

Preparation of raspberry-like polystyrene/carbon black composite microsphere via π – π interactions

Jianfeng Huang · Qiuying Li · Yubing Bao · Chifei Wu

Received: 7 May 2008 / Revised: 23 September 2008 / Accepted: 15 October 2008 / Published online: 5 November 2008
© Springer-Verlag 2008

Abstract Polystyrene (PS)/carbon black (CB) composite microspheres were prepared using a modified CB, which was prepared by blending CB with a hindered phenol antioxidant Irganox 1330 in an internal mixer. Scanning electron microscopy indicated that the modified CB adsorbed on the surface of PS microspheres homogeneously to form a raspberry-like morphology composite. The non-covalent binding of Irganox 1330 on the surface of PS microsphere was observed from the UV-Vis absorption spectrum in ethanol, while the fluorescence of PS was almost totally quenched by the binding of Irganox 1330. These results implied there were aromatic interactions between Irganox 1330 and the PS microspheres, which played a crucial role in the formation of composite microspheres.

Keywords Carbon black · Polystyrene · π – π interaction · Composite particle · Hindered phenyl antioxidant

Introduction

Carbon black is widely used as filler in elastomers, plastics, and paints to modify the mechanical, electrical, and the optical properties of the materials. Conventionally, the polymer/carbon black (CB) composites are prepared by melt blending or solution blending methods. Their proper-

ties are strongly dominated by the dispersion morphology of CB in polymer matrix and interfacial interactions between CB and polymer. In recently years, the synthesis of polymer/CB composite particles has received much attention because the structure and interfacial interactions can be precisely controlled, and more importantly, such hybrid particles have many applications, such as in toners [1–5], conductive film [6], and electrorheological fluid [7].

There are several experiments described in the literature regarding the preparation of polymer/CB composite particles. Katharina Landfester obtained polymer-encapsulated carbon black pigment particles with a size of approximately 120 nm by co-sonication of carbon black dispersion and a typical miniemulsion polymerization recipe [1]. Analogous polymeric microspheres for toner application based on a membrane emulsification method were prepared by Jung-Hyun Kim [2]. Both particle size and microstructure of the composite particles can be tuned. However, these two methods are rather complicated and require special equipments and rigorous conditions. Jun Hasegawa developed a polymerized styrenic-based toner by suspension polymerization in presence of carbon black [3]. This process overcomes the aforementioned problems because of the simplicity of the reaction process and equipment. A major deficiency was that the loading of carbon black in the composite particles was relatively low (<10%), since most types of radical polymerization are adversely influenced by the presence of carbon black, such that the reaction may be retarded or, indeed, completely inhibited as a strong radical scavenger. To solve this problem, Xerox took advantage of electrostatic forces between negatively charged latexes or emulsion resins and positively charged carbon black dispersions to synthesize toner particles [4, 5]. Jaime C. Grunlan prepared a conductive particle by depositing a thin carbon black film on the functionalized polyethylene

Electronic supplementary material The online version of this article (doi:10.1007/s00396-008-1948-1) contains supplementary material, which is available to authorized users.

J. Huang · Q. Li · Y. Bao · C. Wu (✉)
Polymer Alloy Lab., School of Material Science and Engineering,
East China University of Science & Technology,
130 Meilong Road,
Shanghai 200237, China
e-mail: wucf@ecust.edu.cn

particles surface using layer-by-layer electrostatic assembly [6]. The electrostatic interaction between two different particles plays an important role in fabrication such composite particles in both cases.

Other interfacial interactions beside electrostatic force have also been utilized as the driving forces for the preparation of polymer-based hybrid colloidal particles. Wu et al. prepared long stable poly(methyl methacrylate) (PMMA)/SiO₂ nanocomposite particles by strong acid–base interaction between hydroxyl groups (acidic) of silica surfaces and amino groups (basic) of 1-vinylimidazole on PMMA [8]. Choi et al. prepared carbon nanotubes adsorbed polystyrene and poly(methyl methacrylate) microspheres with the aid of hydrophobic interactions provided by the surfactant molecules [9].

