STUDY OF THE EFFECTS OF pH, ELECTROLYTE ADDITIONS AND INCREASING SOLID CONCENTRATION ON THE RHEOLOGICAL BEHAVIOR OF CARBON BLACK SUSPENSIONS

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Abstract

The main aim of this study is to investigate the rheological properties of the flow behavior of carbon black suspensions in order to make particulate Sic-Sic composites by colloidal process.
As OH^- and H^+ are potential determining ions for carbon black, an investigation of the effect of pH on the rheological properties of these suspensions has been carried out.
Above pH 10, in the absence of added NaCl, these suspensions were fully deflocculated. As the pH was decreased below 10, a yield stress was observed. The introduction of the yield stress was accompanied by a change in flow behavior from Newtonian to Pseudoplastic. The presence of a monovalent cation produced a yield stress where one did not previously exist, and increased the size of any existing yield stress. It is shown that suspensions of low solids concentration can be fully deflocculated using alkali alone

Introduction

Carbon black is an intensely black, finely divided powdered form of highly dispersed elemental carbon manufactured by the controlled vapor phase pyrolysis of hydrocarbons [1]. Its principal use is as reinforcing agent in automobile tires and other rubber products, but it is also used as an extremely black pigment with hiding power suitable for use in printing inks, paints, and carbon paper. The blackness and tint properties of such ink coatings are all highly dependent on the particle size distribution, morphology, and structure. Carbon black particles are usually spherical in shape and less crystalline than graphite [2]. The precise structure is intermediate between those of graphite and a truly amorphous material. Small crystallites made up of parallel graphitic layers 0.35-0.38 nm apart. The formation of carbon black involves three important stages. Nucleation of soot precursors produces a particulate system from a molecular system; the precursors subsequently agglomerate to form particles with typical dimension 1-2 nm. The final step involves the association of these particles to form roughly spherical, primary particles. Aggregation of these primary particles thus determines the ultimate morphology of carbon black aggregates, henceforth termed fractal or spherical particles. Average aggregate diameters range from 0.1 to 0.8 µm.
In the manufacture of inks, carbon black is often used in conjunction with waterborne acrylic resins. The resins act as a cross-linking polymer network. Although the printing process involves many high-shear interactions, understanding the low-shear behavior of ink is more relevant to the ink's properties (tack, transference, cohesion, and drying).
The rheological properties of concentrated dispersions are of great importance in many other technological applications, such as food concentrates and pharmaceuticals [3].
Since carbon blacks are produced from hydrocarbons, the dangling bonds at the edges of the carbon layers are saturated mostly by hydrogen. Often, one finds large polycyclic aromatic ring systems on the surface that can be extracted with hot solvents (e.g., xylene). One suspects, therefore, that there are also still larger molecules on the surface that are insoluble, and that there is a gradual transition in size to the layers that can be recognized in HRTEM photographs.
Other elements than hydrogen are also found in carbon blacks. The most important of these is oxygen. Whereas sulfur and nitrogen originate from the\oil precursor, oxygen can also be taken up during carbon black formation or storage. The surface oxides are bounded to the edges of the carbon layers. It has been shown that basal planes of graphite are attacked by molecular oxygen only at their periphery or at defect sites such as vacancies [4]. Carbon black can show basic or acidic pH values in aqueous dispersions. A good correlation between pH and oxygen content of carbon black has been found [5]. The dispersion is the more acidic, the oxygen content is. The acidic surface properties are due to the presence of acidic surface groups. Such carbons have cation exchange properties. Carbons with low oxygen content show basic surface properties and anion exchange behavior. The basic properties are ascribed to the presence of basic surface oxides, but it has been shown that the π electron system of the basal planes of carbon is sufficiently basic to bind protons from aqueous solutions of acids [6]. Figure 1 presents several structures of oxygen functional groups that might be found at the edges of grapheme layers. Carboxyl groups (a)

might give carboxylic anhydrides (b) if they are close together. In close neighborhood to hydroxyl groups or carboxyl groups, carbonyl groups might condense to lactone groups (c) or form lactols (d). Single hydroxyl groups (e) on the edge of "aromatic" layers would be of Phenolic character. The existence of carbonyl groups is very plausible; they could com either isolated (f) or arranged in quinone-like fashion (g). Obviously, other arrangements could be envisaged for quinone-type functions. Finally, oxygen could simply be substituted for edges carbon atoms (h); such xanthene- or ether-type oxygen is very difficult to detect. The groups (a) to (e) react more or less weakly acidic [4].

