica dispersions. Therefore, the stabilities of silica dispersions are different. For good colloidal stability of silica dispersions in organic solvents, a milling process in a suitable dispersant is necessary to comminute the aggregated silica powder by collision energy.

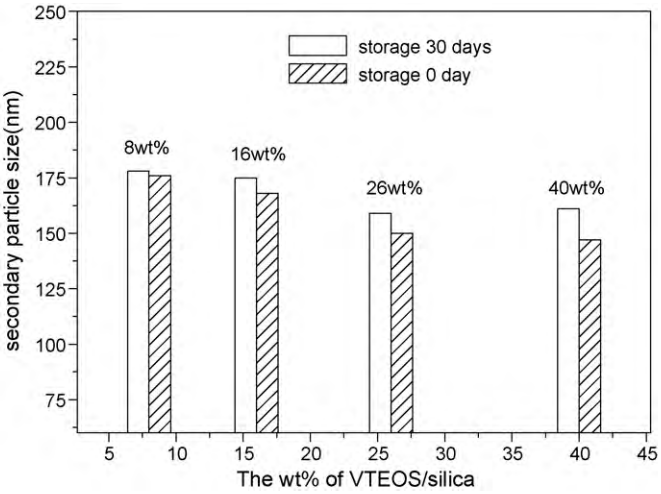

Fig. 6. Comparison of the change of secondary particle size of colloidal silica dispersion with various VTEOS/silica ratios for the storage time of 0 day and 30 days.

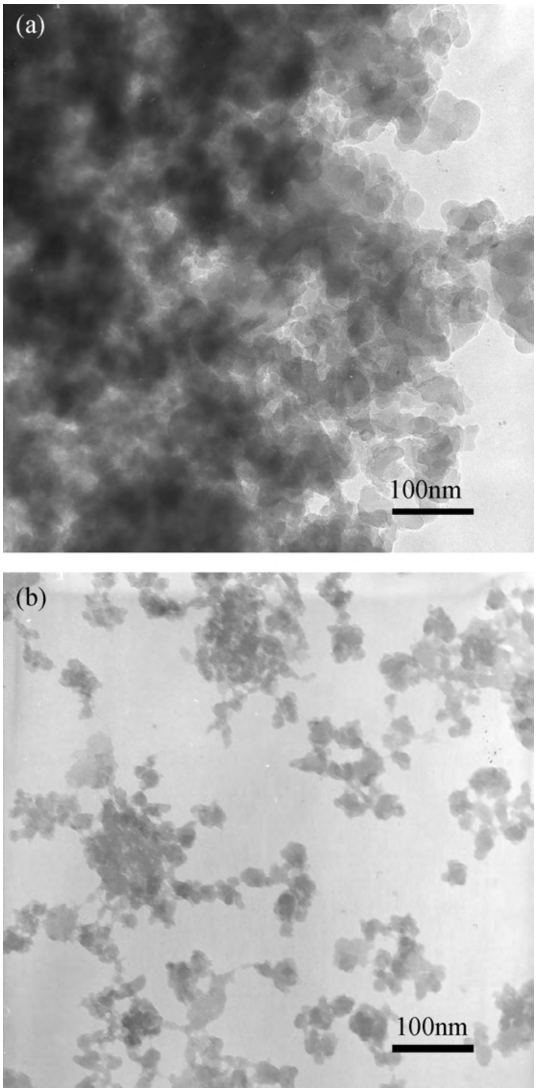

Fig. 7. TEM image of (a) modified-silica particles and (b) modified-silica particles after wet grinding.

Without wet grinding, the aggregation of modified-silica particles was serious and the secondary size of particles was larger than 1 μm (Fig. 7a). Wet grinding can effectively reduce the agglomeration of modified-silica in the medium. After wet grinding, the particles were well dispersed and with no agglomeration (Fig. 7b). Fig. 8 compares the zeta-potentials of milled silica dispersion (VTEO/silica = 40 wt%) and unmilled silica in DI water at various pH values. Zeta-potential is a function of the surface charge of the particles. In dispersions where the value of zeta-potential is close to zero (isoelectric point), particles tend to agglomerate. At highly negative or positive values of zeta-potential (more than 30 mV or less than −30 mV [32]) particles in dispersions tend to repel each other, i.e., no agglomeration occurs. Although the zeta-potentials for both silica dispersions were negative, the zeta-potential of unmilled silica was limited within the range from 0 to −30 mV in a wide pH range of 3–10, which is too small for electrostatic stabilization. It leads to significant aggregation of silica particles. However, the zeta-potential of wet milled silica colloid is much less than −30 mV as the pH value is over 4 and the colloid is quite stable. It implies that electrostatic stabilization plays a determinant role for the dispersion stabilization of silica colloid in this study.

