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ORIGINAL PAPER

The electric response behavior and microencapsulation of the pigment phthalocyanine green G using interfacial polymerization

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Abstract The polyamide microcapsules for the electrophoretic display have been prepared via interfacial polymerization. The core material of the microcapsules is electrophoretic fluid consisted of pigment phthalocyanine green G (CAS No. 1328-53-6) modified with octadecylamine, tetrachloroethylene, and polyoxyethylene octylphenol ether (OP-10). The wall of the polyamide is synthesized from paraphthaloyl chloride and diethylenetriamine. FT-IR indicated that octadecylamine was bonded to pigment phthalocyanine green G with the hydrogen bond. The effect of the amount of octadecylamine on the dispersibility of the pigment suspended in tetrachloroethylene was investigated. Compared to the unmodified pigment, the dispersibility of the modified pigment was improved by 66.7%. The modified pigment migrated to the positive electrode under the direct voltage and the electric response time was about 85 s in 20 V/mm. The average particle size of microcapsules decreased from 834.5 to 258.2 nm as the dosage of OP-10 increased, and the microcapsule yield reached maximum of 83.5% at the OP-10 concentration of 1.5 wt%. With the reduction of the core/wall weight ratio in the range from 1:6 to 1:14, the average particle size improved from 267.4 to 554.4 nm. However, the maximum of the microcapsule yield was 87.6% at the core/wall weight ratio of 1:10. The microcapsule yield reached a peak of 87.6% as the pH value was 12. The average particle size of the microcapsules that obtained at 25 °C was 327.4 nm, which was smaller than those prepared in other temperatures. The formed polyamide microcapsules had a regular spherical shape.

Keywords Phthalocyanine green G microcapsules · Electric response behavior · Interfacial polymerization · Electronic ink · Surface modification

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Introduction

Electrophoretic image display (EPID), which combines many advantages of the traditional paper and electronic displays, is a kind of promising display technology [1–3]. Due to its portability and super capacity, the EPID can be widely applied in magazines, books, newspapers, and large outdoor print advertisements [4]. The microencapsulated display (MC-EPID) is the most popular among the EPIDs, which attributes to its high contrast ratio, flexibility, portability, wide angle view, and especially low power consumption [5–8]. Microencapsulated electronic ink contains electrophoretic particles, suspension, and charge control agent. It works on the basis of the charged pigment particles migrating in the dispersion medium. The technique prevents such shortcomings as reunion and sediment of microcapsule particles beyond the microcapsules [9, 10]. So it can improve the stability and prolong the service life of the displays.

In recent years, many researches have been carried out in the modification of electrophoretic particles, wall materials, and preparation technology. For example, Park et al. [11] studied nano-size cationically charged TiO_2 particles prepared by using amino silane compounds, which had relatively high zeta potential and mobility. Qiao et al. [12] prepared poly (urea–formaldehyde) microcapsules containing modified BY-14 particles dispersed in cyclohexane by in situ polymerization. Jang et al. [13] synthesized microcapsules of high density oil as a core material and melamine formaldehyde (MF) precondensates as a shell material. Song et al. [14] reported that the microcapsules produced via complex coacervation were elastic and stable without breakage during vacuum drying.

Interfacial polymerization is widely used in the preparation of microcapsules. It is convenient and fast to prepare microcapsules by this method. And the requirements to the ratio of raw materials and purity of monomers are inexact. Li et al. [15] studied polyurea microcapsules that fabricated by interfacial polymerization with high impermeability, good transparency, and rough interior face.

In this article, paraphthaloyl chloride and diethylenetriamine were selected as wall materials to fabricate polyamide microcapsules via interfacial polymerization. The polyamide microcapsules prepared own good elasticity, toughness properties, and good optics performance. The obtained microcapsules had nanoparticle sizes, a regular spherical shape and a high microcapsule yield. The effects of emulsifier, the core/wall ratio, pH value, and reaction temperature were all discussed for optimizing the morphologies and improving the microcapsule yield. It is hopeful to provide some references for making the mold MC-EPID device.

Experimental

Materials

Pigment phthalocyanine green G was supplied by Yixing Chentang Pigment Co., Ltd. Octadecylamine, used as the modifier, was purchased from Changzhou Xinhua Active Material Institute. Tetrachloroethylene was bought from Jiangsu Qiangsheng

Chemical Co., Ltd. Besides, triethanolamine, sodium hydroxide (NaOH), terephthaloyl chloride, and diethylenetriamine were all procured from Sinopharm Chemical Reagent Co., Ltd., while polyoxyethylene octylphenol ether (OP-10) was available from Shanghai Lingfeng Chemical Reagent Co., Ltd. All reagents were used directly without further purification.

