Preparation of Gelatin/Alginate Electrophoretic Ink Microcapsules and Electrophoretic Display Prototype

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Abstract

Polystyrene coated TiO_2 particles were prepared by free radical polymerization. Microcapsules containing polystyrene coated TiO_2 and tetrachloroethylene were synthesized via complex coacervation using gelatin and sodium alginate as wall material. The obtained particles and microcapsules were characterized by Contact angle measurement, optical microscope, scanning electron microscopy (SEM) and thermogravimetric analysis, and the results showed the surface behavior of polystyrene/ TiO_2 had been changed to hydrophobic and the wall of microcapsules was compacted and formed from voluble nano-size thread. Electrophoretic display prototype was prepared by coating microcapsules slurry on ITO glass and sealed by UV curable adhesive. The picture was display at a low voltage 3V D.C.

1 Introduction

Electrophoretic displays (EPD), which are one of the most promising display techniques, have attracted a great deal of academic and commercial interests because of the advantages of both electronic displays and conventional paper. They have attributes of flexibility, good contrast ratio, wide-angle view, state bistability, low power consumption. The functioning of EPD is based on the movement of colored pigments inside a colored or transparent liquid when a voltage is applied. Joseph Jacobson first reported a new model of electrophoretic ink, based on microcapsulating the electrophoretic suspension into individual microcapsules [1]. It reduced the unwilling particle movement such as particle clustering and agglomeration on a scale larger than the microcapsule size.

Electrophoretic ink microcapsules can be produced by in-situ polymerization [2-6], interfacial polymerization [7] and complex coacervation [8, 9]. Coacervation has been classified into simple and complex processes depending on the number of participating macromolecules. Veis describes complex coacervation is a two-step process with spontaneous aggregation as a result of interaction of the oppositely charged polyelectrolytes, followed by rearrangement of these aggregates into coacervate phase[10]. Gelatin, zwitterionic macromolecule, is one of the most important wall materials in production of microcapsules. Sodium alginate is linear and anionic polysaccharides, which can interact with positively charged gelatin below the isoelectric point. Both of them are biodegradable, biocompatible and have a natural surface activity. In this study, we adopted complex coacervation technology to prepare gelatin/alginate microcapsules containing tetrachloroethylene and polystyrene coated TiO_2. Furthermore, electrophoretic display prototype was prepared by coating a slurry containing microcapsules on ITO glass and sealed by UV curable adhesive.

2 Experimental

2. 1 Encapsulation of modified TiO2 by polystyrene via free radical polymerization

We followed the procedure reported by Yu Rong to prepare polystyrene coated TiO_2 [10].

5g TiO_2 was dispersed in 150mL ethanol by ultrasonic for 1h, then 3.1g γ–methacryloxypropyltrimethoxysilane (MPS), 6.5g water, 3.4g ammonia (25wt.%) were added. The mixture was under ultrasonic for 1h and stirred at room temperature for 48 hours. Next, filtered and dried.

1.5g TiO_2 modified by MPS was dispersed in 50g ethanol in flask fitted with a condenser, then 4.5g styrene monomer and 0.3g AIBN were added. Polymerization was performed at 70℃ in the nitrogen atmosphere for 24h.

2. 2 Preparation of gelatin/ Alginate microcapsules

30g of tetrachloroethylene dyed by oil red or oil blue was dispersed at 45℃ in 100g of sodium alginate aqueous solution (1wt.%). The equal amount of 1wt.% gelatin aqueous solution at 45℃ was then added into the above solution and adjust pH close to 5.0 with continue stirring. The addition of acetic acid solution induced the complex coacervation for 5h. Next, temperature of the mixture cooled to 5-10℃ slowly with continued vigorous stirring. 25wt.% Glutaraldehyde and 5wt.% $CaCl_2$ solution was added dropwise for crosslinking the microcapsules. The microcapsules were studied in preparation medium without further treatment.

2. 3 preparation of electrophoretic display prototype

Slurry containing electrophoretic ink microcapsules was coated on ITO glass with nearly single layer, then drying for 3h at 80℃, finally sealed by UV curable adhesives.

