



Polyurethane encapsulated carbon black particles and enhanced properties of water polyurethane composite films

Weining Du^a, Jun Liu^b, Yifan Wang^a, Yupeng Li^a, Zhengjun Li^{a,*}

^a National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

^b College of Chemistry & Environmental Protection Engineering, Southwest University for Nationalities, Chengdu 610041, China

ARTICLE INFO

Article history:

Received 10 October 2015

Received in revised form 11 April 2016

Accepted 11 April 2016

Available online 26 April 2016

Keywords:

Carbon black

Encapsulate

Amphiphilic

Waterborne polyurethane

Composite film

ABSTRACT

Polyurethane-encapsulated carbon black (ECB) particles were synthesized successfully through a facile method by encapsulating carbon black (CB) particles in the presence of an amphiphilic isocyanate-terminated polyurethane pre-polymer. Fourier transform infrared spectroscopy demonstrated the existence of a polyurethane layer on the surface of encapsulated CB, and thermo-gravimetric analysis indicated the encapsulation percentage reached 15.77 wt.%. The results of dynamic light scattering, transmission electron microscopy, and UV–vis spectroscopy analyses revealed that the ECBs exhibited better dispersibility and stability in water in comparison with the dispersant-dispersed carbon black (DCB) prepared by simply dispersing CB particles using a polymer super-dispersant. In particular, scanning electron microscope observation of PUB/ECB composite films obtained by blending ECB particles with a waterborne polyurethane binder (PUB), showed enhanced dispersibility and compatibility of the ECBs in the PUB matrix. Therefore, as test results demonstrated, PUB/ECB composite films showed better mechanical, water resistance, and color properties compared with those of PUB/DCB composite film. It is expected that this effective encapsulation method for preparing functional CB dispersions will be used to make waterborne coatings in the leather and textile finishing fields.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Carbon black (CB) has been widely used as an inorganic colorant in the coating industries due to its numerous intriguing merits such as nontoxicity, darkness, chemical stability, electrical conductivity, and heat resistance [1–3]. However, pristine CB particles are typically hydrophobic and exhibit a strong tendency to self-agglomerate owing to the strong van der Waals forces around their surface [4]. This weakens the properties of polymeric materials containing CB particles, thus greatly limiting further practical applications.

To overcome this obstacle, numerous attempts have been made to alter the surface chemistry of CB particles and improve their dispersibility in aqueous solution, in particular, simultaneously enhance their compatibility in the polymeric matrix. Several methods have been developed for this purpose, including dispersant modification [5], oxidation [6], grafting [7–9], and encapsulation [10–16]. Most of these methods, however, suffer from some disadvantages. The major problem of dispersant modification is the

low compatibility of simply dispersed CB particles with the organic polymer matrix. The corresponding polymeric coating properties such as water resistance and gloss are therefore negatively affected because of the hydrophilicity of the dispersing agent. With respect to oxidation modification, the dispersion of modified CB particles is less stable due to the limited hydrophilic groups on the CB particle surface. In particular, the oxidation reaction is not easily controlled and the reaction mechanism is unclear [17]. In the case of grafting modification, the reaction is generally carried out in organic solvent and requires harsh reaction conditions. Moreover, the grafting ratio is not significantly improved [10,13].

Recently, the encapsulation method has been attracting the interest of researchers for improving the properties of CB particles. It is hoped that the polymer shell encapsulated on the CB particle surface can enhance the dispersibility and interfacial adhesion of the CB particles in an organic polymer matrix, and enable them to remain separated during film formation [18], thus improving the performance of the polymeric material. Many supportive strategies can be achieved, such as phase separation [10,11], interfacial polymerization [12], and emulsion or mini-emulsion polymerization [13–16]. With respect to the phase separation method, the major problem is that the polymer shell encapsulated on the CB particle surface is easily eroded by water, and the dispersed CB par-

* Corresponding author.

E-mail address: lizhengjun@scu.edu.cn (Z. Li).

ticles easily aggregate again [19]. Interfacial polymerization also suffers from a few problems such as low encapsulation ratio and low encapsulation efficiency. In particular, the size of modified CB particles is sometimes difficult to control. In the case of emulsion or mini-emulsion polymerization, the prerequisite for successful encapsulation of CB particles is that they are well-dispersed in monomer mini-emulsion droplets [14,20]. Polymerization parameters such as the pH of the polymerization process, the surface properties of CB particles, and initiator types must also be vigilantly controlled. In addition, it is very difficult to implement the encapsulation because CB particles usually act as an efficient radical trap in the free-radical polymerization process [13,18]. Therefore, the development of a facile, efficient, and environmentally friendly encapsulation method is extremely important. To the best of our knowledge, preparation of polyurethane-encapsulated CB particles by the encapsulation method in the presence of an amphiphilic isocyanate-terminated polyurethane pre-polymer has not been reported elsewhere. The amphiphilic isocyanate-terminated polyurethane prepolymer, prepared via condensation polymerization, can be absorbed onto the CB particles surface and reacted with hydroxyl groups located on the CB particle surface to form a stable polymer shell, thus preventing aggregation. It is expected that the dispersibility of the encapsulated CB particles in water and their compatibility with the polymeric matrix can be substantially improved, thereby improving the performance of polymer composite films.