Preparation of modified pigment particles and electrophoretic suspension

Different amounts of octadecylamine and 0.3 wt% phthalocyanine green G were added into 40 mL absolute alcohol in a beaker at the room temperature, and then the mixture was ultrasonicated for 20 min, followed by back flowing and stirring for 1 h at high temperature around 80 °C. Afterward, the mixture was filtrated, washed with distilled water, and dried so as to get rid of absolute alcohol, then phthalocyanine green G modified with octadecylamine was obtained.

1.6 wt% OP-10 as emulsifier, 0.8 wt% triethanolamine as charge control agent, and 0.4 wt% modified phthalocyanine green G were well dispersed in 15 mL tetrachloroethylene by ultrasonification for 10 min to gain electrophoretic suspension.

Preparation of microcapsules

Microcapsules were prepared via interfacial polymerization method. OP-10 was stirred to dissolve in 75 mL distilled water, and the pH of the solution was adjusted by addition of 25 wt% NaOH aqueous solution. Meanwhile, terephthaloyl chloride was sonicated for 10 min, making it uniformly dispersed in the prepared electrophoretic suspension. The oil phase was then dispersed into the aqueous phase in a three-neck flask with agitation for 20 min at the room temperature to obtain an O/W emulsion. The diethylenetriamine aqueous solution, of which the mole ratio of diethylenetriamine and terephthaloyl chloride was 2:1, was dripped into the emulsion to initiate the interfacial polycondensation reaction. The reaction system was kept the stirring rate at 800 rpm for 20 min. The final slurry was filtered, rinsed with distilled water, and dried to gain the microcapsule.

Characterization

Characterization of the unmodified and modified phthalocyanine green G

The unmodified and modified phthalocyanine green G were characterized by a FT-IR (NICOLET NEXUS 470, scan 500–4000 cm^{-1}).

Characterization of the electrophoretic fluid

The dispersibility of the unmodified and modified phthalocyanine green G in tetrachloroethylene was calculated by the following formula [16]:

$$T_D = \frac{T_0 - T_S}{T_0} \times 100\%,$$

where T_D was the dispersibility of phthalocyanine green G, T_0 was the transmittivity of reference solution, and T_S was the transmittivity of dispersion. Both T_0 and T_S were tested by an ultraviolet and visible spectrophotometer (UV-2100, Unico) at maximum absorption wavelength.

The electrophoretic fluid was added into the electrophoretic cell that made by ITO conductive glass. The electric response behavior of the electrophoretic fluid was observed under the direct current (DC).

Characterization of microcapsules

The particle size and the size distribution of microcapsules and zeta potential of pigments were measured on a Nano Particle Size and Zeta potential Analyzer (Nano-ZS90, MALVERN, Britain). Transmission electron microscope (TEM, Hitachi H-7650, Japan) and video-zoom microscope (VZM, DZ-3, Japan) were used to observe the morphology and structure of microcapsules.

Microcapsule yield (*Y*) was defined as the ratio of mass of the finally acquired microcapsules to the initial total mass of ingredients used in formation [17]. The calculated formula was as follows:

$$Y = \frac{W_m}{W_c + W_w} \times 100\%,$$

where W_m was the mass of the acquired microcapsules, W_c was the mass of the core, and W_w was the mass of the wall materials.

Results and discussion

Surface modification of phthalocyanine green G

FT-IR spectra of phthalocyanine green G

Figure 1 presents the FT-IR spectra of pigment phthalocyanine green G unmodified and modified with octadecylamine. For FT-IR spectra of unmodified pigment (a), the broad peak at 3422.39 cm^{-1} is attributed to the O–H stretching vibration, owing to the crystal water in phthalocyanine green G. 2927.69 cm^{-1} is related to C–H asymmetric stretching vibration. C=N stretching vibration in the isoindazole structure appears at 1391.03 and 1326.14 cm^{-1}. Moreover, the characteristic peaks at 948.44 cm^{-1} and around 600–800 cm^{-1}, represent the existences of N–Cu and C–Cl, respectively.