3 Results and discussion

3. 1 Investigation of polystyrene/ TiO2 by free radical polymerization

Yu Rong reported that dispersion stability of electrophoretic suspension depends not only on the density matching between polymer/pigment particles and solvent, but also on the steric stabilization[11]. TiO_2 is commonly used due to its high refractvity and excellent whiteness. However, the density of TiO_2 (rutile) is 4.26g/cm^3 which much higher than most of solvent. Encapsulation of TiO_2 by polystyrene can reduce the density mismatch between

pigments and solvent. On the other hand, polymer coated TiO_2 prevented the particles depart from electrophoretic suspension to water phase during complex coacervation process.

Contact angle measurement was used to research the change of surface behavior of particles. The contact angle of TiO_2 and Polystyrene/ TiO_2 is 0° and 130.3° respectively. It was demonstrated that the surface behavior of polystyrene/ TiO_2 had been changed to hydrophobic.

3. 2 characterization of gelatin/ alginate microcapsule

3.2.1 Particle size characteristics of gelatin/ Alginate microcapsules

At the beginning of experiment, electrophoretic suspension was separate by mechanical agitation to small droplets. Gelatin and sodium alginate were adsorbed at the O/W surface due to their natural surface activity. The adsorption is not only available for stability of droplets, but also prerequisite for coacervation.

If pigments particles are evenly dispersed in solvent, the average microcapsule diameter is controlled by the agitation rate as shown in Fig.1. When the agitation rate increases, the average diameter descends.

3.2.2 Effect of weight ratio of core to wall materials

As shown in Figure 2, as the weight ratio of core to wall materials increases, the wall thickness of microcapsules descends.

When the ratio is 10:1, microcapsules become spindly due to excess of wall materials. Since microcapsules use to break at the thinnest spot, spherical microcapsules are more stable than spindly microcapsules.

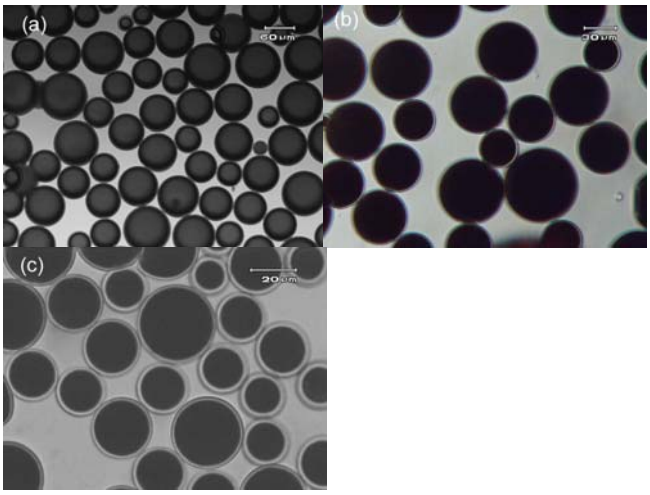

Figure 1 Optical micrographs of microcapsules prepared at different stirring rates (a) 300, (b) 600 and (c) 900rpm

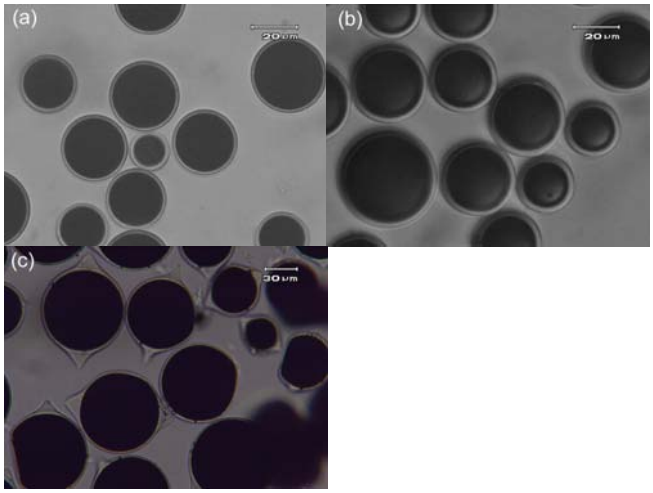

Figure 2 Optical micrographs of microcapsules prepared with different weight ration of core to wall materials (a) 30:1, (b) 20:1 and (c) 10:1

3. 2.3 Surface morphology of gelatin/alginate microcapsule

The surface morphology and microstructure of dried microcapsules have been studied by means of SEM. Figure 3a show the surface of microcapsule is smooth. When the distance between microcapsules was close enough, they usually extrude each other and turn to pentagonal or hexagonal instead of spherical as shown in Figure 3b. It indicates the wall of microcapsules is elastic, which is of advantage to prepare single and compact layer on ITO glass. Fig.3c and 3d depicts cross-section of microcapsule. We can find the wall of microcapsule has compact microstructure, and suggests that the walls are formed from voluble nano-size thread.