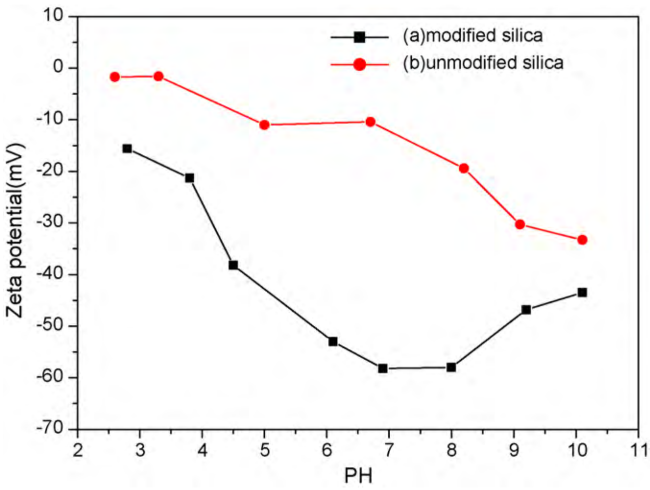

Fig. 8. The zeta-potentials of (a) milled silica dispersion (40 wt%VTEOS/silica) and (b) unmilled silica measured in DI water at various pH values.

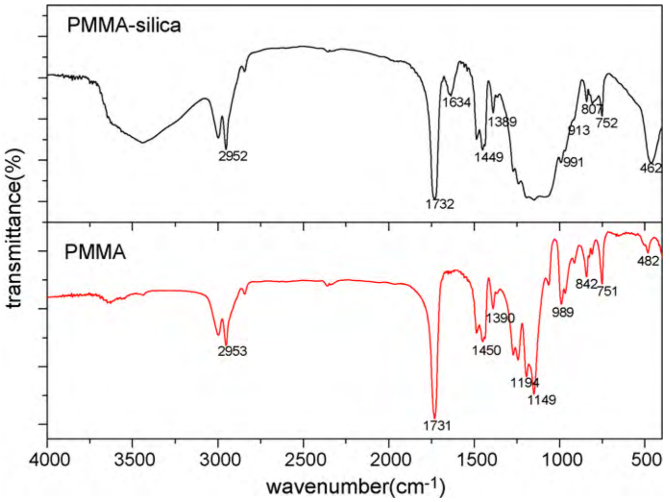

Fig. 10. FTIR spectra of PMMA and PMMA–silica, respectively.

3.3. Morphology of PMMA–silica beads

As seen in Fig. 9, the pristine PMMA beads produced by dispersion polymerization are dispersed with bead diameters within the range of 1–2 μm. Fig. 9 also shows that these PMMA beads are spherical and non-agglomerated, and have a smooth surface. As mentioned in Section 2, the positively charged PMMA was obtained by treating PMMA with the mixture of METMAC and MPTMS solutions. Thus, the milled silica particles with negative charge were readily coated on the surface of PMMA surface owing to the electrostatic interaction.

The successful preparation of core–shell-like PMMA/silica hybrids was confirmed by FTIR spectra. Fig. 10 compares the FTIR spectra for pristine PMMA and PMMA/silica microsphere. The spectrum of PMMA–silica has peaks at 2952, 1732, and 1437 cm^{-1}, which are assigned to CH, C=O, and CH_3 stretching vibrations of PMMA, respectively. The PMMA–silica has a much stronger absorption band at about 1732 cm^{-1}, which is due to the significant increase in the content of the carbonyl group (C=O). The peaks at 1389 and 1449 cm^{-1} are attributed to the vibration bands of the $-CH_2$ and $-CH_3$ groups, and the peaks at 1000–1200 cm^{-1} are assigned to the C–O–C group of PMMA. The additional bands in the spectrum of PMMA–silica at 462 and 807 cm^{-1} and the peak of 1634 cm^{-1} are the characteristic peaks of silica [30], verifying that the as-synthesized composites are made up of silica and PMMA and that silica existed on the surface of PMMA microspheres. The FTIR results indicate that silica has been grafted onto the surface of PMMA beads via electrostatic interactions. One advantage of the proposed method is that the VTEOS–silica can be chemically modified by an addition reaction with the remaining vinyl group [33].

