Investigating the effectiveness of PEO/PPO based copolymers as dispersing agents for graphitic carbon black aqueous dispersions

S. Yasin, P.F. Luckham*

Department of Chemical Engineering & Technology, Imperial College, South Kensington, Post Code: SW7 2AZ, London, United Kingdom

ARTICLE INFO

ABSTRACT

The dispersability of graphitic carbon black, selected as a model for carbon nanotubes, has been investigated using a combination of rheological, conductivity and atomic force microscopy (AFM) techniques. The effectiveness of three PEO/PPO based non-ionic dispersants, namely polyethylene oxide polypropylene oxide ABA copolymers (synperonic PE/F 103 with 2×16 ethylene oxide units and PE/F 108 with 2×148 ethylene oxide units) and NPE1800 (nonyl phenyl polypropylene oxide-polyethylene oxide with 27 ethylene oxide units), is reported. Adsorption isotherms were determined for these dispersants. The adsorption isotherms of PE/F 103 in comparison with PE/F 108 revealed that in molar terms ($\mu mol/m^2$) the adsorption decreases for PE/F 108 with more ethylene oxide units, indicating that adsorption is governed by size of the PEO (polyethylene oxide) chain length. Also, the synperonic PE series which has polypropylene oxide as an anchor group and does not contain any aromatic ring in their anchoring group, gave lower adsorption amounts (in moles) as compared to the NPE 1800 which contains an aromatic ring (nonyl phenyl) in its anchoring group as well as propyleneoxide. The relative viscosity-effective volume fraction Φ' curves are compared with the theoretical curves for the hard sphere dispersions calculated using Krieger–Dougherty equation. For the graphitic carbon black studied here, in an aqueous medium, neither PE/F 103, nor PE/F 108 showed good agreement with the Krieger–Dougherty equation; the viscosities were all much higher than that predicted by that equation. Whilst NPE 1800 produced dispersions of lower viscosity and the viscosity values showed a good agreement with the Krieger–Dougherty equation. The results achieved from oscillatory measurements showed that PE/F 103 and PE/F 108 dispersants showed a frequency cross-over of G' and G'' at lower volume fractions. Also they produced dispersions of high electrical conductivity, suggesting that these systems are aggregated. In the AFM force spectroscopy measurements, the interactions between the adsorbed layers of PE/F103 were initially attractive, whilst somewhat surprisingly the PE/F 108 adsorbed layers only showed repulsive interactions on approach and separation. NPE 1800 stabilised systems exhibited much lower viscosity and elastic modulus than the PE/F stabilised dispersions; produced dispersions of lower electrical conductivity and showed repulsive interactions in AFM, suggesting that these systems are much more stable than the carbon black dispersions bearing adsorbed PE/F polymers.

The results indicated that synperonics (PE/F 103 and PE/F 108) are not a good dispersants for graphitic carbon black and by consequence for carbon nanotubes; whilst NPE 1800 is a suitable dispersant for these dispersions and could be a good dispersant for carbon nanotubes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nanotubes are nanometre scale wires with the potential of benefiting mankind in many ways because of their extraordinary mechanical, electrical, optical and thermal properties [1–4]. Carbon nanotubes pack themselves into ropes which further aggregate and this aggregation is an obstacle to many applications [5]. This problem has motivated considerable recent research to develop methods to disperse the nanotubes more effectively [6].

The use of ultrasound has achieved some success in dispersing carbon nanotubes, but this method tends to damage the internal structure of the tubes [7]. Physical adsorption of polymeric layers that will act as a steric stabilizer is an alternative [8,9]. Graphitic carbon black possesses largely a uniform surface, like carbon nanotubes, composed of aromatic carbon rings owing to crystalline nature of the two materials. Graphitic carbon is chemically inert and stable, hence does not react with the environment. Also graphitic carbon black particles in a solution/suspension, like carbon nanotubes have a tendency to pack themselves and settle

* Corresponding author. Tel.: +44 0 2075945583; fax: +44 0 2075945636.
E-mail addresses: s.yasin@imperial.ac.uk (S. Yasin), p.luckham01@imperial.ac.uk (P.F. Luckham).

Table 1
Characteristics of polymers/dispersants [10].

Dispersant	Molecular weight (kg/mol)	No. of ethylene oxide units	No. of Propylene oxide units	Nonyl phenyl
PE/F 103	4.7	2×16	56	No
PE/F 108	16.2	2×148	56	No
NPE 1800	2.2	27	13	Yes

after some period. Therefore, keeping graphitic particles dispersed in any medium using polymers for longer periods is of considerable interest. Since there are considerable safety issues in working with carbon nanotubes, graphitic carbon black was selected as a model. The model is based on the hypothesis that a good dispersant for graphitic carbon black will also be a good dispersant for carbon nanotubes due to the similarity of the surface structure and properties. In previous studies, Miano and co-workers [10,11] have investigated the dispersion of a non graphitic, amorphous carbon black in water by three classes of dispersants; an ABA polyethylene oxide-polypropylene oxide-polyethylene oxide dispersant; a nonyl phenol ethoxylate dispersant and a novel nonylphenol-polypropylene oxide-polyethylene oxide dispersant. The studies concluded that the later dispersant showed best dispersion properties (although the nonyl phenol ethoxylates dispersants also showed similar dispersing behaviours) and both were considerably better dispersants than the ABA polyethylene oxide-polypropylene oxide-polyethylene oxide PPO-PEO polymers. This is surprising since PPO-PEO polymers (often called by their trade name of Pluronics) are often used to disperse carbon nanotubes [12]. The present work is an extension of the Miano's work to a graphitic carbon black (Monarch 1000).