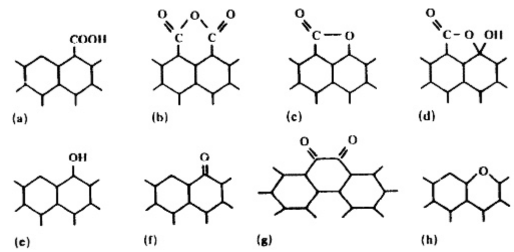


Figure1. Possible structure of surface oxygen groups (see text)

Basic surface oxides are always present on a 1000°C in vacuum or under an inert gas, the existing surface compounds are almost quantitatively decomposed. When this carbon is exposed to dry oxygen after cooling to room temperature, some oxygen is chemisorbed. After submersing this carbon under aqueous acids, the same quantity of oxygen again is taken up, and approximately one equivalent of acid per chemisorbed oxygen atom is bound at the same time. The bound anion of the acid can be exchanged for other anions. Water is a sufficiently strong acid, and OH^- ions are bound when the reaction is conducted in pure water, giving rise to an alkaline pH of the dispersion. As shown in figure. 2 the ether-type oxygen can easily be replaced by nitrogen in the reaction with ammonia. The hydroxyl groups can be methylated with diazomethane, whereas the anion exchange property is preserved.

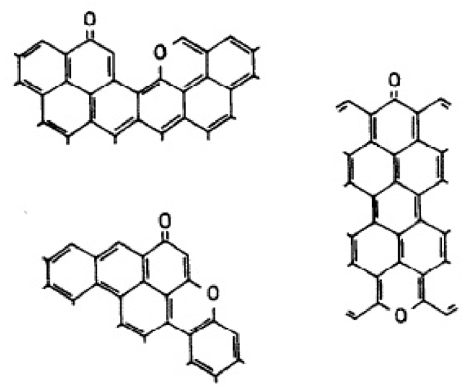


Figure2. Possible structures of basic surface sites on a grapheme layer, derived from the γ-pyrone structure.

Although the main aim of this study is to investigate the rheological properties of carbon black/silicon carbide suspensions order to make particulate Sic-Sic composites by colloidal process, an understanding of the flow behavior of the individual powder suspensions is desirable. This can only be achieved with an understanding of the factors which determine the flow behavior, e.g. the colloidal properties of the suspensions. Therefore the rheological behavior of single component suspensions has been examined as a function of pH and increase the solid concentration. As it was thought that the above properties of two component suspensions would depend mainly on carbon black, due to its finer particle size, a more detailed study of these suspensions has been carried out.

Experimental

Materials

The carbon black used in this study is furnace black manufactured by Iran Carbon Co. with trade name, V-6 and ASTM NO. N-220. The physical and chemical properties of carbon black are given in Table.1

Characterization of the powders

X-ray diffraction patterns of carbon black were obtained using a Philips X'Pert x-ray diffractometer over the range of scattering angles 15° to 90° for carbon black using CoK_α radiation of wavelength 1.7889Å.
Carbon black powders were examined using the scanning electron microscope Cambridge S360, and transmission electron microscope, Philips (FEG) – 200KV, for further analysis.