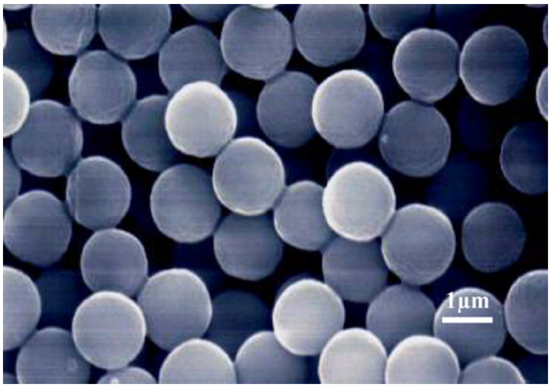

Fig. 9. SEM micrographs of the pristine PMMA microsphere.

Fig. 11a displays the SEM image of PMMA/silica hybrid. The mean diameter of PMMA/silica beads was larger than that of pristine PMMA beads (Fig. 9), indicating that a layer of silica was adsorbed on the surface of PMMA beads. Fig. 11a also shows that the silica shell is very rough, which was further verified by the FESEM image analysis (Fig. 11b). The FESEM image also reveals that the silica particles were dense on the surface of the PMMA beads. The EDX spectrum confirms that substantial amounts of Si and O exist, as shown in Fig. 11c. Note that the relative intensity of the peaks does not necessarily correspond to the true atom ratio in the sample. The EDX result only provides qualitative information regarding the existence of silica, which is composed of Si and O, in the composite particles. The TEM analysis indicates that the electrostatic interaction between villus silica and PMMA beads was sufficiently strong for the formation of stable composite particles (Fig. 11d and e). It shows that most composite particles were spherical in shape with a villus-like morphology and roughly 50–200 nm in size, and the PMMA beads are fully covered by a layer of silica coating.

For comparison, the SEM image of the unmodified PMMA beads, prepared by the same procedure but without using MPTMS and METMAC, is shown in Fig. 12. It is clear from Fig. 12 that the modified-silica particles adsorbed onto unmodified PMMA beads are rare because of the lacking of electrostatic interaction between pristine PMMA beads and silica particles. Furthermore, these unmodified PMMA bead cannot provide any functional group to enhance physicochemical bonding with silica particles.

3.4. TGA analysis and aging measurement

The silica content was quantitatively determined by TGA. Fig. 13 presents the TGA results for (a) unmodified-silica, (b) modified-silica, (c) PMMA/silica, and (d) pristine PMMA. In Fig. 13a, the 10.9% weight loss observed between 25 and 400 °C was attributed to the elimination of the adsorbed water and the dehydroxylation process. In Fig. 13b, a weight loss of 10.0% between 100 and 600 °C was attributed to the decomposition of VTEOS. It is estimated that approximately 22.9 wt% of total VTEOS was grafted onto the surface of silica in the modification process. In Fig. 13c, the weight loss between 200 and 600 °C was 70.8%, which was attributed mainly to the decomposition of VTEOS and PMMA. The balance value repre-