In FT-IR spectrum of modified pigment (b), the bands in 2800–3500 cm^{-1} change obviously. The peak of O–H shifts to present 3426.60 cm^{-1} and turns weaker. The bands of C–H stretching vibration near 2927.69 cm^{-1} turn stronger and convert to 2923.03 and 2861.30 cm^{-1}. The alteration is due to the hydrogen bond

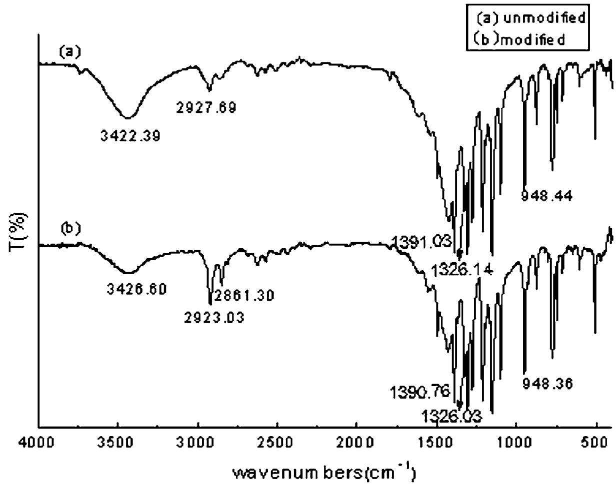


Fig. 1 FT-IR spectra of pigment phthalocyanine green unmodified and modified by octadecylamine

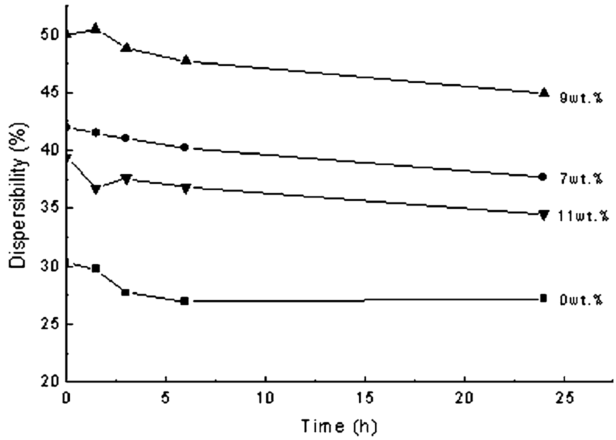


Fig. 2 Dispersing extent of pigment phthalocyanine green G in C_2Cl_4

between the nitrogen atom of the pigment and the hydrogen atom in the amino group of octadecylamine. It can be concluded that pigment phthalocyanine green G is boned by octadecylamine with its long alkyl chain outside.

Effect of the amount of octadecylamine

The unmodified and modified pigment phthalocyanine green G were evaluated in term of the dispersion in tetrachloroethylene. The pigment phthalocyanine green G was coated with different amount of octadecylamine including 0, 7, 9, and 11 wt%. As shown in Fig. 2, the dispersion of the phthalocynine green G modified with 9 wt% of octadecylamine in tetrachloroethylene is improved by 66.7%. The alkyl chain in octadecylamine, which adsorbs onto the surface of the pigment, has good compatibility with tetrachloroethylene. Moreover, the alkyl chain is able to form solvated membrane rapidly around the pigment phthalocyanine green G. The presence of the solvated membrane may prevent the pigment particles from flocculating while they approach to each other. It is observed that the dispersibility of pigment particles modified with 9 wt% octadecylamine is excellent among the pigment particles modified with 0, 7, and 11 wt%.

The electric response behavior of the electrophoretic fluid

Figure 3 shows the electric responses of phthalocyanine green G modified by 9 wt% of octadecylamine in the electrophoretic fluid. The zeta potentials of the modified pigments were −30.2 mV. Figure 3a is a photo of the electrophoretic fluid at $E = 0$ V. From Fig. 3b, d, it was observed that phthalocyanine green G particles

