Preparation and characterization of polyurea microcapsules containing colored electrophoretic responsive fluid

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Abstract A kind of yellow–red microencapsulated electronic ink was prepared by interfacial polymerization. The shell of the polyurea (PU) microcapsules was fabricated from tolyene 2,4-diisocyanate (TDI) and triethylene tetraamine (TETA). Pigment Hansa Yellow 10G, as negatively charged electrophoretic particles, was homodispersed in tetrachloroethylene (TCE)/cyclohexane mixture to make the suspending fluid core. And Oil Red was also added in the core to make a red background. Emulsifiers influencing the dispersing process were experimentally investigated. PU microcapsules were characterized on structure, mean particle size and size distribution, morphology with FT-IR, ESEM and image analyzer. The prepared microcapsules were regular, transparent, smooth and optically clear, and had a wall thickness of around 1.5 μm and an excellent sealing property. The electric response behaviors of the electronic ink were studied under electrostatic field. The yellow particles moved quickly and reversibly inside the microcapsules while the electric field alternated, with a response time of 150 ms approximately at $E = 30$ V/mm.

Introduction

Recently, electronic paper have been the subject of intense research and development for applications in creating a flexible low-cost paper-like display, which involved a twisting ball display [1], a cholesteric liquid crystal display [2], elecrowetting display [3], and electronic ink display [4–6]. Electronic ink displays, also known as electrophoretic displays, are fully reflective type display devices, which utilize electrophoretic phenomena of charged pigment particles dispersed in a colored solvent. Compared with the conventional liquid crystal displays (LCDs) [7], electrophoretic displays have attributes of good brightness and contrast, wide viewing angles, state bistability, and extremely low power consumption.

The early research mainly focused on unencapsulated displays [8], in which, the electrophoretic medium is present as a bulk liquid, typically in the form of a flat film of the liquid present between two parallel spaced electrodes. Such unencapsulated displays typically have problems with their long-term image quality. For example, particles that make up such electrophoretic displays tend to agglomerate, settle, drift laterally, resulting in inadequate service-life for these displays. This could be properly eliminated by confining the particle-containing fluid within the walls of a large number of small capsules, namely an encapsulated display [4], which provides further advantages. The pioneering research into electronic ink and the technology that powers it was conducted at the MIT Media Lab. Barrett Comiskey and his coworkers prepared a kind of encapsulated electronic ink with inorganic pigments [4]. Although the inorganic pigments have a pure color and high reflectivity, their specific gravity is also too high to match the dispersion media and have to be modified by polymers to reduce the specific gravity of the particles and present a modified surface chemistry for charging purposes. Thereafter in 2004, the world's

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first black–white electronic paper display was commercialized by E Ink Corporation, Philips, and Sony, but full-color electronic ink display is still on horizon.

Whereas the development of organic electrophoretic particles, made it possible to produce full-color electronic ink displays based on superimposing the cyan-magenta-yellow (CMY) layers, due to their low-specific gravity, bright color, and easiness of being charged. Tom Bert et al. elaborated the charging property of organic pigment particles, and elaborated the electrical properties of pigment particles in electrophoretic display [9, 10]. Dong-Guk Yu et al. fabricated a kind of acrylic-based electronic ink particles containing oil blue N and charge control additives [11], which had a high electrophoretic mobility. Therefore in this paper, we chose Pigment Hansa Yellow 10G as electrophoretic particles, for its bright tone, low-specific gravity, and good affinity for solvent. On the other hand, the yellow pigments were microencapsulated by interfacial polymerization of polyurea instead of by in situ polycondensation of urea formaldehyde (UF) [4]. This is because PU microcapsule offer better morphology over UF and require lower time for fabrication, usually at room temperature, which is protective to heat sensitive electrophoretic suspension systems. The prepared yellow electronic ink is a vital step towards our full-color microencapsulated electronic ink.

