Colloids and Surfaces A: Physicochem. Eng. Aspects 458 (2014) 187–194

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Control of carbon black aggregate size by using polystyrene-polyethylene oxide non ionic diblock copolymers

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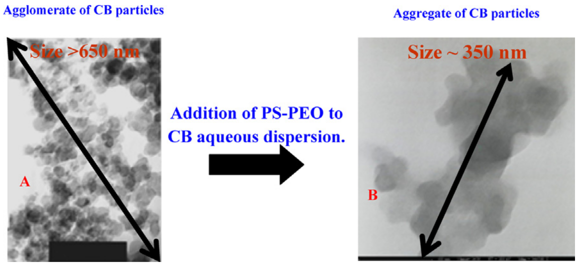
HIGHLIGHTS

- The CB particle results from aggregation process of carbon elemental particles.
- The CB forms in alkaline medium "bunch" of grapes shaped aggregates.
- The CB forms in acidic medium ellipsoidal shaped agglomerates.
- The CB particles are smaller in alkaline, as compared to, acidic media.
- The minimum CB aggregate size is obtained in the presence of PS-PEO copolymer.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 October 2013
Received in revised form 7 March 2014
Accepted 21 March 2014
Available online 31 March 2014

Keywords:
Carbon black
Zeta potential
Aggregates
Particle size
Ellipsoidal shape
Bunch of grapes
Branching shape

ABSTRACT

The fine fraction of carbon black (CB) sample N234, initially prepared by the furnace process, was obtained by sieving and it was then dispersed in aqueous medium at various aqueous phase pH. Further, adsorption from water onto this non porous CB particles, of polystyrene-polyethylene oxide (PS-PEO), non ionic diblock copolymers, having molecular weights, $M_w = 2000$ and $M_w = 4000$ g/mol, were investigated at ambient temperature. For the bare CB particles, prepared in the absence of copolymers, the TEM micrographs show aggregates and/or agglomerates having sizes depending of the aqueous phase pH, and formed from fused primary particles having sizes in the range 13–17 nm. These aggregates develop intra-porosity that result from their branching shape. The CB bare particles prepared in acidic aqueous dispersion form mostly ellipsoidal agglomerates having sizes exceeding 500 nm. However, by increasing the pH of the medium from pH = 3 to pH = 10, and after drying the CB dispersion, aggregates shaped as "bunch" of grapes and having smaller sizes are observed by TEM. The microelectrophoresis studies of these dispersions indicate that the CB particles are positively and negatively surface charged at pH values, respectively, below and above the Isoelectrical point (IEP) which is about pH ~ 6. Such electrokinetic behavior of the CB aqueous dispersion results from the presence on the CB surface of acidic and basic functional groups. However, upon PS-PEO copolymers adsorption onto CB, reduction in the magnitude of zeta potential, and shift of the Isoelectrical point (IEP) to lower pH values were observed. Such IEP shift is related to the copolymer adsorption on the Stern layer and to the position of the shear plane in the electrical double layer. In addition, the copolymer adsorption was found to reduce the CB particle size achieving a minimum value in water of about 200 nm, resulting in sterically stable CB aqueous dispersions.

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http://dx.doi.org/10.1016/j.colsurfa.2014.03.068
0927-7757/

1. Introduction

In the next decade, the carbon black (CB) market volume is expected to increase by more than 3 million tones from 2011 levels, according to several international market research companies. The CB is used mostly, as filler in the production of tires of all sorts, and in numerous rubber products. This pigment is also used in other industrial applications such as adhesives [1], paint and varnish industry [2], inks [3], plastics [4], and in metallurgical applications [5]. In adhesives, CB pigments are used in order to color the adhesive compound deep black, to make it conductive and aging resistant to UV light. In paint and varnish industry, CB is used for tinting paints and primers and for coatings of higher qualities. In inks, CB pigments play an important role in the field of printing inks. CB pigments can be also used to color plastics in the requested shades of gray and black, and to minimize the photo-oxidative degradation of plastics caused by UV light. An antistatic finish or electrical conductivity of the plastics can be achieved by means of a highly structured furnace CB or special high-performance CBs. In metallurgical applications, the CB particles are used to reduce the pore density and slag which improves the life cycle of the refractory materials. In all these industrial applications described above are dependent on the surface properties, the mean size and the size distribution of the CB particles. The structure and the particle size are very important for these industrial applications. Thus, in order to control the CB surface properties, particle size and shape, the present work is aimed to investigate experimental conditions and factors affecting the surface characteristics of CB particles.