The aim of the present research is to prepare polystyrene/CB composite particles by a self-assembled heterocoagulation with the aid of π – π interactions. Non-covalent interactions involving aromatic rings are pivotal to protein-ligand recognition and biomolecular structure conservation [10–13]. The π – π interactions were also used in the supramolecular self-assembly [14–16] but seldom used to prepare polymer/inorganic composite particles. The aromatic interaction in this study derives from the grafting molecules on CB surface and the benzene ring of polystyrene molecules as shown in Fig. S1 in Electronic Supplementary Material. It provides an efficient and simple approach to prepare polymer/CB composite particles with well-controlled raspberry-like morphology. The composite particles may be expected to extend their applications as functional fine particles in a wide variety of ranges, such as in electrorheological fluid, gas sensing materials [17], toner, and reinforcing fillers for elastomer [18].

Materials and methods

Materials

Mogul-L CB was supplied by Cabot. This grade of CB has a nitrogen surface area of 138 m²/g and a primary particle size of 24 nm. A hindered phenol antioxidant, commercial name Irganox 1330 (3,3',3',5,5',5'-hexa-tert-butyl-a,a',a'-(mesitylene-2,4,6-triyl)tri-*p*-cresol), was supplied by Ciba Specialty Chemicals. Its molecule structure is shown in Fig. 1. Styrene (Shanghai Chemical Regent, China) and methyl methacrylate (Lingfeng Chemical, China) were distilled under reduced pressure and stored in a refrigerator prior to use. Poly(*N*-vinyl pyrrolidone) (PVP, Mw=40,000, Sigma Chemical) was used. Ethanol (Shanghai Chemical Regent, China) was used as the reaction medium. The 2,2'-azobisisobutyronitrile (AIBN, Wako Pure Chem., Japan) was used as received.

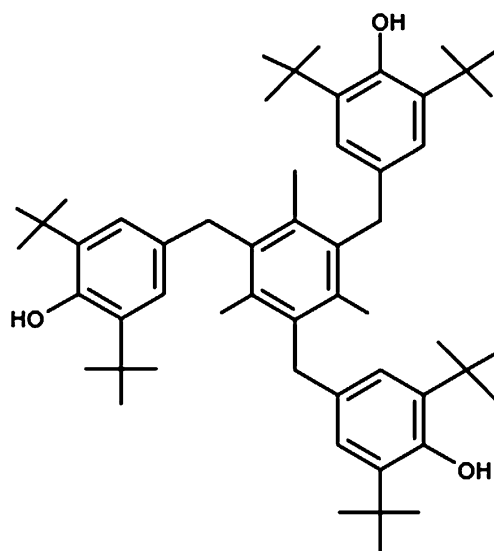


Fig. 1 The chemical structure of Irganox 1330

Modification of carbon black

The modified CB was prepared in an internal mixer (Rheomix 600p, Haake, Germany). Before mixing in the internal mixer, the organic molecules were pre-mixed with CB at ambient condition with a weight ratio of 0.5:1. Then the mixture was treated in the internal mixer at starting temperature of 230 °C for 20 min. Two counter-rotating σ -type rollers ran at a speed of 60 rpm. The product was dispersed in acetone, and the excess unbound organic molecule was removed by filtration and extraction, then it is vacuum-dried at room temperature.

Preparation of polystyrene and PMMA microsphere

Polystyrene (PS) and PMMA were prepared using the dispersion polymerization method [19], which is one of the most popular methods for producing monodispersed polymer particles. The purified styrene and methyl methacrylate monomer and a radical initiator (AIBN) were dissolved in ethanol-containing PVP as a stabilizer at room temperature. After removing the oxygen by nitrogen purging, the reaction mixture was heated to 60 °C and maintained for 24 h. The monodispersed particles obtained were washed by ethanol and then dispersed in ethanol again. The PS and PMMA particles prepared at 60 °C had a narrow size distribution with a particle size of 2 and 10 μ m.

Preparation of polystyrene/CB composite microsphere

The ethanol dispersions of modified CB were dropped into a glass beaker containing the PS dispersion using a syringe

pump at a rate of 2 ml/min. During this process, the PS dispersion was gently stirred. After the dropping of the dispersions of modified CB was completed, the mixture was then stirred rapidly at room temperature for 2 h to allow coupling of the modified CB and PS microspheres. Subsequently, the blended dispersions were kept at ambient conditions for 24 h without stirring. The PMMA dispersion was conducted in the same method as a control.