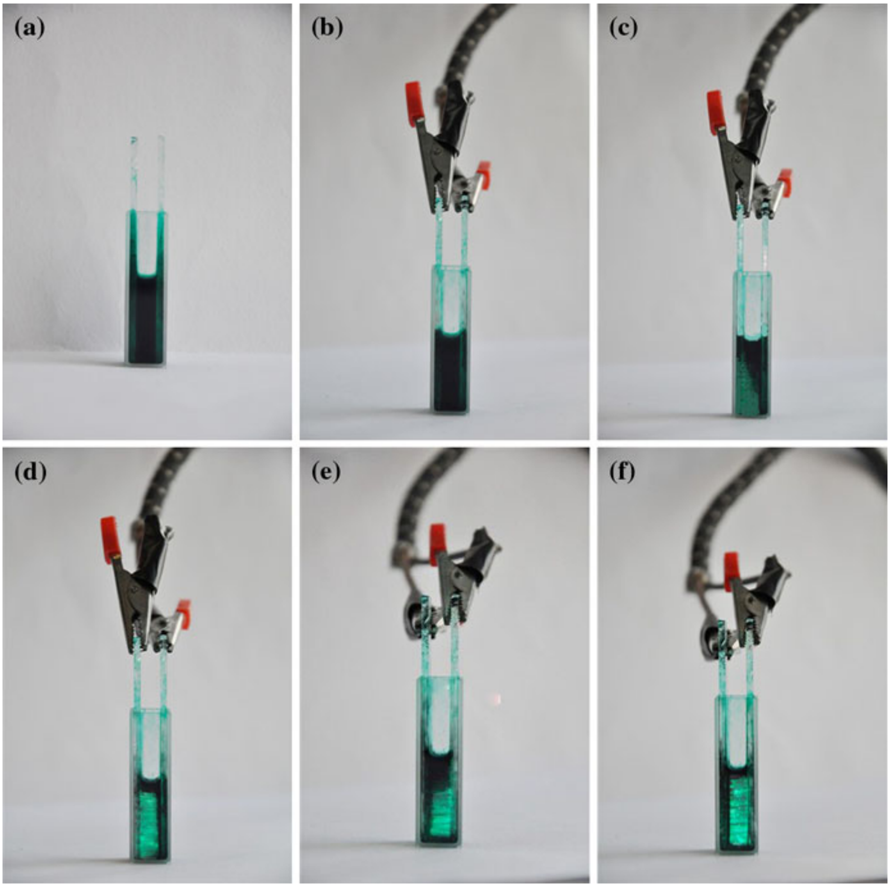


Fig. 3 The electric responses of the electrophoretic fluid. **a** $E = 0$ V/mm, **b**–**d** $E = 20$ V/mm, and the *right side* is positive electrode; **e**–**f** $E = -20$ V/mm and the *left side* is positive electrode

migrated to the positive electrode under a DC electric field. And the phthalocyanine green G particles downside moved before the upside particles. While the positive and negative electrodes were reversed, the phthalocyanine green G particles also shifted to the positive electrode, as presented in Fig. 3e, f. This performance occurred due to the negatively charged phthalocyanine green G that modified by octadecylamine. The particles kept gathering on the positive electrode for more than 7 days after the electric field was turned off. It is evinced that the modified phthalocynine green G particles are able to migrate reversibly and own bistability. The electric response time of the modified phthalocyanine green G particles in the electrophoretic fluid was about 85 s in 20 V/mm.

Influence of OP-10 emulsifier concentration in microcapsulation

Influence of OP-10 concentration on the particle size of microcapsules

The monomer in the organic phase is scattered to the surface of water phase in the presence of the emulsifier in microencapsulation, where the interfacial polymerization takes place. The polycondensates accumulate on the droplet surface bit by bit and wrap up the core material to generate microcapsules. This reveals that the concentration of the emulsifier plays an important role in the process of microencapsulation.

The relationship between the average particle size of microcapsules and the OP-10 concentration is presented in Fig. 4. The average particle size of microcapsules declines from 834.5 to 258.2 nm at the OP-10 content increases from 0.5 to 2.5 wt%. The OP-10 emulsifier is able to produce the interfacial film via adsorbing in the O/W interface, preventing the core material droplet from coalescence in mutual collision. With increasing the OP-10 content, the modified phthalocyanine green G particles are difficult to approach to each other due to the steric hindrance produced by OP-10. So microcapsules with smaller particle sizes were generated.