Table1. Physical and chemical properties of carbon black

Analytical Properties	ASTM Test Method	Result
Iodine Number, mg/g	D 1510	119
DBP Absorption, cc/100g	D 2414	111.5
Solvent Discoloration, T%	D 1618	97
Pour Density. Lb/ft^3	D 1513	20.7
Heat Loss % (as packaged)	D 1509	1.4
Fine Content, 120 M%	D 1508	3.2
Sieve Residue, 325 M%	D 1514	0.04
Tint Strength, %IRB3	D 3265	108.5
Ash (at 550 C), %	D 1506	0.65
Volatile Mater, %	D 1620	0.9
pH	D 1512	8.6
Free Sulfur %		0.008
Toluene Extract %	D 4527	0.06
Sulfur %	D 1619	1.8
N_2 Surface Area (M_2/g)	D 4820	113

Rheological Measurements

Flow curves and viscosities of suspensions were measured using a Rheometer (Physica Paar-GMBH-MCR3000). Prior to carrying out any rheological measurements the pH of all suspensions was determined using a pH meter. The meter was calibrated before use with buffer solutions of pH 4.0, 7.0 and 9 according to the pH value expected.
Throughout the study the pH of suspensions was altered using either 1 M NaOH or 1 M Hcl.

Preparation of suspensions

Suspensions were prepared by adding a known weight of dry powder to distilled water producing the required weight percent (in the range of 5-50%) suspensions. Several techniques were employed to disperse the powder in the fluid, the method and time of mixing depending on the solids concentration, volume and ease of mixing of the suspensions.

Effect of pH

The effect of altering the pH of 20w/o suspensions on their rheological behavior was carried out in the following way. The suspensions were made using 20g powder of carbon black to 100g distilled water, and placed on horizontal rollers for 24 hours, after which time little variation in flow properties was assumed. The pH of batch suspension was raised to 10.94, and a flow curve determined. The pH was then lowered in stages to pH 3.00, and at each point a measurement was taken. Throughout the experiment the pH of the entire batch suspension was altered and a small sample removed from this for measurement. These samples were not returned to the batch but discarded after use.

Effect of electrolyte additions

To examine the effect of Known molarity of a monovalent cation on the rheological properties of 20w/o carbon black suspensions, the above procedure was repeated with sufficient solid sodium chloride added to the batch suspension to give a) 0.05 M and b) 0.1 m sodium ions in suspension. In the former case the batch suspension was rolled for 90 min. before the pH was raised to 11. The suspension containing 0.1 M Na^+ was rolled overnight after the pH had been raised to 11.24.

To investigate and compare the effect which monovalent and divalent cations have on the flow behavior of 20 w/o carbon black suspensions, sodium chloride and calcium chloride were used (as the sources of cations) in the concentration range $\frac{0.05}{z^6}M$ to $\frac{1.0}{z^6}M$, where z is the cation valence. Prior to any addition of electrolyte, the pH of the suspension was raised to 11.50 and maintained at this value throughout the experiment.

Effect of solids concentration

The effect of increasing the solids concentration on the rheological behavior of carbon black suspensions was examined in the high pH range where suspensions of low solids concentrations are deflocculated. The pH of a known quantity of distilled water was raised to 11.4 and adequate amounts of carbon black powder added to equivalent volumes of water to give solids concentrations ranging from 5 to 50 w/o. The suspensions were mixed in a mixer for 15 minutes, after which time adequate dispersion of the powder was achieved. The pH was then raised to 11.5 ±0.15, and a flow curve measured.

Results and discussion

X-ray diffraction

A comparison with x-ray patterns of graphite shows that the diffuse peaks that were evident in the x-ray of carbon black are due to reflections from the 002, 100, 110 and 006 planes. This indicates a turbostratic arrangement (Fig. 3).

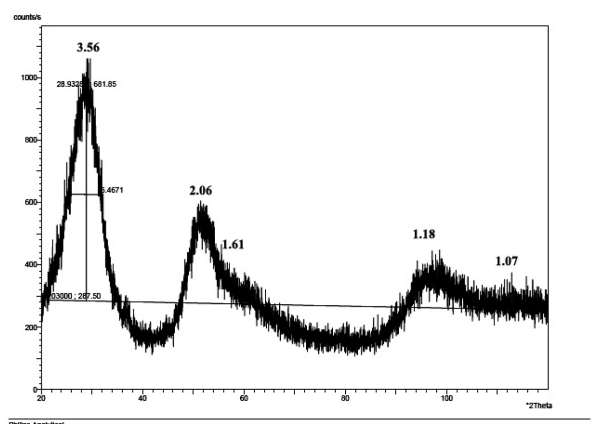


Figure3. X-ray pattern of carbon black

Microscopy

Micrographs of carbon black examined using the scanning electron microscope (SEM) and transmission electron microscope (TEM) and HRTEM are shown in figures 4 and 5. The carbon black particles were spherical with diameters ranging 20-50 nm.