Characterization

Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy (FT-IR) of the samples in KBr pellets were recorded on Nicolet 5700 FTIR spectrophotometer (deuterated triglycine sulfate detector).

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on Netzsch TG and used to estimate the content of Irganox 1330 grafted on CB. The samples were heated from room temperature to 800 °C under N₂ atmosphere with a heating rate of 10 °C/min.

Transmission electron microscopy

Transmission electron microscopy (TEM) was used to investigate the morphology and particle size of the CB powder. It was carried out on a JEOL 2000FX microscope operating at 80 and 200 kV, respectively. The samples for TEM characterization were prepared by transferring a small amount of the CB ethanol dispersions onto a 200-mesh copper grid covered with a FormvarTM (polyvinyl formal) film, and the excess suspension was removed by filter paper and dried by infrared lamp. Then, the sample was vacuumized and analyzed.

Dynamic light scattering

Particle sizes of CB and modified CB were analyzed by a particle sizer (Zeta Potential/Particle Sizer, NicompTM 380 ZLS, PSS, Santa Barbara, CA, USA). Measurements were performed via dynamic light scattering (DLS) analyses of particle suspensions in ethanol at 23 °C. This technique analyses particles in suspensions within the diameter range 3–5,000 nm and operates with a helium–neon laser (wavelength 639 nm); the angle of measurement was 90°. Further, by using diluted carbon solvent dispersions (20 mg L⁻¹), the multiple scattering effects were avoided, and the autocorrelation function was measured correctly [20].

Scanning electron microscopy observation

The sediment from heterocoagulation was re-dispersed in ethanol, then drop cast onto glass slice and sputter-coated with gold in vacuum for scanning electron microscopy (SEM) observation on a SEM (JEOL JSM-35CF) at the accelerating voltage of 15 kV.

UV-Vis absorption spectra

The UV-Vis absorption spectra were measured with a Varian Cary 500 spectrophotometer in ethanol solution.

Fluorescence spectrum

Fluorescence spectra were measured in ethanol solution with a MPF-4 type Hitachi fluorescence spectrophotometer at room temperature. Fluorescence measurements were conducted at excitation frequency of 290 nm with a slit of 2 nm. Conditions were the same for all measurements.

Results and discussion

Preparation of modified CB

As is well known, the primary particles of CB are quite easy to fuse together to form aggregates and further to big agglomerates, which often results in the poor dispersion of CB into solvents or polymers. Thus, the modification of CB is the premise of preparation of polystyrene/CB composite particles. In our previous works [21–24], it is found that some low-molecular-weight compound, such as hindered phenol antioxidant or hindered anime light stabilizers, could be grafted onto CB by simply mixing them in an internal mixer above their melt point. The modified CB can be easily dispersed in the usual organic solvent and formed into a homogeneous dispersion; as shown in Fig. S2a,b in Electronic Supplementary Material, the final suspension of modified CB is stable for weeks, and no sedimentation is observed. Nevertheless, a suspension of pristine CB simply mixed with Irganox 1330 in ethanol sediments to bottom of the bottle quickly. The improved dispersibility is attributed to the grafting molecular layer on CB surface which stabilizes the CB particles and prevents them from aggregating together.

To demonstrate the presence of grafting Irganox 1330 on the carbon surface, the modified CB was filtered with acetone five times and extracted for 72 h to remove the free Irganox 1330 molecules. As reported in literature [25–27], the adsorption of antioxidant in thermoplastics-based formulations onto CB was a recognized phenomenon which was believed to be the interaction of antioxidant molecule

and carbon–oxygen functional group on surface of CB. Allen believed that the adsorption was weak and possibly via hydrogen bonding and dipole–dipole interactions. Thereby, it is believed that the adsorbed molecular could be washed off by selected solvent. The dried power after purification was analyzed with FT-IR. Figure 2 illustrates that the modified CB presents a mixed pattern of pristine CB and Irganox 1330, suggesting the presence of grafting Irganox 1330 molecules on carbon surface.