The aim of this study was to develop a facile and efficient method to encapsulate CB particles with a polyurethane layer, so as to improve their dispersibility and stability in water, and simultaneously enhance their dispersibility and compatibility in a polyurethane matrix. The goal of this is to enhance the mechanical properties, water resistance, and color properties of waterborne polyurethane binder (PUB) composite films. For this purpose, we first prepared polyurethane-encapsulated CB (ECB) dispersions using an amphiphilic isocyanate-terminated polyurethane pre-polymer. The ECBs were then characterized, and compared with dispersant-dispersed carbon black (DCB) prepared by simply dispersing CB using a polymer super-dispersant, using Fourier transform infrared (FTIR), thermo-gravimetric analysis (TGA), dynamic light scattering (DLS), transmission electron microscopy (TEM), and UV-vis spectroscopy, respectively. Subsequently, the dispersibility and compatibility of the CB particles in PUB/ECB composite films were observed using a scanning electron microscope (SEM). Furthermore, the mechanical properties, water resistance, and color properties of the composite films were investigated and compared with those of PUB/DCB composite film. This paper reports a new method for preparing functional carbon black dispersions applied in waterborne coatings, especially for making high-performance pigment paste for leather and textile finishing.

2. Experimental

2.1. Materials

Carbon black (CB) was supplied by Shanghai Coking Plant. Waterborne polyurethane binder (PUB, RU2301) was kindly provided by Sichuan Dowell Co., Ltd. Dispersing agent (X3503) was obtained from Guangzhou Xinlian Chemical Co., Ltd. Polyethylene glycol (PEG, with a molecular weight of about 400), dibutyltin dilaurate (DBTDL), toluene diisocyanate (TDI), dimethylol propionic acid (DMPA), ethylenediamine (EDA), and acetone were purchased from Chengdu Kelong Chemical Co., Ltd. All reagents were of analytical grade. Prior to the experiment, PEG was dehydrated at 110 °C for 2 h under vacuum. CB and DMPA were dried in an oven at 80 °C

for 3 h to remove moisture. All other reagents and chemicals were used as received.

2.2. Methods

2.2.1. Preparation of polymer encapsulated carbon black (ECB)

Fig. 1 depicts the process of preparation of polyurethane-encapsulated CB (ECB) dispersion via the encapsulation method. Detailed procedures were performed as follows.

Step 1: Dispersing agent (12 g) was dissolved in 40 g of deionized water. Then, 8 g of CB was slowly added to the solution under stirring by a high-speed dispersion machine (IKA, China) at 6000 rpm for 1 h at room temperature (27 ± 2 °C). Thus, the aqueous carbon black dispersion was achieved and abbreviated as “DCB”.

Step 2: Dehydrated PEG (36 g) was introduced into a 250 ml triple-necked flask and heated to 50 °C in a water bath with mechanical stirring at 300 rpm. Then, 16 g of TDI and 35 g acetone were slowly dropped into the system and maintained at 50 °C for 1 h. Thereafter the mixture was heated to 60 °C and stirred for 2 h. Subsequently, two droplets of catalyst (DBTDL) were added and allowed to react for 1 h, then 1.5 g of DMPA was added, and allowed to react for a further 2 h. In this way the isocyanate-terminated polyurethane prepolymer (PUP) was obtained.

Step 3: The prepared DCB (60 g) and 0.24 g of EDA were added to a 100-ml flask, then a defined amount of PUP (the mass ratio of PUP:DCB was 1:1 and 0.5:1, respectively) was added with stirring of 6000 rpm at room temperature for 15 min. The encapsulated CB particles were subsequently separated from the obtained dispersion by ultracentrifugation (Wanfeng Instruments, China) at 10,000 rpm for 20 min. The separated residues were dried in a vacuum oven (Yaoshi Instruments, China) at 100 °C overnight and labeled “ECB1” and “ECB2”, respectively.

2.2.2. Preparation of waterborne polyurethane binder/carbon black composite film

Prepared DCB, ECB1 and ECB2 dispersions were mixed with PUB at a solid mass ratio PUB:CB of 2:1, respectively. Then the mixture was treated with an ultrasonic machine (Jili Instruments, China) for 10 min. Finally, the mixture was simply cast in a mold, dried at room temperature overnight and cured at 80 °C for 6 h. The obtained composite films (thickness approximately 1.2 mm) were designated “PUB/DCB”, “PUB/ECB1”, and “PUB/ECB2”, respectively.

2.3. Characterization

Fourier transform infrared (FTIR) spectra of pristine CB and ECB powders (in KBr pellet) were recorded on a Nicoletis10 spectrometer (Thermo Scientific, USA) to confirm the presence of a polyurethane shell on the surface of CB particles. Typically 32 scans over the range 400–4000 cm⁻¹ were utilized for each sample with a resolution of 4 cm⁻¹.

Thermo-gravimetric analysis (TGA) was performed on a TG209-F1 (Netzsch, Germany) to evaluate the content of polyurethane shell on the surface of encapsulated CB particles. Each sample (about 3–5 mg) was analyzed at a heating rate of 10 K/min from 30 to 800 °C under N₂ atmosphere. The encapsulation percentage of the encapsulated CB particles was calculated using Eq. (1) [17].

$$\omega = \frac{W_{CB} - W_{ECB}}{1 - W_{PUP}} \times 100 \quad (1)$$

where ω is the encapsulation percentage (wt.%), W_{CB} , W_{ECB} , and W_{PUP} are the residual weight of pristine CB, ECB, and PUP at 450 °C, respectively.

The particle size and its distribution as well as the polydispersity index (PDI) of DCB and ECB dispersions were measured by dynamic light scattering (DLS) techniques using a Nano-ZS90 laser

Download English Version:

<https://daneshyari.com/en/article/692142>

Download Persian Version:

<https://daneshyari.com/article/692142>

[Daneshyari.com](https://daneshyari.com)