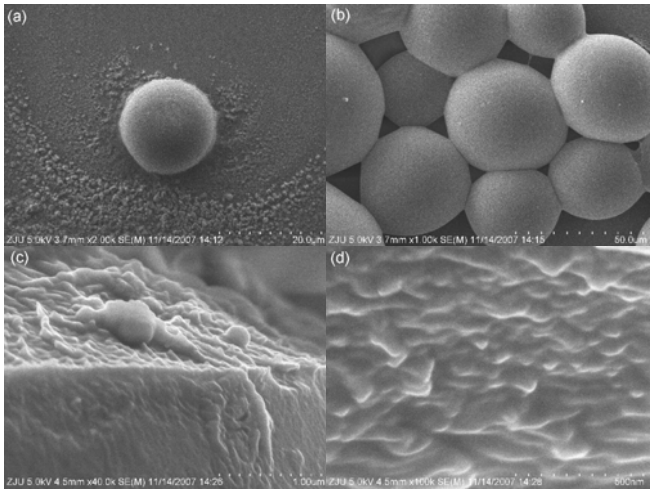

Figure 3 SEM photograph of microcapsules (a)and(b)complete microcapsules (c)and(d)cross-section of microcapsule

3.2.4 Stability of gelatin/alginate microcapsules

Figure 4 shows the changes of gelatin/alginate microcapsules weight as a function of heating temperature. The weight loss of

microcapsules is 9.27% below 215.2℃, which correspond to desorption of small molecules such as H_2O on the surface of microcapsules and a little release of tetrachloroethylene. There is a dramatic weight loss at the range of 215.2-270.1℃, which indicating most of microcapsules were broken and tetrachloroethylene has been released. Since the range of temperature is much higher than the boiling point of tetrachloroethylene (121℃), we can conclude that microcapsules have good thermal property.

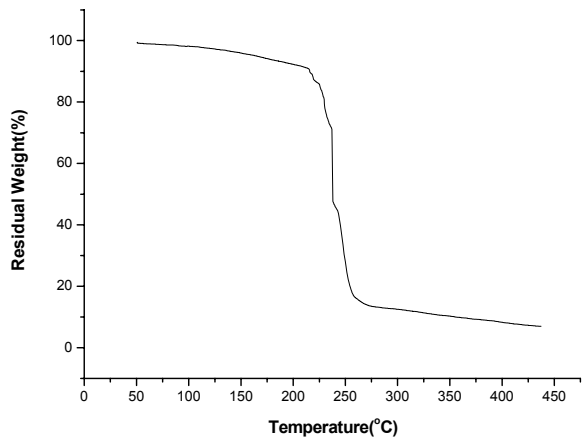

Figure 4 Thermogram of gelatin/alginate microcapsules with tetrachloroethylene as core material

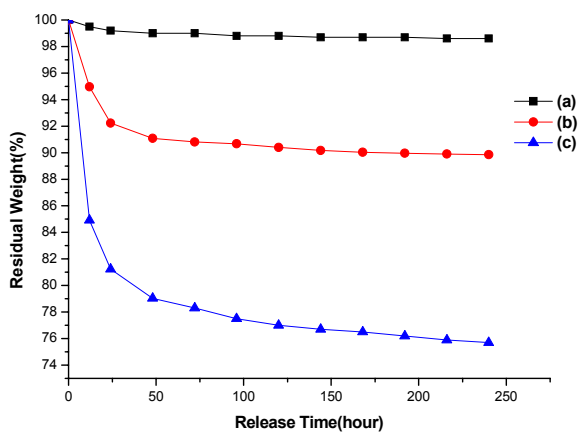

Figure 5 Residual weights (%) of microcapsules after release for 240 hours at (a) 30℃, (b) 60℃ and (c) 90℃

Figure 5 shows the residual weights of microcapsule as a function of release time at different temperature. Microcapsules hardly lose weight at 30℃. The amount of weight lost of microcapsules increases because of temperature elevatation. The majority of weight loss occurred before 48 hours at 60 or 90℃ due to desorption of H_2O on the surface of microcapules and release of tetrachloroethylene. The rate of weight loss become slow after 48 hours.