The percentage of Irganox 1330 grafting onto CB can be determined by TGA. Irganox 1330 was degraded completely below the temperature of 500 °C. The pristine CB and Irganox 1330 modified CB show a weight loss of 1.72% and 9.08%, respectively, as shown in Fig. 3. The weight percentage of grafted organic molecule calculated by the following equations is 7.36%.

$$\text{Grafting wt\%} = \left[\frac{(W_p - W_b)}{W_p} \right] 100\%$$

Where W_p and W_b are the residual weights of CB and Irganox 1330 modified CB particles under the non-isothermal heating on TGA below 500 °C, respectively.

Just for the existence of Irganox 1330 molecule on the surface of CB, the modified CB can be well dispersed in solvent and free from coacervation even at drying conditions. The size ratio of the two different particles is another important parameter influencing the heterocoagulation behavior strongly. According to Furusawa et al. [28], a uniform coverage of spherical core particles can only be obtained when the size ratio is larger than 3. The modified CB particles used here are more than a factor of 10 smaller than the core PS microsphere according to TEM and DLS analysis.

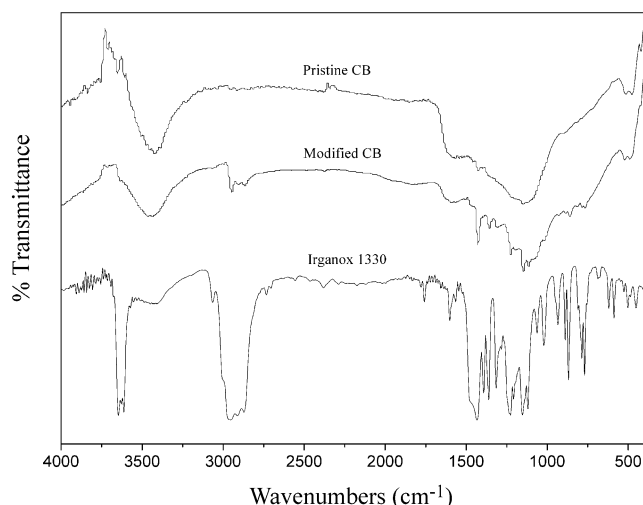


Fig. 2 FT-IR spectra of pristine CB, modified CB and Irganox 1330

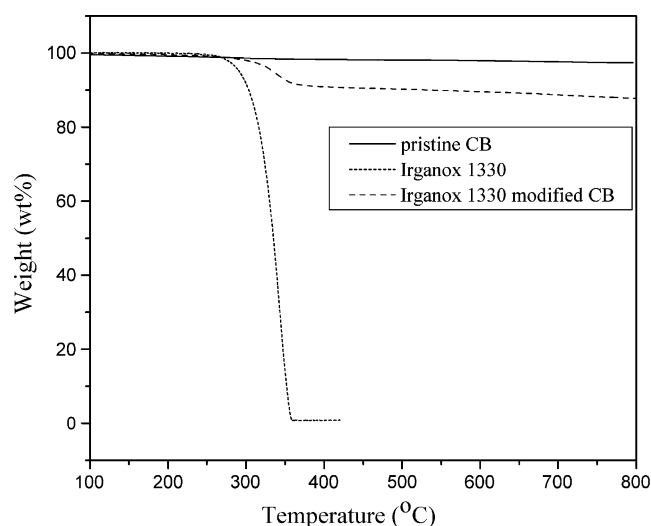


Fig. 3 TGA curves of Irganox 1330, pristine CB, and Irganox 1330 modified CB

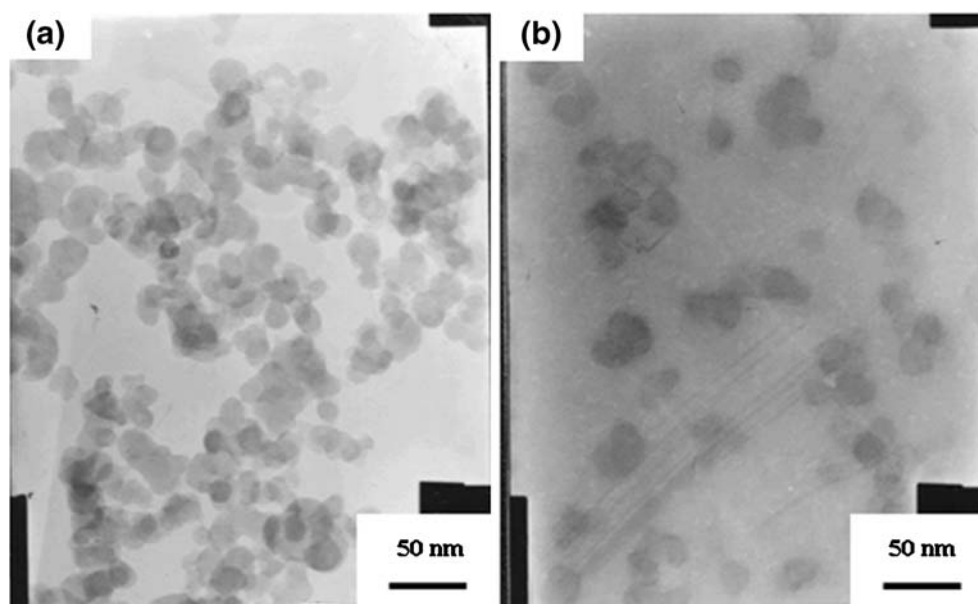
