The preparation of environment friendly gelatin-gum arabic microcapsule for electrophoretic display

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Abstract: The microencapsulated display device is the main choice for electrophoretic display. The application of environment friendly dispersion medium is very critical for the commercialization of this technology. The electrophoretic microcapsules using Isopar L, which is non-toxic, low aromatic concentration and volatilility, as dispersion medium were prepared by complex coacervation between gelatin and acacia. The influence of the weight ratio of capsule material to core material, pH value, dispersion time and rate on the properties of microcapsules was investigated. Optimized technology was defined as follows: the ratio of capsule material to core material is 1:4, the microcapsule wall is cured at pH=8.5 with the temperature of 45 °C, the disperse time and rate was 20 min and 800 rpm, respectively. The particle size and yield of the microcapsule prepared under optimized conditions were 30-60 μm and 83.88%, respectively. The contrast ratio of the electrophoretic display device used the prepared microcapsules was as high as 2.09.

Key Words: Electrophoretic microcapsules; Electrophoretic display; Isopar L; Environmental friendly

1. Introduction

Electrophoretic display (EPD) which bases on the theory of electrophoresis was first introduced by Ota in 1972 [1]. EPD is non-light-emitting display [2-4] and works on the principle that electrophoretic particles with opposite charge dispersed in nonpolar liquid media migrate to the corresponding electrode when an electric filed is applied [5]. Microencapsulated electrophoretic display has attracted much attention due to the combination of the advantages of both electronic display and conventional paper [7], such as wide-viewing angle, flexibility, high contrast ratio, lightweight, portability and low cost [8-13]. The microcapsules encapsulate the electrophoretic suspension containing particles with different color or electric property into individual microcapsule. This technology could overcome many disadvantages during display process, such as the sedimentation of electrophoretic particles, low reflectance and

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transition state (grey state). Currently, it has been commercialized and has achieved mass market success [14].

Nowadays, environmental protection has attracted more and more attention and great effort has been devoted to the exploration of eco-friendly materials. Herein, the development of environmentally friendly materials is one of the key challenges to the further application of EPD. The microcapsules consist of capsule material, electrophoretic particles, dispersion medium, charge control agent (CCA) and dispersant. The halogenated hydrocarbon (tetrachloroethylene [15], polytrifluorochloroethylene, carbon tetrachloride) and epoxide (toluene, naphthaline, et al) [16] have been often used as dispersion medium. However, such reagents are harmful to both human health and environment because of their high volatility and toxicity.

In this work, Isopar L was selected as the desired dispersion medium due to its merits of insulativity, reactionlessness, low volatility and toxicity. The environmental friendly microcapsules were prepared from gelatin and gum arabic, using inorganic materials, that is TiO₂ and carbon black, as white and black pigment, respectively. Innocuity surfactants (T151 and CH-5) were employed as charge control agent and dispersant. Capsule material was prepared from gelatin-gum arabic which are non-toxic water-soluble protein by complex coacervation. The operation parameters such as capsule material/core material ratio, pH value, dispersion time and stirring rate were optimized to obtain microcapsules with high yield and well-distributed particle size.

**2. Experimental**

**2.1 Materials and apparatus**

Gelatin and gum arabic were pharmaceutical grade and purchased from Bai Ling Wei Technology Co., Ltd., China. Carbon black (SB4) purchased from Degussa Co. was dried under 120 °C for 3h before use. Titanium dioxide (TiO₂) was supplied by Beijing Mengtai Youyan technology development center. Isopar L was purchased from Shanghai Huishuo Chemical Co., Ltd China. Glacial acetic acid, sodium dodecyl sulfate (SDS), glutaraldehyde (50%) and sodium carbonate were analytical grade and purchased from Guangfu Chemical Regent Co., Ltd., China. T151 and CH-5 used as charge control agent and dispersant are supplied by Wuxi south oil additive Co., Ltd and Shanghai Sanzheng Co., Ltd., China, respectively. Perfluorobutyl sulfonyl fluoride (HX-8) was purchased from Hubei Hengxin Chemical Co., Ltd., China. A4300 (fatty acid derivatives) was purchased from Tianjin Haiguang Chemical Co.,
The morphology of the microcapsule was observed by BX51 transmission optical microscope (Olympus Corporation, Japan). Contrast ratio of EDP prototype used the prepared microcapsules were measured by Eye-one pro colorimeter (X-Rite, USA). The procedure of coating the microcapsules onto the ITO film was processed by blade coater (home-made).