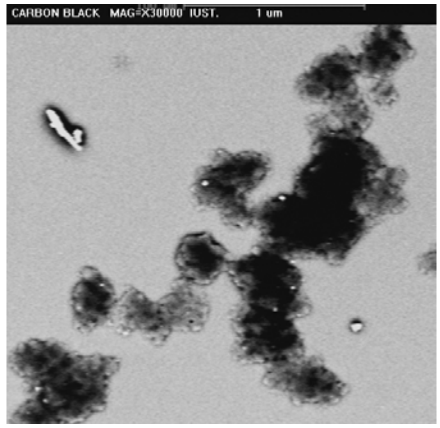
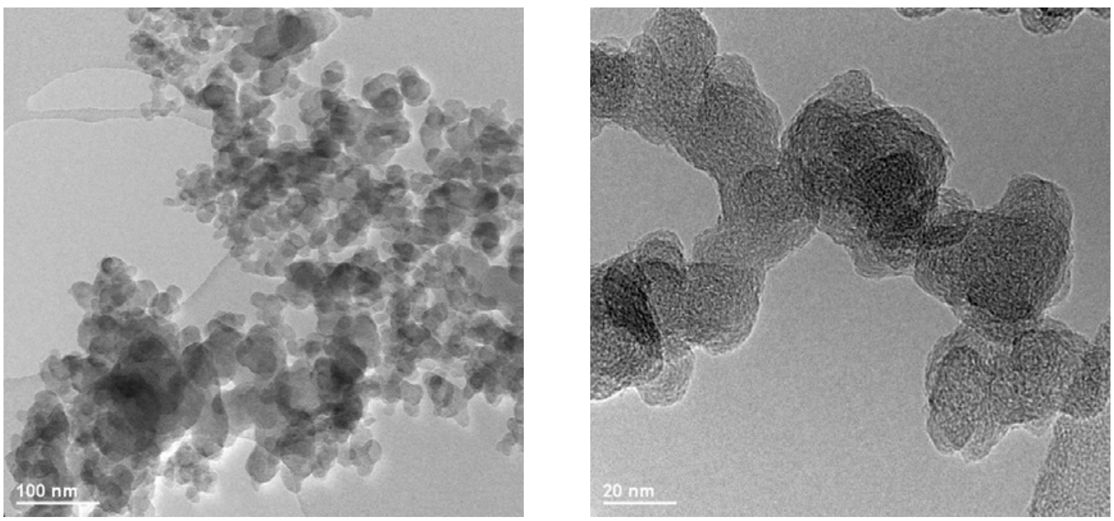


Figure4. SEM micrographs of carbon black



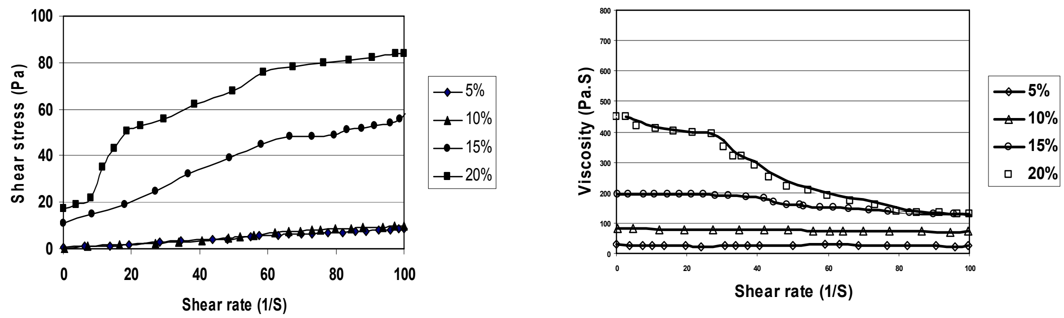
(a) (b)