A TEM image from pristine CB is shown in Fig. 4a. It is found that the average diameter of primary CB particle is about 30 nm and that these primary particles fuse into CB chains and clusters. In Fig. 4b, the morphology of modified CB differs distinctly from that of pristine CB. Large agglomerates are not observed, and the mean aggregate size of modified CB is under 100 nm, indicating modified CB could retain nano-dimension even when its ethanol dispersions were vacuum dried. What is worth noting is that nanoparticles with a size close to primary particle are clearly observed. These nanoparticles are believed to be produced from the pulverizing effect by internal mixer.

DLS analysis is a reliable technique to determine the size and distribution of colloidal particles and aggregates. Figure S3 in Electronic Supplementary Material shows the size distribution of pristine CB and modified CB in ethanol. $P(d)$ is the relative probability of a particle diameter d , describing the log-Gaussian particle size distribution in the unimodal analysis. The maximum of the $P(d)$ curve corresponds to the mean particle diameter, and the $P(d)$ broadness is related to the particle size polydispersity index. As can be observed in Fig. S3 in Electronic Supplementary Material, the pristine CB particles have a mean diameter of 157 nm, while the mean particle diameter of modified CB is 91 nm. No agglomeration seems to occur after stopping the ultrasound treatment. This high stability is essentially due to the irreversible grafted layer of organic molecules on the CB surface, sufficiently stable that even prolonged centrifugation does not lead to a complete settling of the particles.

Preparation of polystyrene/CB composite particles

In a typical process, modified CB and PS microspheres were firstly dispersed in ethanol, respectively. After obtain-