Experimental

Materials

Tolyene 2,4-diisocyanate (TDI) and triethylene tetra-amine (TETA) as wall materials, polyoxyethylene sorbitan monooleate (Tween 80), polyoxyethylene octylphenyl ether (OP-10) and sodium dodecyl sulfate (SDS) as emulsifiers, were obtained from Kewei Chemicals (Tianjin, China), without any further purification. Polyvinylpyrrolidone (PVP, M_w = 30,000) as protective colloid and didecyl dimethyl ammonium chloride (BTC 1010) and sorbitan monooleate (Span 80) as charge control agent were purchased from North Chemical Supplies (China). Pigment Hansa Yellow 10G (C. I. Pigment Yellow 3, PY 3) and Oil Red 301 were obtained from Hoechst (Germany), as electrophoretic particles. All the chemicals, including tetrachloroethylene (TCE) used in this study were a reagent grade.

Pretreatment of particles and preparation of electrophoretic suspension

About 0.05 g BTC 1010 and 0.08 g Oil Red 301 was dissolved in 20 mL TCE/cyclohexane (4:1 [wt/wt], specific gravity = 1.59, 20 °C) in a 100 mL beaker, and then 0.1 g PY 3 powders (specific gravity = 1.59, 20 °C, approximately 1.3 μm in diameter) were added into the beaker with moderate stirring. The mixture was sonicated for 30 min in ultrasonic bath to obtain electrophoretic suspension.

Microencapsulation

Interfacial polymerization method was applied to prepare the microcapsules in this paper. Firstly, 150 mL aqueous solution containing 0.25 wt.% PVP as a protective colloid was added into a 250 mL flask with a PTFE-bladed paddle stirrer. Then 0.002 M TDI was dispersed into 4 mL electrophoretic suspension to obtain internal phase, which was introduced into the reactor. Subsequently, the mixed solution was mechanically emulsified to yield an o/w emulsion by stirring with emulsifier at 20 °C. After stirring for 120 s, 10 mL 0.02 M TETA aqueous solution was added into the emulsion to initiate the interfacial polycondensation reaction between TDI and TETA at the oil–water interface and accordingly droplets of electrophoretic suspension were encapsulated to form the microcapsules. The stirring rate was reduced to 300 rpm after 3 min reaction, and kept for another 10 min. Then the microcapsules were separated from the aqueous phase and rinsed with distilled water to a pH of 7.0.

Characterization

The surface functional groups of the core materials and the microcapsules were obtained with a FT-IR (BIO-RAD3000, scan 400–4,000 cm^{-1}) spectrophotometer. Particle size, particle size distribution, and morphology of the microcapsules were observed using an image analyzer (53-XC Shanghai Forever, China) with CCD (Panasonic, Japan). The morphologies and wall thickness of microcapsules were also measured using an environmental scanning electron microscope (ESEM, XC-30 TMP, Philips) after Au coating with ion sputtering for 180 s.

Electrophoresis test

Microcapsules containing yellow electrophoretic suspension were placed between two parallel copper electrodes with 2 mm apart with 50 wt.% PVP aqueous solution as adhesive. The electrophoretic property was measured with the above image analyzer under direct current (DC) and square wave alternating current (AC) electric field repectively.

Results and discussion

FT-IR spectra of microcapsules

Figure 1 illustrates the FT-IR spectra of tetrachloroethylene as main core material and PU microcapsules of yellow electronic ink. Strong band of N–H stretching vibration at 3,302 cm^{-1}, and C=O stretching vibration at 1,645 cm^{-1}, C–N stretching vibration combined with N-H bond at 1,544 and 1,224 cm^{-1} are observed. The absorption peak at 1,600 cm^{-1} is shown as the N–H bonded with benzene ring. It is known from the literature [12], that signal bonded N–H groups appears at 3,300~3,380 cm^{-1} whereas the free groups at 3,447 ~ 3,600 cm^{-1}. And the hydrogen bond lead to the migration of C=O from normal 1,660 cm^{-1} to present 1,645 cm^{-1}. As one can see, in spectra (b) all the N–H groups appear nearly completely hydrogen bonded, due to the interaction of hydrogen atoms of N–H groups and the carbonyl groups of urea segment. Figure 2 is a schematic model of the hydrogen bonded PU structure, and every carbonyl group is supposed to interact with two N–H groups.