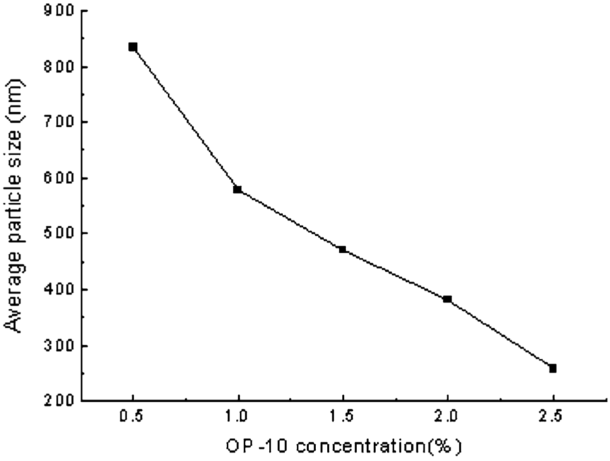


Fig. 4 The influence of the OP-10 emulsion on particle sizes of microcapsules

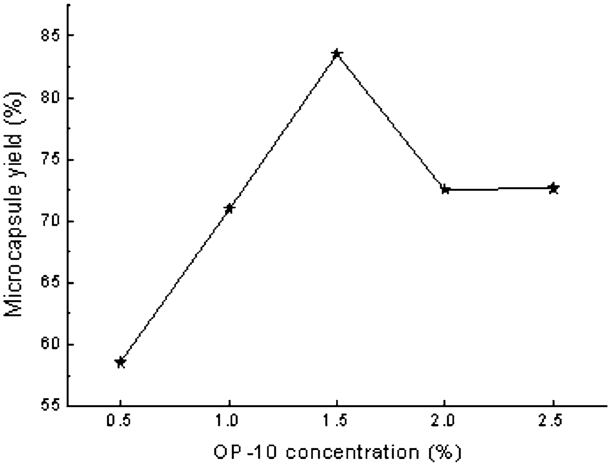


Fig. 5 The influence of the OP-10 emulsion on microencapsulating yield

As the OP-10 concentration is above 1%, organic phase may be emulsified to be very small droplets, which probably results in the increase of the total superficial area and energy in the system. If the attractive force among microcapsules is beyond the repulsive, the small particles are prone to agglomerate. So the declining tendency of particle sizes of microcapsules is weakened.

Influence of OP-10 concentration on the microcapsule yield

Figure 5 shows the relationship between the microcapsule yield and the OP-10 emulsifier concentration. The results indicate that the amount of OP-10 has an evident effect on the microcapsule yield. As the amount of OP-10 increases from 0.5 to 1.5 wt.%, the yield rises from 58.56 to 83.50%, then declines and tends toward stability with further increases of OP-10. It may be interpreted that the higher OP-10 content makes the core materials well dispersed to form a stable O/W emulsion and wrapped by the generated polyamide. Therefore, the microcapsule yield goes up gradually. But while the amount of OP-10 is more than 1.5 wt%, the dispersed core materials with very small particle size and large surface area are hard to be coated by polyamide. This results in the microcapsule yield decreasing from 83.50 to 72.58%. Considering the effect of OP-10 concentration on both the size and the yield of microcapsules, 1.5 wt% was more adaptable to be the appropriate OP-10 concentration in the following experiment.

Effect of the core/wall ratio on microcapsules

Effect of the core/wall ratio on the particle size of microcapsules

It is found that the change of the core/wall weight ratio also has an obvious effect on the microcapsules. As shown in Fig. 6, the average particle size of microcapsules

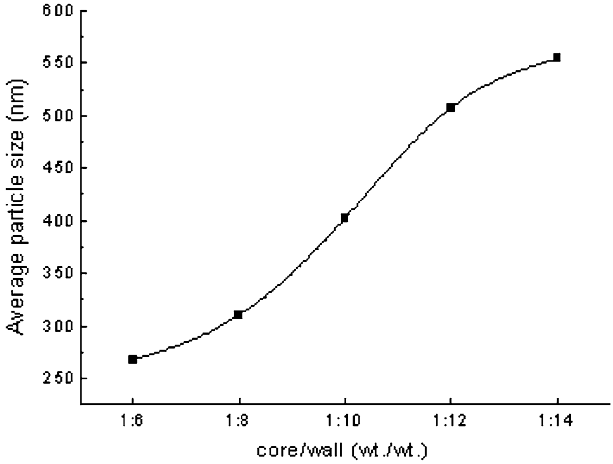


Fig. 6 The effect of the core/wall ratio on the particle size of microcapsules

keeps increasing from 267.4 to 554.4 nm with the decrease of the core/wall weight ratio, namely the increase of wall materials. It is assumed that the high amount of wall materials makes the performed shell of microcapsules thicker, and the average particle size of microcapsules turns much larger accordingly.

