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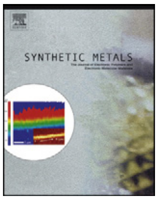

Preparation and characterization of carbon black/acrylic copolymer hybrid particles for dual particle electrophoretic display

Pei-pei Yin, Gang Wu*, Hong-zheng Chen, Mang Wang

MOE Key Laboratory of Macromolecule Synthesis and Functionalization, State Key Lab of Silicon Materials & Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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ABSTRACT

To prepare black electrophoretic particles with good suspension stability in the low dielectric medium for electrophoretic display application, four kinds of carbon black (CB)/acrylic copolymer hybrid particles, CB/poly(2-hydroxyethyl acrylate-co-lauryl methacrylate) (P(HEA–LMA)), CB/poly(2-hydroxyethyl acrylate-co-2-ethylhexyl acrylate) (P(HEA–EHA)), CB/poly(2-(dimethylamino)ethyl methacrylate-co-2-ethylhexyl acrylate) (P(DMA–EHA)) and CB/poly(2-(dimethylamino)ethyl methacrylate-co-lauryl methacrylate) (P(DMA–LMA)), were prepared via polar bonding, the interaction between the carboxyl groups on the surface of CB and the hydroxyl or amino group in copolymers. Structure, morphology as well as electrophoretic properties of the particles were examined. The particle size of the P(HEA–EHA) and P(DMA–EHA) treated CB increases with increasing the storage time. While the particle size of the P(HEA–LMA) and P(DMA–LMA) treated CB is time independent, which can be attributed to the better extension of P(LMA) segments in tetrachloroethylene than P(EHA) and the resulting more effective steric effect. When the feed ratio of DMA/LMA was 3:5 by volume, the maximum values of the electrophoretic mobility and Zeta potential reach 5.44×10^{-10} m^2 V^{-1} s^{-1} and 32.5 mV, respectively. The P(DMA–LMA) anchored CB particles can be applied in the dual-particle electrophoretic dispersion together with negative charged TiO_2 to show black and white images.

1. Introduction

The electrophoretic display (EPD), one of the most promising solutions in the search for electronic paper, has received a great deal of attention because of its interesting properties such as lightweight, good contrast ratio, wide viewing angles, flexible, and low power consumption [1–4]. EPD is a reflective display based on the motion of charged particles suspending in a low dielectric liquid under the effect of an electric field. The charged particles with charges of opposite polarity are required to migrate repeatedly between electrodes without sticking to the electrode surface, sedimenting or changing electrostatic properties by changing polarities of the applied field. Thus, the suspension stability of the electrostatic particles in the media is very important for the practical application of EPD.

The first EPD was introduced in 1973 by Ota et al. [5]. Although the research of EPD has made such a rapid progress in the last decade [6] that the products such as e-books were on the market, the efforts on improving the contrast and response speed never stopped. TiO_2 and carbon black (CB) particles were commonly selected to act as pigment for white and black display. Many studies were focused on the surface modification of TiO_2 [7–15] through physical/chemical methods including polymer encapsulation, grafting and adsorption to anchor charge control agent onto the surface of TiO_2 on the one hand, decrease the density of the pigment to match the media for image stability in the off state on the other hand. As to CB applied as electrophoretic particles, there are only a few studies reported before [16–19].

CB is one of the most important black pigments, the high specific area of which makes it susceptible to flocculate and deposit. Thus, it is difficult to disperse CB evenly in an organic medium to obtain stable suspension. The strategy widely utilized is to modify the surface properties of CB in order to improve their dispersibility in nonaqueous medium. Several methods of CB surface modification are reported. One is physical absorption. Surfactants [20–22] and block polymers [23] can be applied to stabilize CB dispersions for the reason that they can adsorb onto the CB surface by means of hydrogen bonding, ionic interactions, van der Waals forces and acid–base interactions [24]. Previous studies have focused on the interactions between a variety of surfactant with different head group structures, such as succinimide ester [25], azacarboxylate [26], poly(ethylene glycols) [27], and model carbonaceous deposits, in particular, CB. The second is surface grafting. CB/polymer hybrids can be prepared by 'grafting from' [28–30] and 'grafting to' [31]

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* Corresponding author. Tel.: +86 571 8795 2557; fax: +86 571 8795 3733.
E-mail address: wmang@zju.edu.cn (G. Wu).