Spectra (b) also contains an absorption band at 2,275 cm^{-1}, which is assigned to an isocyanate group, this may because of the excess of TDI the wall-forming monomer. While the specific absorption of bands of tetrachloroethylene is not observed in spectra (b). So it is clearly found that PU microcapsules were formed and the internal phase was sealed into the microcapsule.

Effect of surfactant in electrophoretic suspension

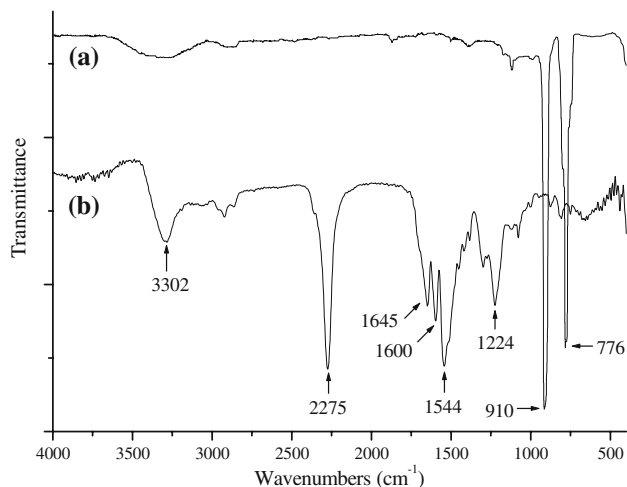All through the process of the preparation of electronic ink, dispersibility of particles is one of the key parameters. It is found that the majority of PY 3 particles agglomerated in the absence of oil-soluble surfactant which led to incomplete electrophoretic response. In our system Span 80 and BTC 1010 were applied respectively. Both exhibited excellent effect on improving the stability and dispersibility of the suspension fluid. However, considering the possible cross-linking reaction between Span 80 and TDI as it happens in making polyurethane, BTC 1010 was chosen. This was proved by experiment result that the introduction of TDI into the suspension with Span 80 caused a noticeable bridging flocculation. On the contrary, BTC 1010 provided the PY 3 particles with good dispersibility and excellent electrophoretic mobility, because it also acted an excellent charge control additive which is another key parameter.

Effect of emulsifier in microencapsulation

The strength of the interfacial membrane is the main factor affecting the characteristic of the interfacial polymerization. Normally introducing certain surfactant can reduce the interfacial tension. Meanwhile a protective membrane will form at the interface between oil and water, and thus improving stability of emulsion system [13]. In this paper, three emulsifiers including Tween 80, OP-10 and SDS were added into the water phase at the concentration of 0.0192 M, 0.0261 M, and 0.0120 M respectively, to improve the dispersion of the oil phase in the water phase and control the wall-forming process. Figure 3 shows the microcapsules prepared by different emulsifiers using an image analyzer, in which PY 3 was not added in order to make a clear morphology. In Tween 80, the surface of the capsules is wrinkled and rough (Fig. 3a) due to polymeric cross-linkages between TDI and the surfactant, similar to the case of Span 80. Consequently the protective membrane is damaged partially and therefore the interfacial tension becomes nonuniform across the interface between the oil droplets and the water phase, leading to the forming of defected microcapsules. In SDS, flocculation and cluster are observed and no

Fig. 1 FT-IR spectra of (a) tetrachloroethylene, and (b) PU microcapsules
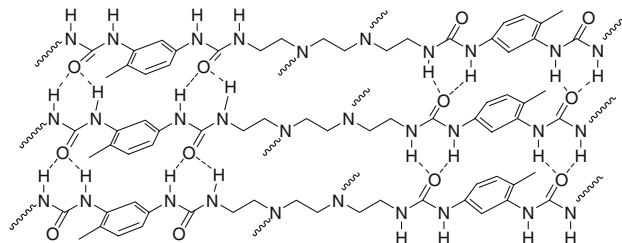