Furthermore, gelatin/alginate microcapsules, reserved in water for more than one year at room temperature, have the same electrophoretic property as new products.

3.3 Electrophoretic display prototype

Gelatin/alginate microcapsules coated on ITO glass were compactly conterminal each other due to the elastic wall. The phenomenon increased the contrast of prototype and area of display. The picture was displayed at low volt of 3V D.C as shown in Fig 5, which was much lower than displays made by Satoshi Inoue (18V)[12] and arrived at request of commercial use.

Figure 6 The university mark was displayed at low volts (3V) D.C.

4 Conclusions

Polystyrene coated TiO_2 particles were prepared by free radical polymerization. Contact angle measurement showed that the surface behavior of polystyrene/ TiO_2 had been changed to hydrophobic. Gelatin/alginate Microcapsules containing PS/ TiO_2 and tetrachloroethylene were synthesized via complex coacervation. The average microcapsule diameter was controlled by the agitation rate. As the weight ratio of core to wall materials increases, the wall thickness of microcapsules descends. SEM showed the wall of microcapsule has compact microstructure, and suggests that the walls are formed from voluble nano-size thread. Thermogram of gelatin/alginate microcapsules indicates that they have good thermal property.

5 Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant No. 50433020, 50520150165, 50503021, 50773067).

References

[1] Barrett Comiskey, J. D. Albert, Hidekazu Yoshizawa, Joseph Jacobson, An Electrophoretic Ink for All-Printed Reflective Electronic Displays, Nature, 394,253（1998）

[2] Jacobson Joseph, Comiskey Barrett, Albert Jonathan, Microencapsulated Electrophoretic Display, US Patent, 5961804, 1999.10.5
[3] Chul Am Kim, Meyoung Ju Joung, et.al, Microcapsules as An Electronic Ink to Fabricate Color Electrophoretic Displays, Synthetic Metals, 151,181(2005)
[4] K. S. Kim, J. Y. Lee, B. J. Park,et al, Synthesis and Characteristics of Microcapsules Containing Electrophoretic Particle Suspensions, 284, 813(2006)
[5] Huilin Guo, Xiaopeng Zhao, Jianping Wang, Synthesis of Functional Microcapsules Containing Suspensions Responsive to Electric Fields, 284,646(2005)
[6] Jonathan Albert, Barrett Comiskey, Non-spherical Cavity Electrophoretic Displays and Methods and Materials for Making the Same, US0112491A1, 2003
[7] Eiji Nakamura, Hideyuki Kawai, Norihiko Kanae, Hirokazu Yamamoto. Development of Electrophoretic Display Using Microencapsulated Suspension, Proceedings of SID '98 International Symposium, 1014(1998)
[8] Yu Rong, Hong-Zheng Chen, Da-Cheng Wei,Jing-Zhi Sun,Mang Wang, Microcapsules with Compact Membrane Structure from Gelatin and Styrene-Maleic Anhydride Copolymer by Complex Coacervation, Colloids and Surfaces A: Physicochem.Eng. Aspects, 242,17(2004)
[9] A. Veis, C. Aranyi, Phase Separation in Polyelectrolyte Systems. Ⅰ.Complex Coacervates of Gelatin, J. Phys. Chem., 64, 1203(1960)
[10] Yu Rong, Hong-zheng Chen, Han-ying Li, Mang Wang, Encapsulation of titanium dioxide particles by polystyrene via radical polymerization, Colloids and Surfaces A: physicochem. Eng. Aspect, 253,193(2005)
[11] Yu Rong. Preparation of materials for electrophoretic display and electrophoretic display prototype. PhD Paper,79,2005
[12] Satoshi Inoue, Hideyuki Kawai, Sadao Kanbe, et.al. High-Resolution Microencapsulated Electrophoretic Display (EPD) Driven by Poly-Si TFTs with Four-level Grayscale, IEEE Transactions on Electron Devices, 49, 1532(2002)

Author Biography

Weigang Li received his M.D. in chemistry from Southwest University of Science and Technology (2004) and is presently a Ph. D. student in the Organic Semiconductor Laboratory in Zhejiang University. His research focuses on the electrophoretic display.