Fabrication and charge properties of polymer particles for electrophoretic display

Ming Wang, Sakiko Nakamura, Nobukazu Miyagawa and Takashi Kitamura; Information and Image Sciences Department, Graduate School of Advanced Integration Science, Chiba University; 1-33 Yayoicho, inage-ku, Chiba 263-8522, Japan

Abstract

In recent years, Electrophoretic Image Displays (EPIDs) have been the subject of intense research and development due to the promising solution in the search for low-power, high contrast paper like reflective displays. Mature EPIDs system usually bases on the electrophoresis of charged particles in suspending fluid. But the problems of EPIDs display, especially particles sedimentation, make their widely usage limited.. Using polymer particles whose specific density is low as charged particles can solve this problem to a certain extent. In this paper, the fabrication of several kind of pigment involved styrene-acryl co-polymer particle for EPIDs by dry in liquid method was reported. The influence of stirring speed on particles diameter distribution was studied. The surface properties of different pigment and surfactant involved co-polymer particles were investigated by SEM and the size distribution. At last the charge properties of particles in suspending fluid were tested by Zeta Sizer.

Introduction

It has long been the ambition of display technology researchers to create the electronic paper which possesses not only traditional paper-like high contrast appearance but also the function of being able to be rewritten, low power consumption, flexibility and portability^[1]. The first e-paper product "Librie" from SONY corp. was introduced in 2004, and after that many prototypes and products have been followed published yet and the e-paper technologies have been evolved diversely. There are several categories now, such as Twisting ball display, Electrophoretic image display(EPID), Toner Display, liquid powder display (LPD), flexible LCD display^[2], Electrowetting display, Electrochromic display, MEMS and etc^[3,5].

The electrophoretic image display technology is reflective display technology which requires no backlight and is viewable under a wide range of lighting conditions, including direct sunlight, and requires no power to maintain an image. This kind of technology enabled by electrophoretic media that consist of charged particles, surfactant and dispersant liquid. As the electrically charged particle, TiO2 and carbon black pigment are commonly used due to their excellent whiteness and blackness. Surfactant provides the pigment with a charge and also improves the dispersion stability of the mixture. Dispersant liquid usually is transparent or colored dielectric medium. The function of display based on the movement of charged particles inside the colored or transparent liquid under the influence of applied electrical field. The mixture was placed between two transparent electrodes which are separated by a spacer and the image is formed or changed when the charged particles move towards the electrode closest to the observer or opposite by applied different voltage between two electrodes.

Experimental

2.1 The relationship between stirring speed and particles size

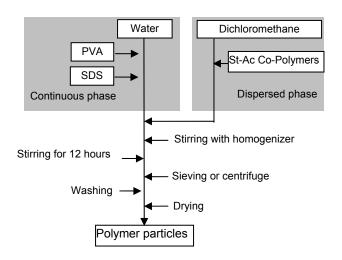


Figure 1. Process of drying in liquid method

Fig.1 shows the process of co-polymer particles fabrication by drying in liquid process. First, co-polymers was dissolved into dichloromethane as dispersed phase (in this stage the pigment and surfactant can be added in) and poly-vinyl alcohol (PVA) and sodium dodecyl sulfate (SDS) were dissolved in distilled water as continuous phase. Emulsion was prepared by mixing and stirring dispersion phase in continuous phase by homogenizer. And then, dichloromethane was vaporized in emulsion. Finally, the polymer particles were prepared by centrifuge and dry [4].

However, the most important factor for this system is that the pigment particles have a problem with suspension stability due to their high density. Thereby improvement of the dispersion stability of charged particles has been investigated by many researchers and most of the improved technology is about polymer coating process. However we tried to find a way to fabricate pigment involved polymer particles with low specific density.

In the paper, the preparation of styrene acryl co-polymer with different pigment and surfactant by dry in liquid method was investigated. It have been verified that by this method we can fabricate polymer particles which has size distribution from several micro-meters to hundreds of nano-meters. And after adding some different surfactants and pigment in the particles, their

surface properties and charge properties were studied by SEM and Zetasizer.