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methods. 'Grafting to' involves the reaction of reactive macromolecules with surface groups. 'Grafting from' involves surface initiation and subsequent polymer grow from the surface. Another method [32–34] used to prepare polymer-grafted CB is based on the well-known fact that CB is a strong radical scavenger because of the presence of polycondensed aromatic rings, quinonic and phenolic oxygens on its surface. Propagating polymeric radicals can be easily trapped by CB surfaces during polymerization. Preformed polymers can also be grafted onto CB if they can dissociate and form radicals. The functionalization of CB by surface grafting of polymers has been reviewed by Tsubokawa in 2002 [35]. After adsorption or grafting onto the surface of the particles, the polymer chains create repulsive forces between the particles, which are essentially for the steric nature in nonpolar medium [36].

Among the above methods, physical absorption is the simplest method to form a stable suspension and suitable to large-scaled production. It is reported that polyalkyl acrylates and methacrylates can be used in fuels and lubricants in order to avoid or decrease deposit adhesion on metallic surfaces and prevent deposit aggregation [37]. In the present study, in order to prevent the agglomeration and sedimentation of CB in nonpolar medium and prepare a stable CB suspension, CB particles were respectively treated by four kinds of acrylic copolymers, poly(2-hydroxyethyl acrylate-co-lauryl methacrylate), poly(2-hydroxyethyl acrylate-co-2-ethylhexyl acrylate), poly(2-(dimethylamino)ethyl methacrylate-co-2-ethylhexyl acrylate) and poly(2-(dimethylamino)ethyl methacrylate-co-lauryl methacrylate), in which the 2-hydroxyethyl acrylate (HEA) and 2-(dimethylamino)ethyl methacrylate (DMA) units can be anchored onto the surface of CB through polar bonding, the absorbed poly(lauryl methacrylate) and poly(2-ethylhexyl acrylate) segments were expected to extend in tetrachloroethylene to prevent CB particles from agglomeration and sedimentation. Characteristics of the CB/acrylic copolymer hybrid particles such as chemical structure, loadings of polymer, morphology, particle size as well as the electrophoretic properties were examined by FI-IR, TGA, TEM and dynamic light scattering (DLS), respectively. It is found that the chain structure of the acrylic copolymer has great influence on the electrophoretic mobility, Zeta potential and the dispersion stability. The P(DMA–LMA) treated CB particles were applied as black electrophoretic particle in the dual-particle electrophoretic system together with the negative charged poly(lauryl methacrylate)-grafted TiO_2 particles. Under the DC field of 0.075 V/μm, the positive/negative charged electrophoretic particles can move towards opposite direction and white/black image can display.

2. Experimental

2.1. Materials

Lauryl methacrylate (LMA), 2-ethylhexyl acrylate (EHA), 2-hydroxyethyl acrylate (HEA), 2-(dimethylamino)ethyl methacrylate (DMA) were purchased from Sinopharm Group Chemical Reagent Co., and distilled under vacuum to remove the inhibitor before use. 2,2′-Azobis(isobutyronitribe) (AIBN) was obtained from Sigma–Aldrich and recrystallized from ethanol before use. Carboxylate-stabilized carbon black, CB-COONa, with 0.52 mmol carboxylate per gram of carbon black was supplied by Cabot Co. Toluene was purchased from Sinopharm Group Chemical Reagent Co. and used as received.