Effect of the core/wall ratio on the microcapsule yield

Figure 7 illustrates the effect of the core/wall weight ratio on the microcapsule yield. The result shows that the microcapsule yield rises up 74.54–87.60% while the core/wall weight ratio decreases from 1:6 to 1:10. It is most likely that much more core droplets are coated by polyamide as the decrease of the core/wall weight ratio.

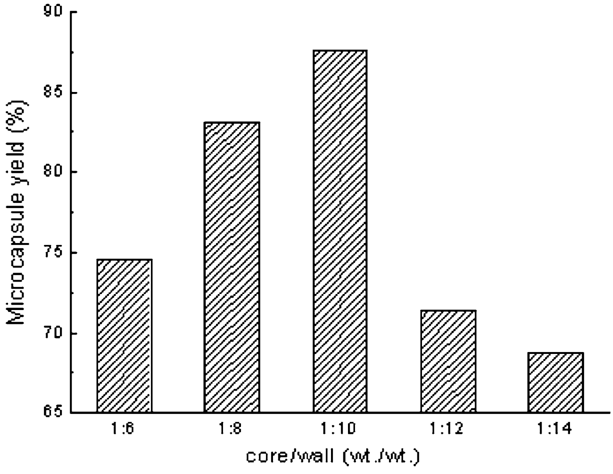


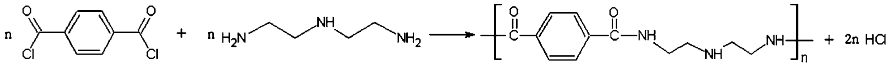
Fig. 7 The effect of the core/wall ratio on microcapsule yield

But the yield declines to 68.80% with further reduction of the ratio. The core materials are not enough to be coated by polyamide prepared from the excess paraphthaloyl chloride and diethylenetriamine. It was supposed that the microcapsules without core materials were obtained, which reduced the efficiency of wall materials and the microcapsule yield correspondingly.

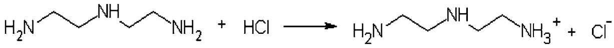
Effect of process parameters in microencapsulation

pH value

It is well known that pH value has a great influence on the production and the performance of polyamide microcapsules. Figure 8 presents the relationship between the microcapsule yield and pH value. The result demonstrates that the yields of microcapsules prepared in the alkaline range are beyond 70%, while the yield is only 23.83% at pH of 6. Moreover, the yields go up from 71.8 to 87.60% with pH value varied from 8 to 12 and then turn down slightly to 83.98% with pH value increasing to 14. This can be interpreted from the reaction principle, as shown with the following equations, among which the Eqs. 2, 3 are side reactions.



(1)



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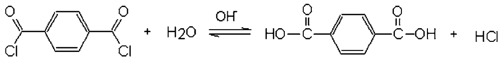

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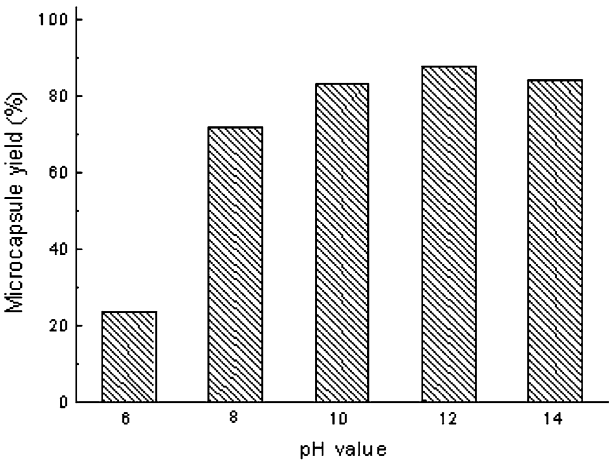

Fig. 8 The effect of pH value on microcapsule yield

The Eq. 2 reveals that the acylation reaction rate will be reduced in the presence of hydrogen chloride. So it is necessary to add NaOH as the acid-binding agent in the emulsification and microencapsulation. In addition, removing hydrogen chloride is also able to promote the film forming reaction successfully. Since the polycondensation reaction occurs inadequately in the alkalescent condition (pH = 8), most core materials are not able to be coated by the generated polyamide, leading to the decline of the microcapsule yield. However, if the alkalinity is too strong (pH = 14), terephthaloyl chloride converts to carboxylate by hydrolysis, as Eq. 3 shows. Carboxylate can not react with diethylenetriamine, resulting in decrease of the amount of generated polyamide and the yield accordingly. Therefore, the pH value of 12 is suitable for the experiment.