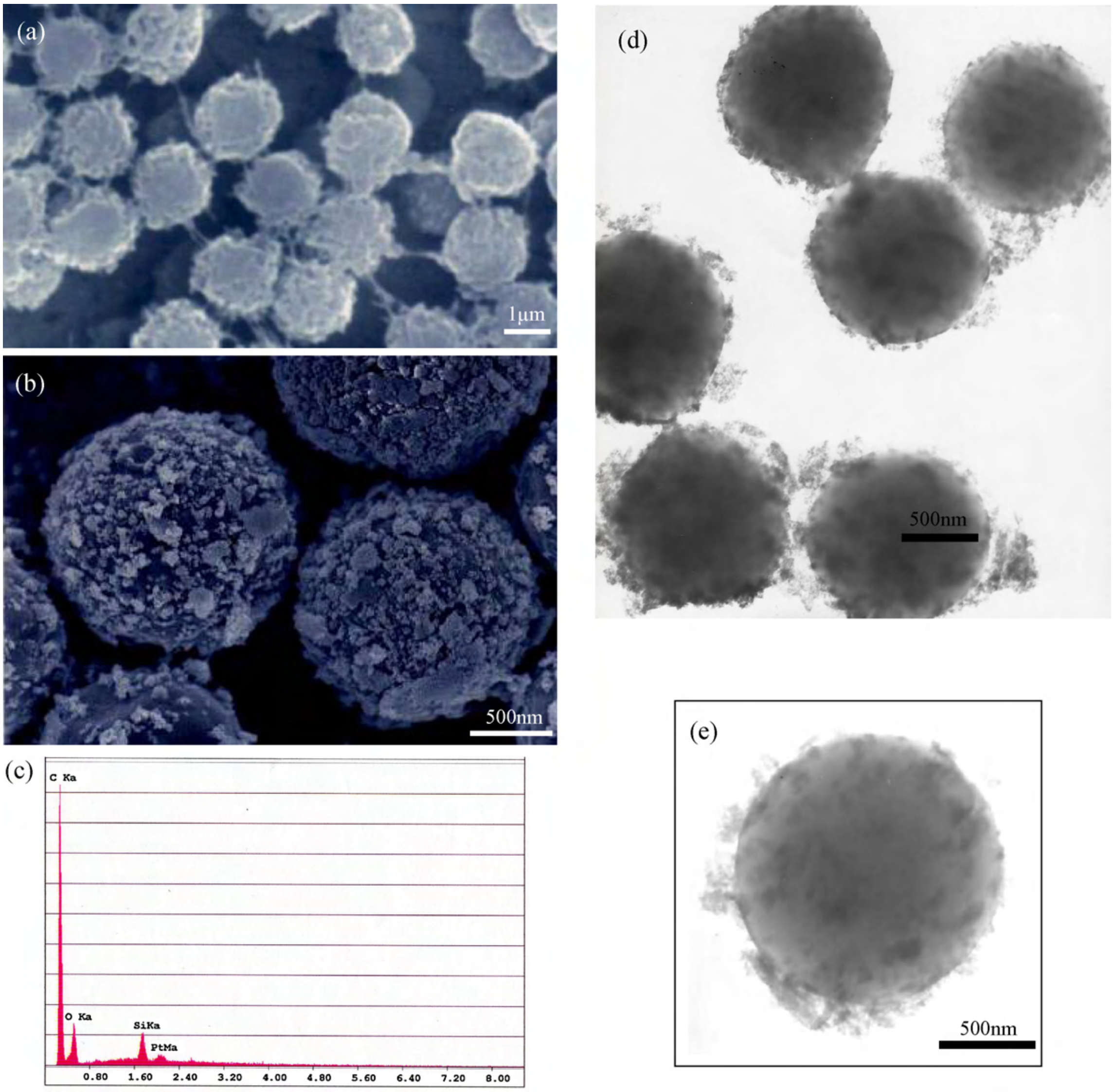

Fig. 11. (a) SEM micrographs of the PMMA–silica microsphere, (b) FESEM micrographs of the PMMA–silica microsphere, (c) the EDX spectrum of the PMMA–silica microsphere and (d) and (e) TEM micrographs of the magnified PMMA–silica microsphere.

sents the silica content of the hybrid, which is 18.5% for PMMA/silica hybrids. In Fig. 13d, the TGA results for PMMA particles show that the final weight close to 1000 °C was about zero, confirming that the microspheres comprise mostly pure PMMA.

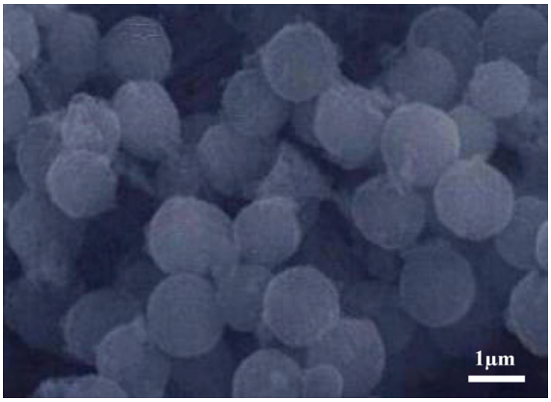

Fig. 12. SEM micrograph of the PMMA–silica microsphere with unmodified PMMA.