1.1. Furnace process and CB particle size

The CB is an organic solid which is produced by incomplete combustion, mainly by using the furnace process [6]. This process is continuous and operates in a closed reactor characterized by high velocities and turbulent flows. Hence in this process, a feedstock is heated and injected continuously into the combustion zone of a natural gas-fired furnace, where it is decomposed to form the CB. Quench water cools the gas to stop cracking and the black is separated from the gas stream by a fabric filter. CB is hydrophobic in nature, and tends to form aggregates and/or agglomerates when suspended in water. Thus, the addition to the aqueous media of dispersing agents, such as block copolymers or ionic surfactants, can improve the dispersion in water of the CB particles. The CB particles may be described in term of three sets of size range [7]. The primary particles have the smallest size, which are typically 13–100 nm in diameter depending on the parameters set in CB processing. Such primary particles fuse and form in the furnace reactor a second larger level of structure or aggregates having size in the range 200–1000 nm. The morphologies of these aggregates can vary from linear, branched to completely compact and roughly spherical domain. Further, these carbon aggregates may percolate and form agglomerates, which have the largest size (exceeding 1000 nm). The easily formation of aggregate of the furnace carbon is due to the strong attractive interparticle forces, while agglomerates result from weakly bound aggregates, and might be broken down into smaller aggregates, by using appropriate dispersing agents such as ionic molecular surfactants [8] or non-ionic PS-PEO copolymers.

1.2. PS-PEO copolymers

Polystyrene-polyethylene oxide (PS-PEO) diblock copolymers exhibit amphiphilic behavior in water, which is a selective solvent for PEO and a precipitant for PS blocks [9–13]. In dilute solution and above the Critical Micelle concentration (CMC), PS-PEO copolymers associate to give micelles in which the core formed from PS blocks is surrounded by a shell consisting of molten PEO blocks [14]. Therefore, these copolymers are useful for the solubilization and/or the stabilization of hydrophobic compounds, such as CB particles, in aqueous medium. Thus, at the CB–water interface, the insoluble PS block should adsorb onto the CB surface, and the soluble PEO block, which has no affinity for the surface, is in contact with water forming the stabilizing layer. In addition, taking into account the non-ionic character of the PS-PEO copolymers, the aqueous dispersion stability, should result from the steric interactions that occur between PEO layers in contact with the surrounding water molecules and covering the hydrophobic particles. Experimental and theoretical studies dealing with adsorption at solid–liquid interface of A_nB_m diblock copolymers have been developed by several authors [15–21]. According to these models, the insoluble (A) blocks form a molten film, whereas the soluble (B) blocks stretch into the solution to build up a brush having surface density, σ_{theo}, which scales as Eq. (1):

$$\sigma_{\text{theo}} * a^2 \sim N_A^{-12/23} N_B^{-6/23} \tag{1}$$

where 'a' is the monomer length, N_A and N_B, are respectively, the number of repeat units of the A and B blocks.

Further, upon the adsorption from liquid onto on the solid surface, of the A_nB_m diblock copolymer as compared to homopolymers, it is expected that the formed polymer brush will have higher surface density, and larger thickness, L, on the solid surface, enhancing the stability of the dispersed solid particles. The PS-PEO copolymers were selected here for two main reasons. Firstly, in previous works (see for instance Ref. [14]), we have investigated the amphiphilic behaviors of these copolymers in water, and secondly these polymers can adsorb on the CB hydrophobic surfaces, reduce their sizes, and bring sterically stability to the CB aqueous dispersions.

It is now clearly established that the size and/or the fractal dimension of the CB aggregates are powerful tools to characterize such solid particles, in order to use them suitably in various applications. In addition the specific surface area and the surface activity of the CB particles are important parameters that control also the various properties of the particle reinforced-composite materials [22,23].

In the present work, we have used Dynamic light scattering (DLS) to measure CB particle sizes. This method is a suited for the measurement of the particle mean size, the size distribution, and the translational diffusion coefficient of macromolecules and submicron-sized particles suspended in a liquid [24]. It should be noted that DLS can analyze the size of particles from about 2 up to about 5000 nm in diameter [25]. Thus, CB aqueous dispersions were prepared by dispersing CB powder in aqueous media containing polystyrene-polyethylene oxide (PS-PEO), non ionic diblock copolymers dispersing agents. The adsorption of such copolymers, from water onto CB particle surface, and there effects on the CB mean size reduction and the surface charge modification, are described.

2. Experimental

2.1. Materials

The CB sample studied and referenced as N234 was an oil-furnace having a surface area of 119 $m^2 g^{-1}$ as measured by the BET method [8]. It should be emphasized that in the furnace process [6], fuel and feedstock raw materials such as carbochemical and petrochemical by-products are used. Further, the combustion reaction, which takes place in a closed reactor, is controlled by various parameters such as the feedstock/air ratio, the reactor temperature and the feedstock composition. The combustion reaction is stopped