Fig. 4 TEM images of **a** pristine CB and **b** modified CB

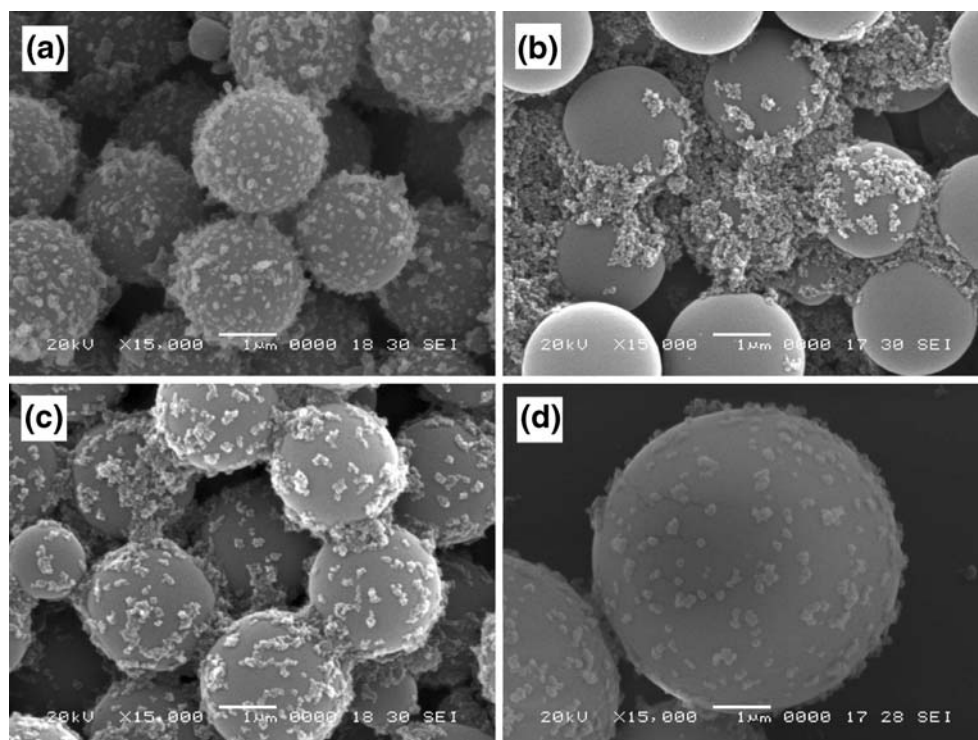


ing the homogenous dispersion with the aid of ultrasonic separation, the modified CB dispersion was dropped into a glass beaker containing the PS microsphere dispersion at a speed of 2 ml/min. During this process, the PS microsphere dispersion was gently stirred. The overall weight ratio of modified CB to PS microsphere was 1:10. Once the dropping of modified CB dispersion was completed, the blended dispersions were kept in ambient conditions for 24 h without stirring. During this time, the modified CB adsorbed PS microspheres underwent slow sedimentation

to the bottom of glass vials. At the same time of the sedimentation composite particles, the supernatant of the modified CB dispersion turned into a clear solution. The modified CB adsorbed PS microspheres were withdrawn and air-dried and vacuum-dried at room temperature overnight.

The surface morphology of the microspheres was observed by SEM. Figure 5a shows representative SEM images of the resulting composite particles upon adsorption of modified CB on PS microspheres. The adsorbed

Fig. 5 SEM images: **a** modified CB adsorbed clean PS, **b** pristine CB and clean PS, **c** modified CB adsorbed crude PS containing PVP, **d** modified CB adsorbed clean PMMA



modified CB particles are clearly seen at the exterior of the particles and form a raspberry-like morphology. The small particles, regarded as modified CB, show homogeneous distribution, without obvious aggregation. By contrast, there is no CB adsorbed PS microsphere generated by replacing the modified CB with pristine CB (Fig. 5b). These morphology observations indicate that a stronger interaction existed between modified CB and PS particles, and the grafting molecule of Irganox 1330 possibly plays a crucial role during the heterocoagulation.

Mechanism for the formation of composite particles

Imhof [29] prepared polystyrene/silica (PS/SiO₂) core-shell nanocomposite particles by using poly(*N*-vinylpyrrolidone) as a coupling agent. Thus, a suppositional mechanism for the adsorbing of modified CB on PS microsphere is the formation of hydrogen bond between Irganox 1330 and trace amount of PVP used as stabilizer in the preparation of PS. To prove the suppositional mechanism, crude PS microsphere without washing after the dispersion polymerization was used as control. In this case, PVP molecule was believed to be anchored on the surface of PS microsphere. On the other way round, the modified CB aggregated together and was sparsely adsorbed on the PS microsphere surface (Fig. 5c). These results indicate that the possible hydrogen bonding between Irganox1330 and PVP is not the cause of the assembly. A direct interaction between grafting molecule Irganox 1330 and PS molecule might be the driving force for the formation of such raspberry-like microspheres.