2.2 Characterization

The size distribution of co-polymer particles with different emulsifying stirring speed were determined by Zetasizer3000 (Malvern Instrument Ltd).

In order to fabricate color and chargeable particles, three different pigments and surfactant Solsperse17000 were added in dispersed phase before emulsion stage. The pigments are Carbon black pigment and 2-ethylhexyl methacrylate coated carbon black and magenta pigment. The surface shape and charge property of pigment and surfactant involved particles were measured by SEM and Zetasizer.

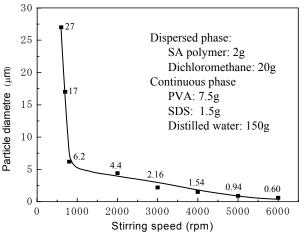


Figure.2 Relationship between particle size and stirring speed.

Result and discussion

3.1 The relationship between stirring speed and particles size

As shown in Fig.2, by drying in liquid method, the copolymer particles with average diameter from several micrometers to hundreds of nanometers could be fabricated by changing the stirring speed in emulsion stage. However, the air bubble will form in the emulsion if the stirring speed is increased beyond 6000rmp, and it had bad effect on fabricate particles with average diameter distribution. Co-polymer particles which have size distribution less than 500nm can be made by adding other surfactants in the system. In our lab, polymer particles with 350nm diameter were synthesized by adding Solsperse17000 in dispersed phase.

3.2 The surface characters of pigment involved polymer particles

The PMMA-PS co-polymer used in this paper is highly transparent material which usually used in making windows, paints and toner. It is transparent enough to have a color view of the

internal pigment. So the color particles can be made by embedding pigment in it.

Fig.3 represents the SEM image of different co-polymer particles:

- (a) The co-polymer particles without any pigment and surfactant in it. Particles have spherical shapes, smooth surface and average size distribution from 1 μ m to 3 μ m (emulsion stirring speed was 3000rpm).
- (b)The co-polymer particles with carbon black pigment were observed to be great different with (a), many carbon black pigments whose size were about 200nm are absorbed or half embedded on surface of the co-polymer particles. And from the background many dispersed carbon black can be seen.

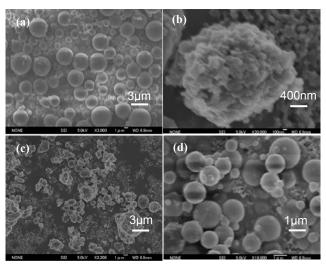


Figure.3 SEM image of (a) co-polymer particles, (b)co-polymer particles with carbon black pigment, (c)co-polymer particles with magenta pigment, (d)co-polymer particles with polymer coated carbon black pigment and surfactant solsperse17000

- (c)The co-polymer particles with magenta pigment. The particles exhibited a somewhat irregular morphology and potato shape. The particles diameters are various due to the bad affinity between pigment and polymer.
- (d) The co-polymer particles with polymer coated carbon black pigment and surfactant solsperse17000. Most of the pigments were embedded into co-polymer so that the particles shapes keep smooth and spherical ^[6,7].

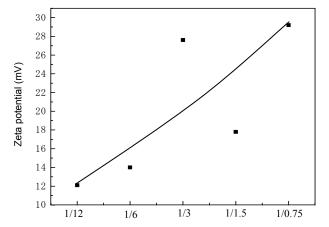
3.3 Surface charge property of co-polymer particles with surfactant

For the application of co-polymer particles in EPID system, there are two important problems should be solved: color and surface charge property of the particle. The former one can be handled by adding pigment in. at the same time, we supposed that the later one also can be solved by adding surfactant into particles.

Fig.4 shows the surfactant dependence of the zeta potentials of co-polymer particle which have polymer coated carbon black pigment in it. The dispersant liquid is Isopar G with CCA. From sample 1 to 5 the surfactant

solsperse17000: polymer coated carbon black pigment in dispersed phase are 1:12, 1:6, 1:3, 1:1.5, 1: 0.75 in weight.