Among the wide range of dispersants available, three PEO/PPO based non-ionic dispersants named polyethoxylated PE/F 103, PE/F 108 and nonyl phenyl polypropylene oxide-polyethylene oxide were selected. The anchoring chain, polypropylene oxide, is same for PE/F 103 and PE/F 108 except in NPE 1800 where the anchoring chain consists of a nonyl phenyl group and polypropylene oxide. Whilst the size of stabilising chain, i.e. polyethylene oxide is different for all dispersants. Therefore, effect of the size of stabilising chain is investigated by keeping the anchoring chain same in synperonics (PE/F 103 and PE/F 108). As well effect of a nonyl phenyl in NPE 1800 is studied on dispersion properties. The quality of carbon black dispersions is evaluated based on rheological measurements, electrical conductivity measurements and AFM (atomic force microscopy) operating in the so-called force spectroscopy mode.

2. Experimental

2.1. Materials

Graphitic carbon black (Monarch 1000 jet black in colour) with a density of $1.8 \, g/cm^3$ was kindly supplied by Cabot Chemical Corporation, UK. PE/F 103, PE/F 108 and NPE 1800 were supplied by ICI Speciality Chemicals, now known as Croda Chemicals. Characteristics of dispersants are given in Table 1.

2.2. Surface area measurements

In order to determine the maximum amount of dispersant adsorbed onto the carbon black particles, the surface area of the particles was determined using two different methods. First, the surface area was calculated by nitrogen adsorption method (BET) [13]. Using this method the surface area of Monarch 1000 was found to be $301 \, m^2/g$ with a porosity of $0.96 \, cm^3/g$. Nitrogen gas is a simple diatomic molecule, able to access the smallest pores of the carbon black and is much smaller than any of the polymeric

dispersants. Therefore, the surface area based on gas adsorption method is not a good estimate for the area available to the dispersants. Thus a wet surface area based on methylene blue adsorption method was determined as well; using this method the surface area of the particles was found to be $163 \, m^2/g$ [10,11,14]. As expected, the surface area based on methylene blue adsorption is much less than that measured by nitrogen adsorption method. Therefore, the wet surface area is more accurate estimate for the available surface area of the particles for adsorption of dispersants. Hence, the wet surface area is used to estimate the amount of polymer adsorbed per square metre of surface for present work.

2.3. Adsorption measurements

Carbon black (Monarch 1000) dispersions of 0.15 weight percent were prepared using dispersants of different concentrations. After 30 min vigorous stirring using a Silverson mixer, all dispersions were shaken for at least two days to establish adsorption equilibrium. All solutions were then centrifuged in order to separate the carbon black and determine the equilibrium concentration of the polymer. However it was noticed that centrifugation alone did not give a clear supernatant at the top of the centrifuge tubes and that some carbon black particles were still present in solution. Therefore, micro filters (Millex Millipore syringe driven filter unit, 0.2 μm) were used to filter any remaining carbon black from the solution and hence a clear supernatant solution was obtained. The concentration of polymer remaining in the supernatant was determined using an UV/vis spectrometer. In case of PE/F polymeric dispersants a colourimetric method was used by forming a coloured complex of iodine (I_2) and potassium iodide (KI) [10,11]. For each 10 ml supernatant solution 0.25 ml of a freshly prepared complexing solution consisting of 1 g of I_2 and 2 g of KI in 100 ml of distilled water) was added. The absorbance values were then determined using an UV/vis spectrometer at a wavelength of 460 nm which was compared with the calibration curves. The equilibrium concentrations of NPE 1800 were obtained by measuring the absorbance of the phenyl ring at 274 nm.

2.4. Rheology measurements

Aqueous dispersions of Monarch 1000 (8–22 wt%) were prepared using the surfactant solutions of known concentrations. The dispersion was first stirred manually and then in a Silverson mixer for about one hour followed by ball milling for 16 h. After screening the balls, the dispersions were taken for rheological experiments. Bead milling for more than 16 h did not result in any change in the viscosity.

Steady state and oscillatory measurements were carried out with a PAAR UDS rheometer using concentric cylinder geometry. The rheometer is capable of varying the shear rates in a range of 0.001–$1000 \, s^{-1}$ and oscillatory strain frequencies in a range of 0.001 to 100 Hz. The oscillatory measurements were more complex, requiring as a first step, determination of a linear viscoelastic region. This was obtained by performing a strain sweep test whereby the amplitude of the strain was ramped in order to determine the critical strain where G' (elastic modulus) and G'' (loss modulus) begin to be dependent on the strain and start to decrease