2.2 Preparation of the microcapsules

2.2.1 Preparation of electrophoretic liquid

Carbon black 0.5 g, hyperdisperant T151 0.1 g and CH-5 0.2 g were dispersed in 10 mL Isopar L as black electrophoretic slurry. Then the black electrophoretic liquid were ball-milled for 36 h at 300 rpm. The white electrophoretic slurry consist of TiO$_2$ (36 g), T151 (1.2 g) and CH-5 (2.4 g) and Isopar L (120 mL) were ball-milled for 48 h at 300 rpm. Then, the black and white electrophoretic slurry were mixed together according to a certain proportion. Furthermore, 1.91 wt.% perfluorobutyl sulfonic fluoride and 0.75 wt.% A4300 served as dispersant and charge control agent were added to the electrophoretic liquid and then the mixture was sonicated for 2 h in a bath sonicator to ensure dispersion.

2.2.2 Preparation of gelatin-gum arabic Microcapsules

Gelatin (2.5 g) and gum acacia (2.5 g) were dissolved in 125 mL deionized water with stirring at 45 °C for 30 min. 15 g of the electrophoretic fluid served as core material was dispersed at 45 °C in gelatin aqueous solution which commixed with 0.1 g SDS. The emulsion was agitated at 800 rpm for 20 min. Gum acacia aqueous solution blended with 0.1 g SDS was added to the above solution at 45 °C. Then the pH value was adjusted to 5.0 with 5 wt.% acetic acid to induce complex coacervation. After cooling to 10 °C with continuous vigorous stirring, 100 mL glutaraldehyde aqueous solution (5 wt.%) was added dropwise to crosslink the microcapsule and the reaction mixture was stirred at 0 °C for 2 h. Afterward, the pH value was regulated to 8.5 using 10 wt.% sodium carbonate aqueous solution. Then the reactant was stirred at 45 °C for 70 min. The microcapsules were washed by deionized water several times, classified into different size by sieve and then collected from the water by filtration.

The yield of the microcapsule (Y) is defined as below:

\[ Y = \frac{W_{\text{capsule}}}{W_{\text{gelatin}} + W_{\text{gum acacia}}} \times 100\% \]

in which $W_{\text{capsule}}$ was the mass of the microcapsule with the diameter in 30-60 μm; $W_{\text{gelatin}}$ and $W_{\text{gum acacia}}$ were the mass of gelatin and gum acacia, respectively.

2.3 Preparation of prototype EPD
Microcapsules with diameter in 30-60 μm were uniformly coated on indium tin oxide (ITO) with 611 (polyurethane) served as adhesive by blade coater. The weight ratio of microcapsule to 611 was 2:1. After drying at room temperature, the microcapsule coating film was pasted onto a patterned electrode coated with anisotropic conductive adhesive. The microcapsule EPD was obtained after employing 1.5 kg/cm² of vertical pressure on it and drying at room temperature for 24 h.

3. Result and discussion

3.1 Preparation of microcapsules

In this paper, Isopar L with low toxicity, low aromatic concentration and volatility was employed as dispersion medium, which permit the prepared microcapsules is environmental friendly while suffering no yield penalty.

For the EPD, preferable display image will be obtained when the microcapsule size in 30-60 μm [17]. In order to improve the yield of microcapsule with diameter in 30-60 μm, the ratio of capsule material (gelatin + gum acacia) to core material (electrophoretic fluid) was studied.

![Image](image_url)

**Fig. 1** Effect of the ratio of core material to capsule material on the particle size (a) and yield (b) of microcapsules.