Fig.4 exhibits that with the increasing of surfactant in dispersed phase, the zeta potential of final particles firstly increase and then declined, at last increase to about positive 30mV. This kind of particle shows stable dispersion in dielectric medium because of smooth surface and charging state.



The proportion of surfactant to pigment Figure.4 The surfactant dependence of the zeta potentials of polymer coated carbon black involved co-polymer particles, from left to right, the proportion of surfactant solsperse 17000 to polymer coated carbon black pigment in dispersed phase are 1:12, 1:6, 1:3, 1:1.5, 1: 0.75 in weight.

The PS-PMMA co-polymer itself can not be charged in dispersant liquid. However the polymer coated carbon black is chargeable in dispersant liquid. As show in Fig.5, after the pigment and surfactant were added in dispersed phase before emulsion stage, some of the pigment will half embed on the surface of final co-polymer particle. And the particle was charged by bonding with surfactant. With the increasing of surfactant added in, more and more pigment will get to interior of polymer. On the other hand, the charge of individual pigment will increase. So the surfactant dependence of particle's zeta potential shows us such a curve in Fig.4 [8].

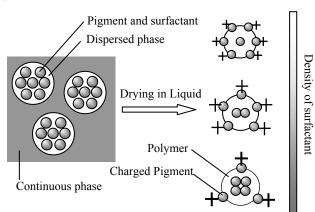


Figure.5 Co-polymer particle charge mechanism

Conclusion

The pigment involved chargeable PS-PMMA co-polymer particles which were used for EPID were successfully prepared. The particle size can be easily changed from several micro-meters to hundreds of nanometers only by adjusting stirring speed in emulsion stage. In addition, the surface properties and charge properties of pigment and surfactant involved co-polymer also been investigated. With polymer coated carbon black pigment and surfactant17000 adding in dispersed phase, the final co-polymer particles can be charge to about 30mV and show stable dispersion in electrophoretic medium. Even though we have analyzed the mechanism of pigment involved styrene-acryl co-particles, we still need to find other chargeable functional polymer to instead styrene-acryl polymer, and try other surfactants at the same time.

Reference

- B. Chomiskey, J.D. Albert, H. Yoshizawa, J. Jacobson, Nature 394 (1998) 253.
- [2] Asad Khan, Kent Displays Inc. Applications and Review of Rigid and Flexible Cholesteric Displays, Asia Display 2007, 877
- [3] Itsuo TANUMA,Flexible Electronic Paper using Electronic Liquid Power Technology, The Imaging Society of Japan,Vol.46,No.5,pg 396-400
- [4] Seiji Sunohara and Takashi Kitamura, Preparation of Polyvinylpyrrolidone Fine Particles be Inverse Emulsification-Evaporation Process in Solvent, Japanese Journal of Polymer Science and Technology, Vol. 62, No.7, pg 310-315(Jul. 2005)
- [5] Akira SUZUKI, Latest Trend 2007 for E-paper, The Imaging Society of Japan, Vol.46, No.5, pg 372-384
- [6] H.Ridaoui, A.Jada.L.Vidal, J.-B.Donnet, Effect of cationic surfactant and block copolymer on carbon black particle surface charge and size, Colloids and Surfaces A: Physicochem. Eng. Aspects 278(2006)149-150
- [7] Jyh-Ping Hsu, Zheng-Syun Chen, Ming-Hong Ku, Li-Hsien Yeh, Effect of charged boundary on electrophoresis: Sphere in spherical cavity at arbitrary potential and double-layer thickness, Journal of Colloid and Interface Science 314 (2007) 256–263
- [8] Yanmei Wang, Caiyuan Pan, Dielectric behavior and magnetic properties of poly(styrene-coacrylic acid)metal microspheres, European Polymer Journal 37 (2001) 699-704

Author Biography

Ming Wang received his BS in Material Physics and Chemistry from Beijing Institute of Graphic Communication (2007.4). Since then he has continued his study for PhD in Kitamura Lab., Chiba University. His work has focused on the electronic paper technology, especially Electrophoretic Images Display and microcapsules