Figure5. a) TEM, and b) HRTEM micrographs of carbon black

Rheological behavior of suspensions

Viscosity and yield stress measurements

Various forms of the flow curve were obtained with carbon black suspensions, some of which exhibited a yield stress. For systems other than Bingham, this can be expressed in terms of a yield stress. The true viscosity of Newtonian systems (10w/o carbon black suspensions) and the plastic viscosity of Bingham and pseudoplastic suspensions (15-20 w/o carbon black suspensions) have been measured by taking the inverse of the slope of the first ascending branch of the flow curve which has been extrapolated back to zero shear rates (Fig.6). For suspensions deviating from linear flow behavior, i.e. thixotropic, antitixotropic and Shear thickening suspensions, an apparent viscosity term has been determined, by taking the ratio of the value of shear stress to shear rate at the maximum shear rate of the system.



(a) **(b)**

Figure6. - Variation in a) Shear Stress and b) Viscosity with Shear rate for 5-20 w/o carbon black suspensions

Effect of pH and electrolyte additions

Figure.7 shows the effect of pH on the yield stress of 20 w/o carbon black suspensions containing different amounts of NaCl. Above pH 10, in the absence of added any electrolyte, these suspension were fully deflocculated, i.e. no yield stress was apparent. As the pH was decreased below 10, a yield stress was observed, which gradually increased as the pH was lowered further. The introduction of the yield stress was accompanied by a change in flow behavior from Newtonian to pseudoplastic. The presence of a monovalent cation produced a yield stress where one did not previously exist, and increased the size of any existing yield stress. This effect was more pronounced as the concentration was increased. This indicates that the more highly charged particles, i.e. the greater pH value, the lower shear stress which has to be applied to break down any interparticle structure, and the suspension flows a Newtonian fluid.

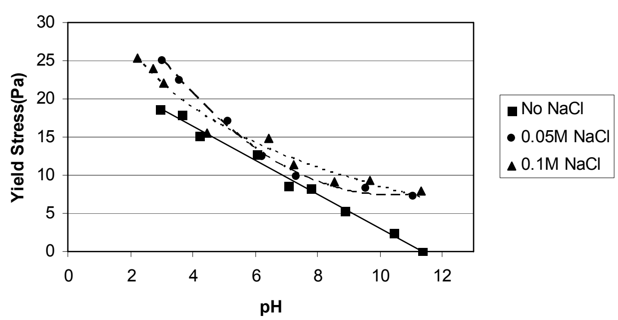


Figure7. Variation in Yield stress with pH and Sodium Ion concentration for a 20w/o carbon black suspension

The effect of pH and electrolyte additions on the yield stress value of carbon black suspensions can be explained in terms of the potential energy diagram (Fig.8). at pH values >10, in the absence of any electrolyte, the carbon black particles have a high surface charge density and potential and, since K[1] is low, repulsion forces between them are such that coagulation is prevented, by an energy barrier. As the pH is decreased below 10, a reduction in the surface charge density of the particles occurs, reducing the magnitude of the repulsion forces. This, and a simultaneous decrease in the height of the energy barrier allows the particles to approach closer to each other, resulting in coagulation, indicated by the appearance of a yield stress in the flow curve.