From the chemical structure view, PS mainly contains benzene ring on its backbone. For this reason, PMMA microspheres without aromatic ring were mixed in the same

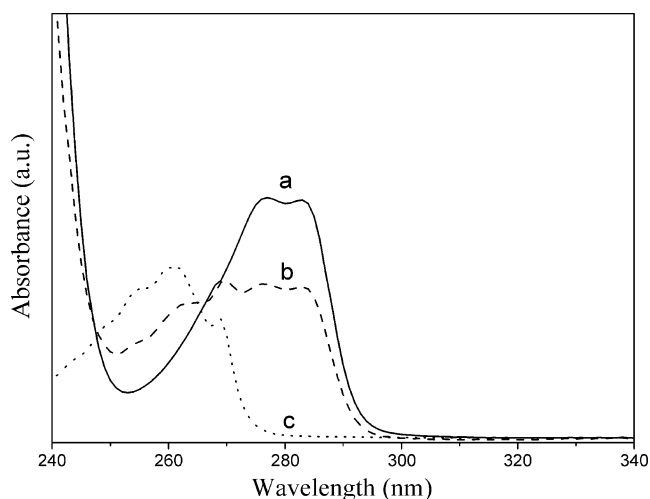


Fig. 6 The UV-Vis absorption spectra of **a** Irganox 1330, **b** PS microspheres bound with Irganox 1330, and **c** PS microspheres in ethanol

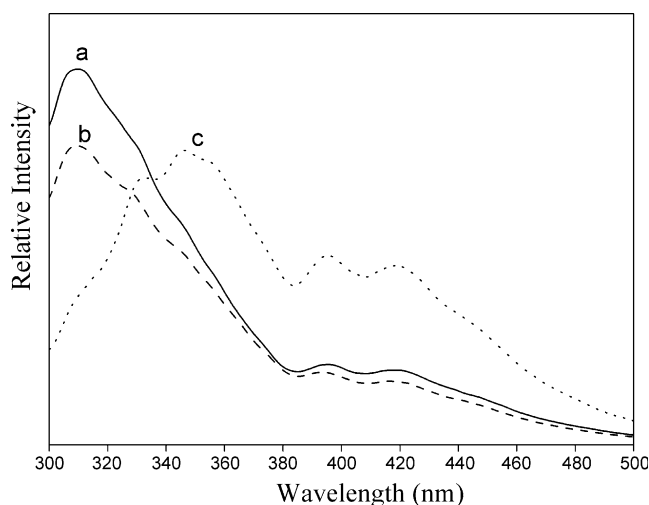


Fig. 7 Fluorescence emission spectra of **a** Irganox 1330, **b** PS microspheres bound with Irganox 1330, and **c** PS microspheres in ethanol

methods of PS microspheres as a control. As seen in Fig. 5d, dropping modified CB dispersion into the PMMA microsphere dispersion produced homogeneous dark black blend dispersion as above PS system. The blended dispersions were kept in ambient conditions for 24 h without stirring. During this time, the PMMA microsphere underwent slow sedimentation to the bottom of glass vials but left the supernatant still black (Fig. S4 in Electronic Supplementary Material). It indicated that the modified CB was not adsorbed on PMMA microsphere completely. The SEM observation also revealed that the amount of modified CB deposited on PMMA microsphere is much lower than PS microsphere (Fig. 5d).

Lastly, based on the results mentioned above, a speculated mechanism of the formation of raspberry-like polystyrene/CB composite particle is presented in Fig. S1. The π - π interactions between the aromatic groups on grafting molecule Irganox 1330 and polystyrene are supposed to be the primary driving force of this assembly. The non-covalent binding of Irganox 1330 on the surface of PS microsphere can be observed from the UV-Vis absorption spectrum in ethanol (Fig. 6). As the mixture of PS microsphere and Irganox 1330 has been washed thoroughly to get rid of free Irganox 1330 before redispersing in ethanol, which was monitored by UV-Vis absorption spectroscopy, there should be no free Irganox 1330 in the ethanol solution. Thus, the existence of the feature peaks of Irganox 1330 strongly suggest the binding of Irganox 1330 on the surface of PS microsphere, most presumably through π - π interactions between the phenyl units of Irganox 1330 and the PS. These aromatic interactions can be further testified by the fluorescence emission spectra (Fig. 7). The emission of PS is almost totally quenched by binding of Irganox 1330. The observed quenching may be attributed to

static quenching due to the formation of the ground state complexes and the excited state exciplexs. Therefore, the phenomenon implied there were π – π interactions between the aromatic groups on PS and Irganox 1330, which played a crucial role in the formation of composite microspheres.