Fig. 2 A schematic model of the hydrogen bonded PU structure

microcapsule forms. This is because the water-soluble anionic surfactant SDS and the oil-soluble cationic surfactant BTC 1010 (as charge control agent) has a strong electrostatic interaction on the interface between oil droplets and water phase based on opposite charges. As a result the emulsion effect of the emulsifier is inhibited and the interface is destroyed. In OP-10, microcapsules are regular, transparent, smooth and clear (Fig. 3b). So in this study, Op-10 seems adequate for the preparation of PU microcapsules with regard to the morphology of the capsules.

Morphologies of OP-10 concentration on microcapsules

Figure 4 shows the particle size distribution of microcapsules at different OP-10 contents, i.e., 0.00033, 0.00130, 0.00261, 0.01042 M, at 800 rpm. As we can see, on one hand, the particle sizes are getting smaller with increasing emulsifier content, and the particle size
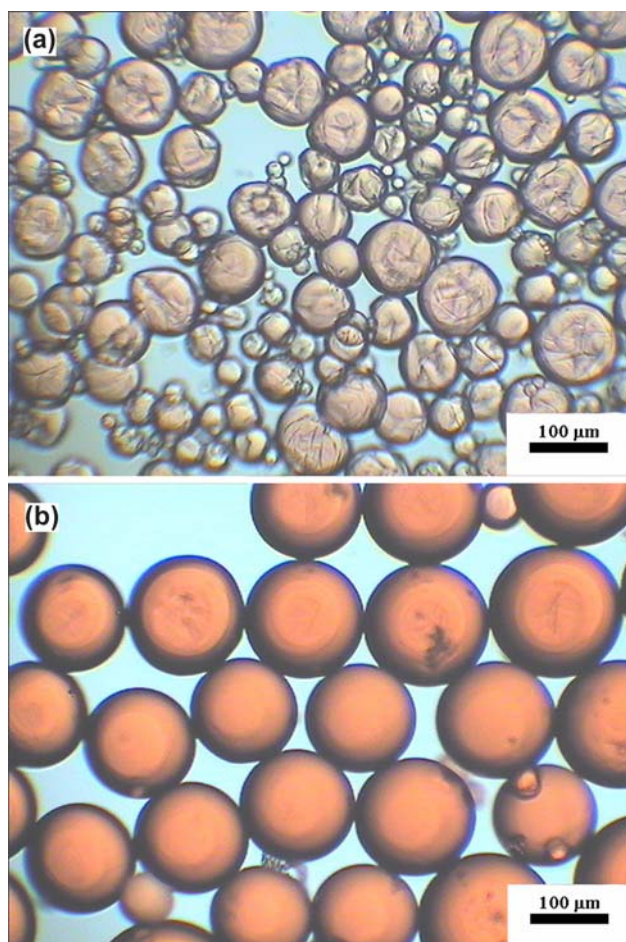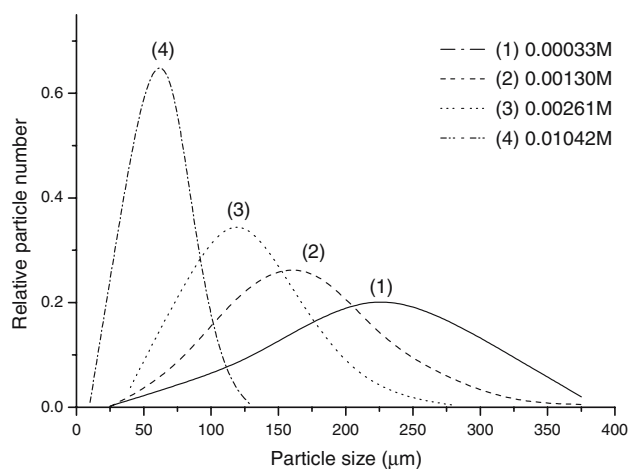