[1] 1/K= The thickness of electrical double layer

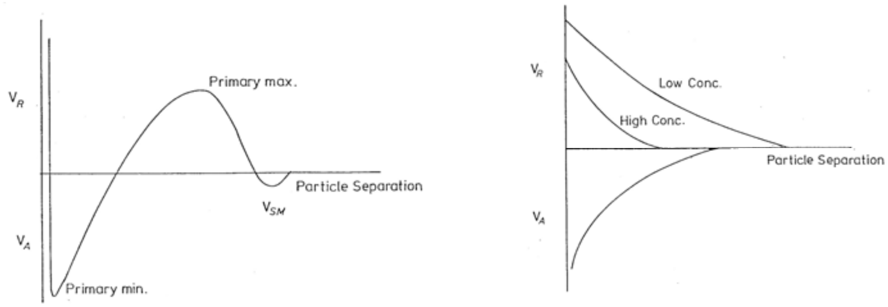


Figure8. Diagram of potential energy

A further reduction in pH will eventually result in the elimination of the energy barrier, together with an increase in the depth of primary minimum. This latter is a measure of the energy required to break any interparticle links, which in turn partly determines the yield stress of the system. Consequently an increase in the yield stress will be observed. The presence of electrolyte has the additional effect of compressing the electrical double layer around the particles, which reduces the range of the repulsion forces, and thus decreases the height of the energy barrier to coagulation. Thus at high pH, in the presence of electrolyte, there are two effects contributing to the elimination of the energy barrier and further increase in the yield stress will be observed. From the above results it is concluded that the rheological behavior of carbon black suspensions is very dependent on pH; therefore OH^- and H^+ are potential determining ions. The effect of cation additions on the yield stress indicate that they are in fact counter ions for carbon black particles, confirming previous finding that the surface is negatively charged. Consequently, the addition of divalent cations to carbon black suspensions should result in a far more pronounced effect on the yield stress than observed with Na^+, and this was examined as follows.
According to the DLVO theory, the critical coagulation concentration:

$$C \propto \frac{1}{z^6}$$

where z is the counter ion valance. Therefore the required concentrations of Na^+ and Ca^{2+} which should produce the same coagulation effect were added to 20w/o carbon black suspensions [7]. Figure9 clearly shows that in fact a concentration of divalent cations 64 times less than that of a monovalent cation does have a similar effect on the yield stress of these suspensions, as predicted.

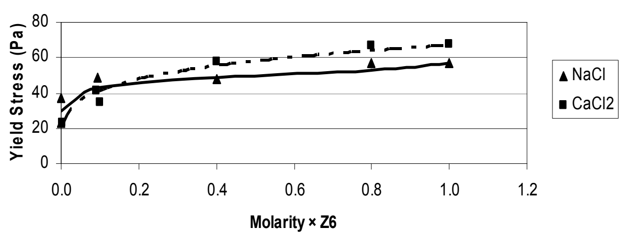
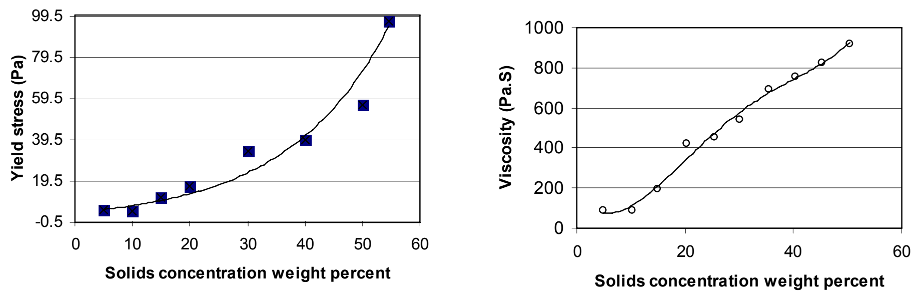


Figure9. Effect of increasing conc. of monovalent and divalent cation additions on the yield stress of a 20w/o carbon black suspension (pH=11.5)

Effect of increasing solids concentration

It has been shown that suspension of low solids concentration can be fully deflocculated using alkali alone. The work is now extended to determine whether suspensions of higher solids concentrations can also be deflocculated in this way, as in the slip casting industry, slips of as high solids concentration as possible are required to give a maximum density product.
Variation in yield stress and viscosity with increasing solids concentration are shown in Figure 10. At pH values of approx. 11.5, suspensions of up to 15 w/o exhibited Newtonian flow behavior.