Summary

In summary, polystyrene/CB composite microspheres were successfully prepared by a novel self-assembly process from modified CB and PS microspheres through a π – π interaction. The SEM results demonstrated that modified CB can be homogenously adsorbed on the surface of PS microspheres and formed the raspberry-like morphology. The π – π interactions between Irganox 1330 and PS were supported by the fluorescence emission spectra. The Irganox 1330 modified CB with specific affinity to benzene ring contained in polymer are expected to be used as building blocks in the rational design of new types of composite particles. These points made this preparation method for polymer/CB composite particles worth investigating further.

Acknowledgments We acknowledge funding support from Konica Minolta and National Natural Science Foundation of China (NSFC50733001).

References

1. Tiarks F, Landfester K, Antonietti M (2001) *Macromol Chem Phys* 202:51
2. Ha YK, Song HS, Lee HJ, Kim JH (1999) *Colloid Surface A* 162:289
3. Hasegawa J, Yanagida N, Tamura M (1999) *Colloid Surface A* 153:215
4. US Patent 5,604,076 (1997)
5. US Patent 5,766,817 (1998)
6. Kim YS, Liao KS, Jan CJ, Bergbreiter DE, Grunlan JC (2006) *Chem Mater* 18:2997
7. Jin HJ, Choi HJ, Yoon SH, Myung SJ, Shim SE (2005) *Chem Mater* 17:4034
8. Chen M, Wu L, Zhou S, You B (2004) *Macromolecules* 37:9613
9. Jin HJ, Choi HJ, Yoon SH, Myung SJ, Shim SE (2005) *Chem Mater* 17:4034
10. Meyer EA, Castellano RK, Diederich F (2003) *Angew Chem Int Ed* 42:1210
11. Mignon P, Loverix S, Steyaert J, Geerlings P (2005) *Nucleic Acids Res* 33:1779
12. Versees W, Loverix S, Vandemeulebroucke A, Geerlings P, Steyaert JJ (2004) *Mol Biol* 338:1
13. Mignon P, Loverix S, De Proft F, Geerlings P (2004) *J. Phys. Chem. A* 108:6038
14. Nguyen TQ, Martel R, Avouris P, Bushey ML, Brus L, Nuckolls C (2004) *J Am Chem Soc* 126:5234
15. Yeh CW, Yen YS, Lin WB, Su CW, Chen JD, Wang JC (2005) *Struct Chem* 16:141
16. Dou RF, Ma XC, Xi L, Yip HL, Wong KY, Lau WM, Jia JF, Xue QK (2006) *Langmuir* 22:3049
17. Li J, Xu J, Zhang M, Rong M (2003) *Carbon* 41:2353
18. Qi D, Wu M, Yang L, Shao J, Bao Y (2008) *Front Chem Eng China* 2:127
19. Shen S, Sudol ED, El-Aasser MS (1994) *J Polym Sci, Part A: Polym Chem* 32:1087
20. Ridaoui H, Jada A, Vidal L, Donnet JB (2006) *Colloids Surf A* 149:278
21. Xu R, Wu C, Xu H (2007) *Carbon* 45:2806
22. Li Q, Yu N, Qiu Z, Zhou X, Wu C (2008) *Colloids Surf A* 317:87
23. Qian S, Huang J, Guo W, Wu C (2007) *J Macromol Sci Phys* 46:453
24. Huang J, Shen F, Li X, Zhou X, Li B, Xu R, Wu C (2008) *J Colloid Interface Sci* 328:92
25. Pena JM, Allen NS, Edge M, Liauw CM, Santamaria F, Noiset O, Valange B (2001) *J Mater Sci* 36:2885
26. Pena JM, Allen NS, Edge M, Liauw CM, Noiset O, Valange B (2001) *J Mater Sci* 36:4419
27. Pena JM, Allen NS, Liauw CM, Edge M, Valange B, Santamaria F (2001) *J Mater Sci* 36:4443
28. Furusawa K, Anzai C (1987) *Colloid Polym Sci* 265:882
29. Graf C, Vossen DLJ, Imhof A, van Blaaderen A (2003) *Langmuir* 19:6693