Temperature

Temperature plays an important part in the particle size and the wall performance of microcapsules, due to the effect of temperature on the rates of the hydrolytic reaction and the polycondensation reaction. Table 1 gives the mean particle sizes and the particle size distributions of microcapsules prepared at different temperatures. The results show that with the increase of the temperature at 15–25 °C, the average particle size changes from 525.4 to 327.4 nm, and the particle size distribution of microcapsules also gets narrower. The ratio of formed microcapsules also increases from approximately 80% to above 90%. But as the temperature rises up (25–45 °C), the particle size and distribution turn larger and broader, respectively, while the number of microcapsules declines to about 40%. In addition, a few of small sized microcapsules were obtained beyond 60 °C. It was supposed that the rate of the polycondensation between terephthaloyl chloride and diethylenetriamine at the low temperature was relatively slow. Then the small relative molecular mass of polyamide was obtained and the particle size distribution of microcapsules was not uniform. As the temperature went up, both the rate of the polycondensation reaction and the hydrolytic reaction of terephthaloyl chloride were increased. Then more HCl was generated, which made the amount of terephthaloyl chloride and diethylenetriamine reacting actually in the polycondensation lessened. At last, few microcapsules were synthesized.

So, in order to get the microcapsules with small particle size and narrow particle size distribution as well as reduce the side reaction, it is appropriate to select 25 °C as the reaction temperature.

Table 1 The influence of the temperature on microcapsules

T (°C)	Mean particle size (nm)	Distribution	Number of capsules (%)
15	525.4	Narrow	80
25	327.4	Narrow	>90
35	435.6	Wide	75
45	578.6	Wide	40
65	443.8	Narrow	<10

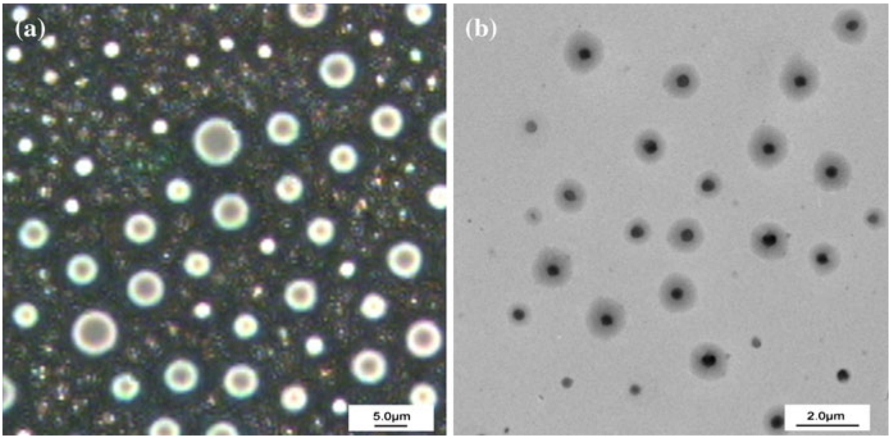

Fig. 9 Micrograph of microcapsules. **a** Video-zoom, **b** TEM

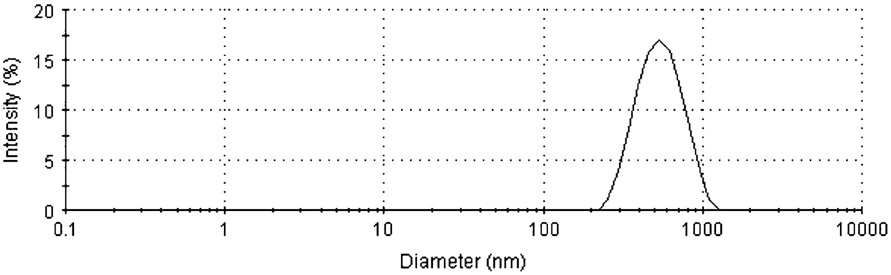

Fig. 10 The size distribution of microcapsules

Morphology and size distribution of microcapsules

Figure 9 displays the VZM (a) and TEM (b) images of the microcapsules fabricated in the condition of OP-10 emulsifier at 1.5 wt%, the core/wall ratio at 1:10, pH at 12 and the reaction temperature at 25 °C. As shown in the figures, the light circle stands for the polyamide wall of microcapsules and the dark section inside represents the core of microcapsules. The sizes of the modified pigment and the microcapsule wall are about 298 and 245 nm, respectively. It is visible that the prepared microcapsules possess small particle sizes, relatively thick shell as well as a regular spherical shape, as seen from Fig. 9b. Figure 10 shows the size distribution of microcapsules. The PDI value is 0.153.