2.2. Preparation of CB/acrylic polymer hybrid particles

The preparation of acrylic polymer was described as follows: 30 ml of toluene, 0.3 g of AIBN, 1 ml of HEA or DMA and 5 ml of LMA or EHA were charged into a 100 ml three-necked round-bottom flask equipped with a mechanical stirrer, thermometer, N_2 inlet, and condenser. The reaction solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. The reaction temperature was heated up to 65 °C under a stirring rate of 350 rpm and kept for 24 h. The molecular weight and molecular weight distribution of the resultant copolymers were $Mn = 1.32 \times 10^4$ and $Mw/Mn = 2.84$ for P(HEA–LMA), $Mn = 1.28 \times 10^4$ and $Mw/Mn = 3.62$ for P(HEA–EHA), $Mn = 0.83 \times 10^4$ and $Mw/Mn = 2.95$ for P(DMA–EHA), $Mn = 1.20 \times 10^4$ and $Mw/Mn = 2.18$ for P(DMA–LMA), respectively.

The mixture of CB (0.5 g), synthesized copolymer (0.2 g) and toluene (30 mL) was treated by ultrasonication for 5 h. The suspension was refined from the free copolymer by cycles of centrifugation and redispersion in toluene and the CB/acrylic copolymer hybrid particles can be obtained.

2.3. Characterization

The chemical structure of hybrid particle was verified by FIIR spectrum (VECTOR 22, Bruker). Thermal properties were examined via thermogravimetric analysis (TGA, TA SDT Q600) with a heating rate of 10 °C/min in a stream of nitrogen. The transmission electron microscopy (TEM, JEOL 200CX) and dynamic light scattering (DLS 90Plus particle size analyzer, Brookhaven instrument Corp.) were applied to observe the morphology and the size of the particles, respectively. Electrophoretic mobility and Zeta potential were measured by the Brookhave Zeta-PALS.

3. Results and discussion

FTIR spectra of the acrylic copolymers together with the CB particles with and without copolymer treatment are shown in Fig. 1. Crude CB samples show a strong peak at 1630 cm^{-1} corresponding to the sp^2 C═C stretching vibration. Two peaks at 2930 cm^{-1} and 2850 cm^{-1}, associated with sp^3 C–H stretching, can be assigned to the open edges of the graphitic flakes. The characteristic C═O vibration peaks at approximately 1730 cm^{-1} can be observed because of the existence of carbonyl group on CB surfaces. The acrylic copolymers can anchor onto the surface of CB through polar bonding, the interaction between the carboxyl groups and the hydroxyl or amino group, as a result, two new peaks at 1460 cm^{-1} and 1166 cm^{-1} can be found in the FTIR spectra of the treated CB particles, which were assigned to the absorption of $-CH_2-$, $-CH_3$ and C–O–C groups in the copolymers.

TGA curves of CB, copolymers and hybrid particles are presented in Fig. 2. It is obvious that no distinguishable main weight loss region can be found for the CB sample, except for a continuous weight loss of about 9% in temperature region from 50 to 600 °C, which can be attributed to the decomposition of carboxyl groups and CB fragments [26]. For the hybrid particles, two main temperature regions of weight loss can be found, as shown in Fig. 2a. The weight loss below 200 °C could be attributed to the evaporation of physically absorbed water and residual solvent in the samples, the weight loss in the temperature region beyond 200 °C can be assigned to the decomposition of copolymers. From curves in Fig. 2b, the main weight loss of the four kinds of acrylic polymer treated CB particles starts from the almost same temperature at about 200 °C, from which the corresponding amount of the copolymer anchored on the CB surface can be estimated, namely about 9.6 wt%, 10.1 wt%, 11.6 wt%, and 12.3 wt% for P(DMA–LMA), P(HEA–LMA), P(DMA–EHA), and P(HEA–EHA), respectively.

From the FTIR and TGA results, we can conclude that the four copolymers have been successfully anchored onto the CB surfaces.

The dispersion and suspension stability of the CB particles in the media is very important for its application in the area of EPD. Fig. 3