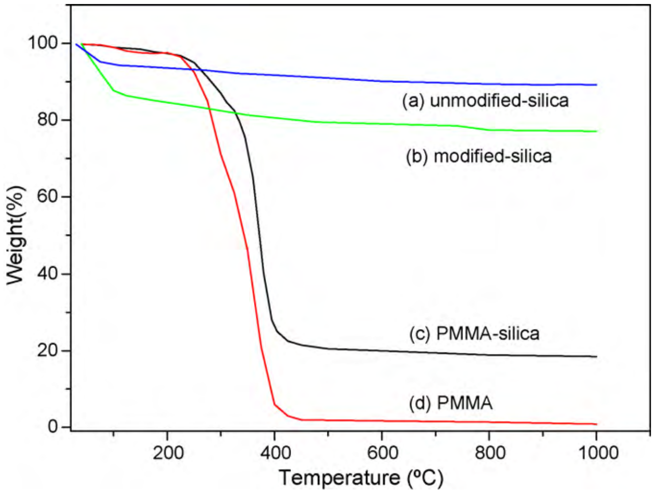

Fig. 13. TGA curve of (a) unmodified-silica, (b) modified-silica, (c) PMMA–silica, and (d) pristine PMMA.

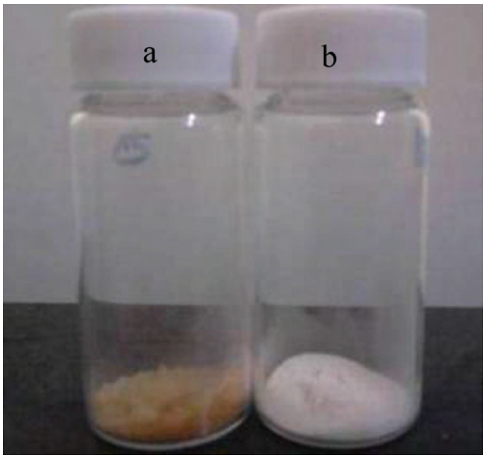

Fig. 14. Photographs of aging measurement after heat treatment at 513 K for 1 h: (a) pristine PMMA powder and (b) PMMA–silica powder.

Fig. 14 presents the heat treatment results for pristine PMMA powder and PMMA–silica powder under the same conditions. These particles were treated at a temperature above the glass transition temperature (T_g) of polymer. After heat treatment, at a temperature of 513 K for 1 h, pristine PMMA powder changed color from white to yellow, whereas PMMA–silica powder did not change color (white). The thermal stability of polymer particles is significantly enhanced by coating a layer of silica, and it would be due to the increase in Si–O–Si bonding and the change in surface structure of microsphere.

4. Conclusions

PMMA beads with a size ranging between 1 and 2 μm were synthesized by dispersion polymerization. Adsorption of METMAC on PMMA beads leads to positively charged PMMA surface. On the other hand, a wet milling process with a suitable dispersant (VTEOS) was successfully utilized to comminute the aggregated silica powder to obtain a good colloidal stability. The zeta-potentials of these milled silica powders are negative in a wide range of pH values from 4 to 10 and are much less than −30 mV. Thus, the negatively charged silica particles were coated directly on the surface of PMMA surface owing to the electrostatic interaction. The PMMA/silica hybrids are, thus, formed with a villus-like morphology. The thermal resistance of the hybrid microspheres, confirmed by TGA analysis and thermal aging experiment, is tremendously enhanced by the coated silica layer. The silica content of the resulting hybrid particles was 18.5% and the surface of PMMA was fully covered by silica. It provides a facile route for the preparation of inorganic–organic hybrid for various optical applications such as used as an effective diffuser and photonic crystal.

Acknowledgement

The authors would like to thank Chung Shan Institute of Science and Technology, Taiwan, for financially supporting this research.