Conclusions

Polyamide microcapsules, which contain pigment phthalocyanine green G modified with octadecylamine and tetrachloroethylene as core materials, were prepared from paraphthaloyl chloride and diethylenetriamine by interfacial polymerization.

The dispersability of phthalocyanine green G modified with octadecylamine was improved by 66.7% at the concentration of octadecylamine of 9 wt%. The amount of OP-10 emulsifier, the core/wall ratio, pH, and reaction temperature all played a vital role in the process of preparing microcapsules. The formed polyamide microcapsules had a small particle size, a regular spherical shape and a high yield of 87.60% in the condition that the weight ratio of core/wall was 1:10 and the pH value was 12.

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References

1. Yu DG, An JH, Bae JY, Jung DJ, Kim S et al (2004) Preparation and characterization of acrylic-based electronic inks by in situ emulsifier-free emulsion polymerization for electrophoretic displays. Chem Mater 16:4693–4698
2. Li WG, Wu G, Chen HZ, Wang M (2009) Preparation and characterization of gelatin/SDS/NaCMC microcapsules with compact wall structure by complex coacervation. Colloids Surf A Physicochem Eng Aspects 333:133–137
3. Kim CA, Kim MK, Joung MJ (2003) Amino resin microcapsules containing polystyrene-coated electrophoretic titanium oxide particle suspension. J Ind Eng Chem 9:674–678
4. Chan YN, Craig GSW, Schrock RR, Cohen RE (1992) Synthesis of palladium and platinum nanoclusters within microphase-separated diblock copolymers. Chem Mater 4:885–894
5. Lee YH, Kim CA, Jang WH, Choi HJ, Jhon MS (2001) Synthesis and electorheological characteristics of microencapsulated polyaniline particles with melamine-formaldehyde resins. Polymer 42:8277–8283
6. Kim K, Sung JH, Lee JY, Song JK, Chin IJ, Choi HJ (2006) Microencapsulation of electrophoretic TiO_2 nanoparticles for electronic ink. Mol Cryst Liq Cryst 445:43–48
7. Kim KS, Lee JY, Bae JY, Park BJ, Sung JH et al (2006) Synthesis and characteristics of microcapsules containing electrophoretic particle suspensions. Colloid Polym Sci 284:813–816
8. Kim CA, Joung MJ, Ahn SD, Kim GH, Kang SY et al (2005) Microcapsules as an electronic ink to fabricate color electrophoretic displays. Synth Met 151:181–185
9. Badila M, Brochon C, Hebrand A, Hadziioannou G (2008) Encapsulation of TiO_2 in poly (4-vinyl pyridine)-based cationic microparticles for electrophoretic inks. Polymer 49:4529–4533
10. Jang IB, Sung JH, Choi HJ, Chin I (2005) Synthesis and characterization of titania coated polystyrene core–shell spheres for electronic ink. Synth Met 152:9–12
11. Park LS, Park JW, Choi HY, Han YS, Kwon Y et al (2006) Fabrication of charged particles for electrophoretic display. Curr Appl Phys 6:644–648
12. Qiao R, Zhang XL, Qiu R, Kang YS (2008) Synthesis of functional microcapsules by in situ polymerization for electrophoretic image display elements. Colloids Surf A: Physicochem Eng Aspects 313–314:347–350
13. Jang IB, Sung JH, Choi HJ (2005) Synthesis of microcapsule containing oil phase via in situ polymerization. J Mater Sci 40:1031–1033
14. Song JK, Kang HC, Kim KS, Chin IJ (2007) Microcapsules by complex coacervation for electronic ink. Mol Cryst Liq Cryst 464:263–269
15. Li G, Feng YQ, Li XG, Gao P, Wang J et al (2007) Preparation and characterization of polyurea microcapsules containing colored electrophoretic responsive fluid. J Mater Sci 42:4838–4844
16. Guo HL, Zhao XP, Wang JP (2005) Synthesis of functional microcapsules containing suspensions responsive to electric fields. Colloid Interface Sci 284:646–651
17. Leclercq S, Harlander KR, Reineccius GA (2009) Formation and characterization of microcapsules by complex coacervation with liquid or solid aroma cores. Flavour Fragr J 24:17–24