Fig. 4 The particle size distribution of microcapsules at different OP-10 contents

distribution becomes narrower. On the other hand, the morphology of microcapsules is getting worse and flocculation is detected gradually with increasing emulsifier content. It is supposed that during the wall-forming process, polymer segments form and condense at the interface between oil droplets and water phase, thus replacing the original protecting membrane competitively. With the increase of content of OP-10, the interfacial adsorption of the emulsifier becomes stronger and it's getting more difficult for the replacement of the protecting membrane during the polymerization step. As a result, coalescence will occur, leading to irregularity and flocculation of the microcapsules. In this study, it was found that the optimum concentration of OP-10 was 0.00261 M, and the attachment of the pigment particles onto capsule wall was also eliminated with the increase of OP-10 content.

The effect of stirring condition on microcapsules

Figure 5 shows the particle size distribution of the prepared PU microcapsules containing electrophoretic suspension at different stirring rates in the emulsion. i.e., 600, 800, 1,000, 1,200 rpm. The particle size distribution becomes narrower and the average particle size becomes smaller with increasing stirring rate, due to the increase of shearing force. Slight agglomeration of the microcapsules is also observed at a stirring rate above 1,000 rpm, because the increasing specific surface of the capsules weakened the stability of the system. Therefore the stirring rate of 800 rpm is adequate for this work. In this study, a stirring time of 120 s was taken as sufficient in emulsion process according to literature [14].
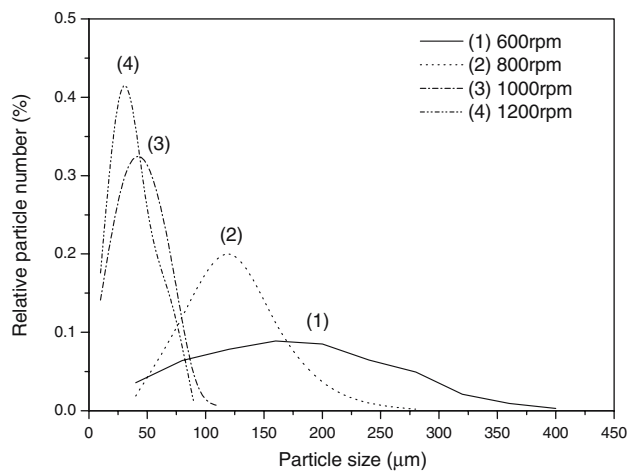

Fig. 3 Micrograph of microcapsules prepared from systems with different emulsifiers: (**a**) Tween 80; (**b**) OP-10

Fig. 5 The particle size distribution of microcapsules at different stirring rates

The morphologies and configuration of microcapsules

ESEM photographs of morphologies of the microcapsules are shown in Fig. 6a, b. As shown in the figure, the microcapsules have a very regular shape, and the wall is characterized by a smooth and dense outer surface, and a rough and cellular inner surface. Figure 6c, d show the micrographs of the microcapsules under an optical microscope with an image analyzer. As we can see from the figure, pigment particles are well-dispersed in TCE/cyclohexane inside the microcapsule (Fig. 6c) and the microcapsules are optically clear. The cross section graph (Fig. 6d) clearly illustrates that the wall of the

capsule is regular, clean and uniform in thickness. Furthermore, we can see both from Fig. 6b and d that the wall thickness of the PU microcapsules is around 1.5 μm, and it gives an excellent sealing property, for no leakage of inner phase was observed whether the capsules were wet or dry.