(a) **(b)**

Figure10. a) Yield stress and b) Viscosity variation with solids concentration for carbon black suspensions (At pH 11.5)

However, an increase in the solids concentration beyond this level produced a change in this behavior: 20 and 25 w/o suspensions were pseudoplastic, whilst 30 to 45 w/o suspensions were thixotropic, and lastly, 50 w/o systems habited antithixotropy. The flow behavior of 30 and 50 w/o systems is illustrated in Figure 11. An increase in the viscosity and the introduction of a yield stress with increasing solids concentration was expected and can be explained as follows. Although at pH 11.5 the particles are highly charged, on increasing the solids concentration the suspension becomes 'over- crowded', and attraction forces between the particles become appreciable due to their close contact. The magnitude of the energy barrier is insufficient to prevent the particles entering the primary minimum, resulting in an appearance of the yield stress. As the number of particle is increased, the number of particle links which must be broken during shear, is increased, resulting in a greater value of the yield stress. Similarly, an increase in the volume fraction of particles in a suspension will lead to a gradual increase in the viscosity.

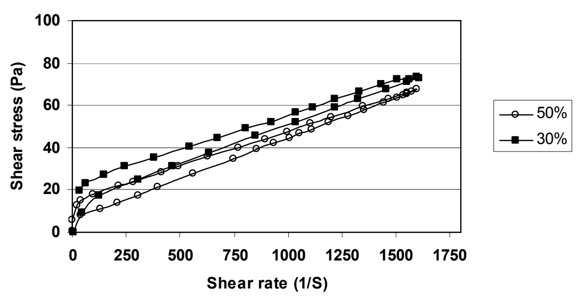


Figure11. Variation in flow behavior with increasing solids concentration of carbon black suspensions

The above results show that altering the pH alone is insufficient to deflocculate carbon black suspensions of high solids concentration, as the energy barrier to coagulation is of insufficient magnitude to prevent coagulation. It would thus appear that a deflocculating agent is necessary to confer stability on these suspensions.

Conclusion

1. As the pH of carbon black suspensions is increased the adsorption of OH^- or release of H^+ increases. This indicates an increase in the surface charge density of the carbon black particles which are negatively charged.

2. The rheological behavior of carbon black suspensions is markedly dependent on pH, which is in agreement with the concept that OH^- and H^+ are potential determining ions. At pH values > 10, suspensions of low solids concentration, (up to 15 w/o), are fully deflocculated, and the flow behavior is Newtonian. Below this value of pH, recoagulation of the suspensions is apparent and the flow behavior becomes pseudoplastic.

3. An increase in the yield stress and viscosity parameter was observed on increasing the solids concentration of carbon black suspensions beyond 15 w/o.

4. At pH values of approx. 11.5, suspensions of up to 15 w/o exhibited Newtonian flow behavior. However, an increase in the solids concentration beyond this level produced a change in this behavior: 20 and 25 w/o suspensions were pseudoplastic, whilst 30 to 45 w/o suspensions were thixotropic, and lastly, 50 w/o systems habited antithixotropy.

5. The addition of monovalent and divalent cations to carbon black suspensions results in coagulation in suspension which were originally Newtonian. The relative concentrations of cations required to produce the same yield stress are in agreement with the DLVO theory.

References

[1] Barrie, C.L., Griffith, P.C., Abbott, R.J., Grillo, I..,.Kudryashov, E, and Smyth, C.2004. Journal of Colloid and Interface Science (272): 210-217.
[2] Donnet, J., Bansal, R., Wang, M.1993."Carbon Black",., (second ed): 89-163.
[3] Luckham, P.F., UKEJE, M.A. 1999. Journal of Colloid and Interface Science (220): 347-356.
[4] Boehm, H.P. 1994. Carbon, (Vol.32):759-769.
[5] Studebaker, M.L. 1957. Rubber Chem. Tech. 30, 1400.
[6] Leon y Leon, C.A., Solar, J.M., Calemma, V. and Radovic, L.R. 1992. Carbon (30): 797.
[7] Wiley, J. and sons, edited by Holmbedge, K. 2001. Handbook of Applied surface and colloid chemistry, (Vol.1): 239-242.