References

[1] S.I. Chang, J.B. Yoon, H. Kim, J.J. Kim, B.K. Lee, D.H. Shin, Opt. Lett. 31 (2006) 3016–3018.
[2] S.L. Yeh, Opt. Commun. 264 (2006) 1–8.
[3] T.K. Shih, C.F. Chen, J.R. Ho, F.T. Chuang, Microelectron. Eng. 83 (2006) 2499–2503.
[4] E.E. García-Guerrero, E.R. Mnédez, H.M. Escamilla, Opt. Express 15 (2007) 910–923.
[5] G.H. Kim, J.H. Park, Appl. Phys. A: Mater. Sci. Process. 86 (2007) 347–351.
[6] G.H. Kim, Eur. Polym. J. 41 (2005) 1729–1737.
[7] A. Zhu, Z. Shi, A. Cai, F. Zhao, T. Liao, Polym. Test. 27 (2008) 540–547.
[8] N. Katsikis, F. Zahradnik, A. Helmschrott, H. Munstedt, A. Vital, Polym. Degrad. Stab. 92 (2007) 1966–1976.
[9] S. Gu, T. Kondo, M. Konno, J. Colloid Interface Sci. 272 (2004) 314–320.
[10] J. Luna-Xavier, A. Guyot, E. Bourgeat-Lami, J. Colloid Interface Sci. 250 (2002) 82–92.
[11] H. Sertchook, D. Avnir, Chem. Mater. 15 (2003) 1690–1694.
[12] V.G. Pol, H. Grisaru, A. Gedanken, Langmuir 2 (2005) 3635–3640.
[13] C. Song, D. Wang, Y. Lin, Z. Hu, G. Gu, X. Fu, Nanotechnology 15 (2004) 962–965.
[14] H.S. Mohammed, D.A. Shipp, Macromol. Rapid Commun. 27 (2006) 1774–1778.
[15] H. Shiho, N. Kawahashi, J. Colloid Interface Sci. 226 (2000) 91–97.
[16] N.L. Lala, T.C. Deivaraj, J.Y. Lee, Colloids Surf. A: Physicochem. Eng. Asp. 269 (2005) 119–124.
[17] K. Zhang, W. Wu, H. Meng, K. Guo, J.F. Chen, Powder Technol. 190 (2009) 393–400.
[18] H. Ma, L.L. Dai, J. Colloid Interface Sci. 333 (2009) 807–811.
[19] S.J. Han, K. Shin, K.D. Suh, J.H. Ryu, Macromol. Res. 16 (2008) 399–403.
[20] M. Chen, S. Zhou, B. You, L. Wu, Macromolecule 38 (2005) 6411–6417.
[21] X. Ding, Y. Jiang, K. Yu, Hari-Bala, N. Tao, J. Zhao, Z. Wang, Mater. Lett. 58 (2004) 1722–1725.
[22] H. Ihara, S. Kubota, A. Uchimura, Y. Sakai, T. Wakiya, M.M. Rahman, S. Nagaoka, M. Takafuji, Mater. Chem. Phys. 114 (2009) 1–5.
[23] D.R. Hwang, J.H. Hong, J. Lee, S.E. Shim, Macromol. Res. 16 (2008) 329–336.
[24] Y. Zhang, H. Chen, X. Shu, Q. Zou, M. Chen, Colloids Surf. A: Physicochem. Eng. Asp. 350 (2009) 26–32.
[25] J. Lee, C.K. Hong, S. Choe, S.E. Shim, J. Colloid Interface Sci. 310 (2007) 112–120.
[26] M. Chen, L. Wu, S. Zhou, B. You, Macromolecules 37 (2004) 9613–9619.
[27] M. Chen, S. Zhou, B. You, L. Wu, Macromolecules 38 (2005) 6411–6417.
[28] H. Bel Fadhel, C. Frances, Powder Technol. 99 (1998) 147–153.
[29] Y. Wang, E. Forssberg, Int. J. Miner. Process. 81 (2006) 1–14.
[30] M. Marini, B. Pourabbas, F. Pilati, P. Fabbri, Colloids Surf. A: Physicochem. Eng. Asp. 317 (2008) 473–481.
[31] S. Vitry, A. Mezzino, C. Gauthier, J.Y. Cavaillé, F. Lefebvre, É.B. Lami, C. R. Chimie 6 (2003) 1285–1293.
[32] www.malvern.co.uk (lecture Dispersion Stability and Zeta Potential).
[33] M.A. Zulfikar, A.W. Mohammad, A.A. Kadhum, N. Hilal, Mater. Sci. Eng. A 452–453 (2007) 422–426.