The electric response behavior of electronic ink

The response behavior of the microencapsulated electronic ink was investigated under a DC electric field first. As shown in Fig. 7a, the pigment particles were dispersed uniformly in the capsules under no electric field. When the field was applied at $E = 30$ V/mm, the pigment particles migrated to the electropositive side of the microcapsules (Fig. 7b), by the electroosmotic and electrophoretic forces [15]. This indicates that the particles were negatively charged. When the direction of the field was reversed, the particles were pulled back to the opposite side of the capsules (Fig. 7c). The response time was 150 ms approximately. The switching behavior was not so symmetric, probably due to deformation of electric field around microcapsules and interreaction of particles in adjacent capsules. If the applied voltage is removed, the yellow particles will remain at the position where they have been moved to. Actually such a stationary state kept for hours, for dispersion of the particles mainly depends on Brownian motion which was quite slow. This means the microencapsulated electronic ink has a property of bistability.

Fig. 6 Micrographs of the microcapsules: (**a**) outer surface (1,000×), and (**b**) cross section (10,000×) by ESEM; (**c**) profile in reflective mode (100×), and (d) cross section (1,000×) by image analyzer in transmissive mode
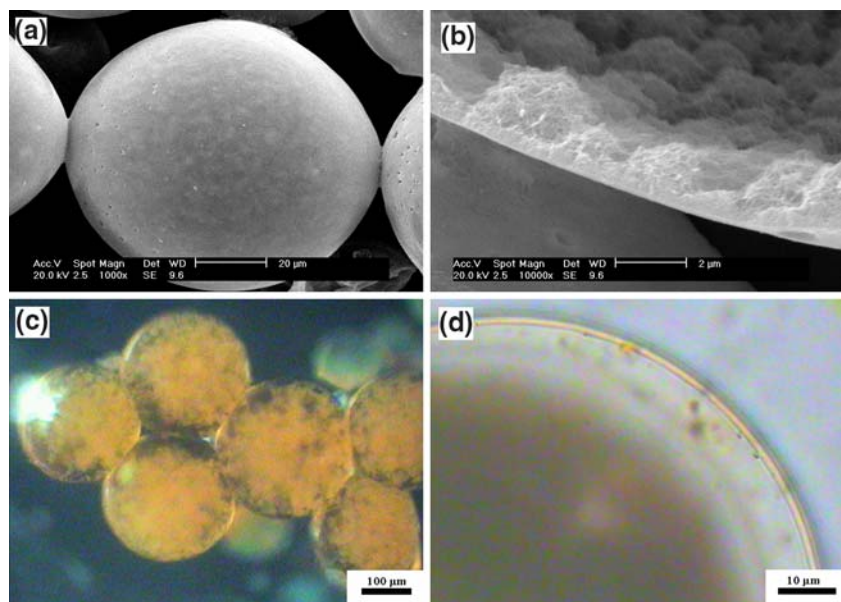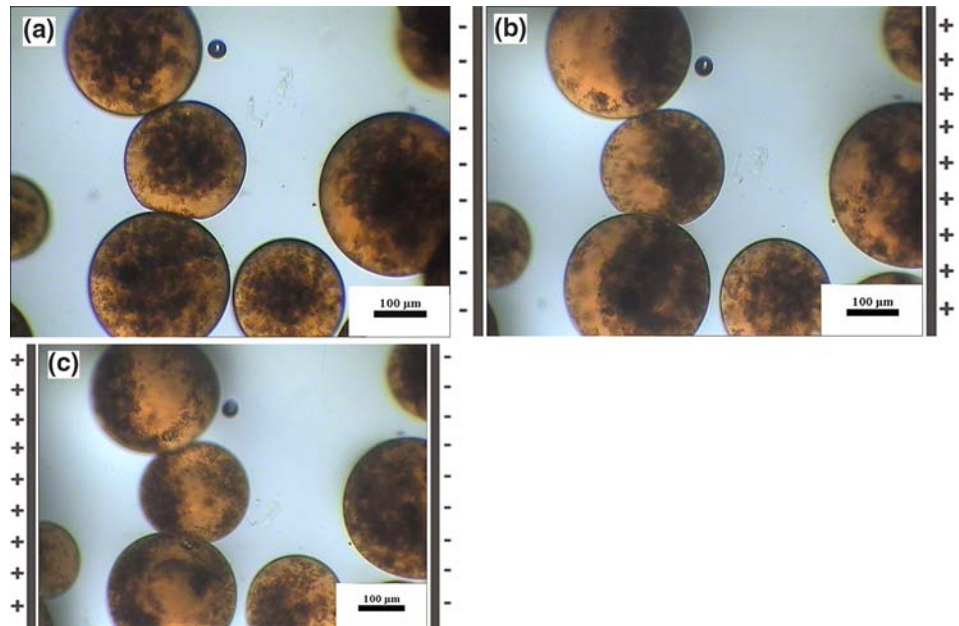
Fig. 7 Microcapsules under the electric field, in transmissive mode (100×): (**a**) $E = 0$; (**b**) $E = 30$ V/mm; (**c**) $E = –30$ V/mm