Fig. 1 (a) represents the effect of capsule material/core material ratio on microcapsule size. The particle size of microcapsules decreases and then increases with the increase of core material. When the ratio is 1:3 and 1:4, the particle size of microcapsule is mainly in the range of 30-60 μm. Especially, the standard deviation reaches the local minimum at the ratio of 1:4. More capsule material could deposit on the interface of core material as less core material used, which lead to the increase of microcapsule size. While if the core material is too much, the microcapsules diameter also increases because the core material in the capsule was more. The yield of the microcapsule increases as the capsule material/core material ratio changes from 1:1 to
1:5, as shown in Fig. 1 (b).

Fig. 2 shows the contrast ratio of the prototype EPD used microcapsules prepared at different capsule material/core material ratio. It is found that the highest point reached when the core material is 1:4.

![Graph showing contrast ratio vs. core material/capsule material ratio]

Fig. 2 Effect of the ratio of core material/capsule material on the contrast ration of prototype EPD.

Fig. 3 represents the morphology of the microcapsules prepared at different stirring rate. It shows that the microcapsules possess the uniform particle size and little fragments when prepared at 700 and 800 rpm.

![Optical microscopy images of microcapsules prepared with different stirring rates]

Fig. 3 Optical microscopy images of microcapsules prepared with the stirring rate of (A) 600 rpm, (B) 700 rpm, (C) 800 rpm and (D) 900 rpm.
As shown in Fig. 4, the particle size was mainly in the range of 30-60 μm when the stirring rate was 700 and 800 rpm. Big particle size of the microcapsules at low stirring rate can be attributed to the weaker shear force between agitator blade and microcapsules, and vice versa. At the stirring rate of 800 rpm, the standard deviation is as small as 27.14 μm and the yield is up to 83.40%.

![Graph 4](image4.png)

**Fig. 4** Effect of stirring rate on the particle size (a) and yield (b) of microcapsules.

The size of microcapsules mainly distributes in 30-60 μm when the dispersion time is 20 min, as shown in Fig. 5. The particle size of microcapsules is oversize for short dispersion time, which could be ascribed to that the microcapsules do not be dispersed adequately by the shear force, and vice versa.

![Graph 5](image5.png)

**Fig. 5** Effect of dispersion time on the particle size (a) and yield (b) of microcapsules.

According to the reaction process, as shown in equation (2) [17], the capsule wall of microcapsule is cured by the crosslinking between formyl group of glutaraldehyde and amino group of gelatin. The curing process will not complete until the formation of network polymer [18].
Fig. 6 indicates that when the pH is 8.5, the yield of the microcapsule is as high as 83.88%. Low yield at low pH could be due to the fact that some amino groups of gelatin still exist as $-\text{NH}_3^+$ and hence cannot crosslink with formyl group. While parts of gelatin will deteriorate if the pH is too high, this is responsible for the low yield of the microcapsules.

Fig. 7 represents the optical microscopy images of the microcapsules prepared under the optimized condition discussed above. It is clearly found the microcapsules show smooth surface, plump granule, uniform particle size distribution and no adhesion.

3.2 Preparation of EPD device prototype

Fig. 7 represents the optical microscopy images of the microcapsules prepared under the optimized condition discussed above. It is clearly found the microcapsules show smooth surface, plump granule, uniform particle size distribution and no adhesion.
Fig. 7 Optical microscopy images of microcapsules prepared under the optimum technology.

Fig. 8 is a clock display prototype exhibiting the black patterns with white background (a) and white patterns with black background (b). The prototype is driven by direct current (DC) with 5V. It is found that the image shown by the display is clear and can change with the time.

4. Conclusion

Smooth, plump and uniform microcapsules with Isopar L which is environmental friendly as dispersion medium, selecting gelatin-gum acacia as capsule wall were prepared by complex coacervation technique. It is observed that the capsule
material/core material ratio, dispersion time, stirring rate and curing pH deeply affect the particle size distribution and yield of the microcapsules. The highest yield and uniform particle size distribution is obtained under the optimized technology: the ratio of capsule material to core material is 1:4; the disperse time and stirring rate was 20 min and 800 rpm, respectively; the microcapsules wall is cured at pH=8.5 with the temperature of 45 °C. The clock display panel prototype prepared by the prepared microcapsules can display clear image when operated under 5V DC.

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References