By applying a block wave AC electric field at frequency of 1 Hz, the electrophoretic particles moved back and forth inside the microcapsule. The electrophoretic motion of the particles is generally considered as laminar flow [4]. The electrical force on the particle is instantaneous and proportional to the applied field [10]. By applying the Stoke's law, the electrical force equates with the frictional resistance of the medium [16]. Therefore particles move at constant velocity during every single trip as illustrated in Fig. 8. The particles migrated from position A (in accordance to Fig. 7a) to position B (in accordance to Fig. 7b) and kept stationary to position D in the first half of the cycle, even though the electric field was removed in the course of C → D. When direction of the field inverted, the particles moved back to position E (in accordance to Fig. 7c) and remained still. Therein, the time of first trip (A → B) was much shorter than the actual response time (D → E) of 150 ms, because particles migrated only half the width of the capsules.

It was also found that under a stronger DC field ($E > 50$ V/mm), pigment particles swirled inside the capsules, and even solid agglomeration of pigment formed which could not be re-dispersed by any means, possibly due to over-compaction of particles.

Conclusions

In this work, polyurea microcapsules containing yellow pigment particles uniformly dispersed in red TCE/cyclohexane were successfully prepared as a kind of electronic ink by interfacial polymerization from TDI and TETA. BTC 1010 was applied as oil phase surfactant and charge control additive. The OP-10 emulsifier seemed to be adequate for the preparation of polyurea microcapsules, and the optimum concentration was 0.00261 M at 800 rpm. The prepared microcapsules were regular, transparent, smooth and optically clear, and had a wall thickness of around 1.5 μm and an excellent sealing property. The pigment particles were negatively charged, and could move reversibly at a constant velocity in the capsules under a block wave AC field ($E = \pm30$ V/mm), with a response time of about 150 ms. Therefore, it could be applied to pigment-in-dye type electronic ink.
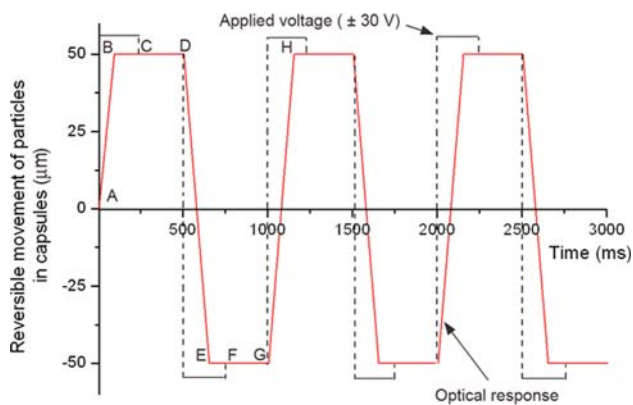

Fig. 8 Schematic presentation of optical response of particles in a typical microcapsule of approximately 100 μm in diameter, under a block wave AC electric field with $E = \pm30$ V/mm and at frequency of 1 Hz

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