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Selection of water-dispersible carbon black for fabrication of uranium oxicarbide microspheres

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Abstract

Fabrication of uranium oxicarbide microspheres, a component of TRISO fuel particles for high temperature nuclear power systems, is based on the internal gelation of uranium salts in the presence of carbon black. In order to obtain a high quality product, carbon black should remain dispersed during all phases of the gelation process. In this study, the surface and structural properties of several commercial carbon black materials, and the use of dispersing agents was examined with the goal of finding optimal conditions for stabilizing submicron-sized carbon black dispersions. Traditional methods for stabilizing dispersions, based on the use of dispersing agents, failed to stabilize carbon dispersions against large pH variations, typical for the internal gelation process. An alternate dispersing method was proposed, based on using surface-modified carbons functionalized with strongly ionized surface groups (sodium sulfonate). With a proper choice of surface modifiers, these advanced carbons disperse easily to particles in the range of 0.15–0.20 μm and the dispersions remain stable during the conditions of internal gelation.
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1. Introduction

The nuclear fuel for Generation IV very high temperature gas cooled reactors (VHTR) is based on microspheres containing a mixture of uranium oxide (UO_2) and uranium carbide (UC_2) coated with carbon and silicon carbide. This structure represents a significant improvement in efficiency, longevity, and safety of nuclear fuels. The interest in production of UO_2–UC_2 kernels has been revived in the last few years. In the late 1970s, laboratory-scale ($UO_3 \cdot 2H_2O$–C) gel spheres were first prepared at Oak Ridge National Laboratory (ORNL) [1,2]. The process was based on the sol–gel reaction between an acid-deficient uranyl nitrate (ADUN) aqueous solution (pH 1.9–2.0) and a solution of hexamethylenetetramine (HMTA) and urea in water (pH 10–10.5), a process referred to as internal gelation. In the early studies at ORNL, carbon black was dispersed with a surfactant and was introduced in the process before the gelation step. Several batches of dried gel spheres were prepared with C/U mole ratios of 0.8–1.2:1, which were sintered to make uranium 'oxicarbide' ($UO_2 + UC_2$) kernels. However, no optimization of formulation or of process conditions was attempted at that time. Subsequently, more in-depth studies on the chemistry of internal gelation in the ADUN–HMTA/urea system [3,4] led to a better understanding of process variables, and made possible production of several batches of good quality UO_2 kernels at ORNL in 2004 [5].

Production of high quality carbon-containing kernels was not without difficulty. A key requirement to obtain

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high kernel density is the uniform distribution of carbon in the UO_2 gel spheres before the thermochemical step; i.e. during the gel formation step. Uranium carbide is formed by direct reduction of UO_2 with carbon, and therefore the presence of large carbon particles or agglomerates is undesirable because they will create voids during sintering. It was proposed that, in order to obtain good kernel density, carbon particles should be dispersed to smaller than 5 μm in size, and preferably smaller than 1 μm in size. Carbon dispersions must withstand large pH variations between the initial pH of HMTA/urea solutions (pH 10–10.5), or alternately that of ADUN solutions (pH 1.9–2.0), and the final pH in the mixed broth at gelation conditions (pH 4.4–4.5). Dispersions must also withstand a large background ionic concentration from dissolved electrolytes (about 2.6–2.9 M for UO_2^{2+} and about 4.4 M for NO_3^- in the ADUN solution) and competition from high concentrations of HMTA and urea (about 3.18 M each in the initial solution).

The correct choice of carbon black and of dispersing conditions is critical for producing dispersions with the required properties and high stability needed for preparation of uniform uranium oxicarbide kernels. Stabilizing the dispersions through all stages of the sol–gel process requires a good match of surface properties of carbon black with the solution parameters and the nature of the dispersing agent used. This paper reports on the results of a thorough characterization of several types of carbon black, selected as possible candidates for the process. Characterization of the surface chemistry of carbon black by potentiometric titration measurements (pK_a spectra) provided a comprehensive picture of pH effects on the factors influencing the dispersion stability. The results were complemented by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy. The best results were obtained by using surface-modified carbons with strongly ionized surface functions chemically grafted on their surface [6].

2. Background

Carbon blacks consist of nanometer-size particles which are bound together into aggregates of various shapes and structures. The aggregates, which are the characteristic units of carbon black, may cluster into larger agglomerates forming fluffy free-flowing powders, or may be bonded into beads. Under ideal dispersion conditions, the agglomerates are broken down into primary aggregates (usually of sub-micrometer sizes). Methods to stabilize dispersions against re-agglomeration include promotion of surface wetting of aggregates, development of electrostatic repulsions, or coating with adsorbed bulky polymer molecules.

Both physical and surface chemical properties of carbon black affect its dispersability. Carbon blacks with small particles (high surface area) are more difficult to disperse. Carbons with a compact structure of aggregates ('low-structure carbons') are more difficult to disperse than carbons with open, complex structures ('high-structure carbons'). The presence of polar chemical groups on the carbon's surface (carboxyls, phenols, lactones, and quinones) is beneficial because they improve wetting and aid in the development of electrostatic charges. All physical factors being constant, carbon blacks with higher volatile content would disperse easier. Some carbons are specially treated (oxidized) in the manufacturing process to improve water dispersability. However, not all surface groups are identical: the pH response of surface groups (or their acid–base character) is an important, but often overlooked, factor that should be considered in a discussion of carbon black dispersability.

Traditionally, dispersability is improved by using dispersing agents (surfactants). Their action is based on dynamic adsorption of the surfactant's non-polar tail segments at the hydrophobic surface of carbon black, and solvation of the hydrophilic heads oriented outwards. Surfactants with ionisable groups (weak acids or bases) develop a pH-dependent charge at the carbon–water interface; their effectiveness is strongly pH-dependent, such that anionic surfactants can only be used in basic solutions, and cationic surfactants are limited to acidic solutions. Non-ionic surfactants contain polar groups (e.g., polyethers) and their dispersing action is not pH-dependent; the drawback is that these bulky surfactant molecules must be used at high concentrations because of the lower hydrophilizing effect of non-ionic polar groups [7]. A newer alternative to the traditional dispersing methods based on dynamic surfactant adsorption is the use of surface modified carbons with suitable chemical groups grafted on their surface by strong chemical bonds. This makes possible a better tuning of surface properties through selection of grafted chemical groups, and allows better control of the surface concentration of modifiers. Because surface modifiers are chemically bonded to carbon the dispersions are more stable against variation of solution conditions (pH, ionic strength).

3. Materials and methods

The materials selected for this study were low surface area, high purity carbon blacks available commercially from Columbian Chemical Company (Raven 1000, Raven 1040, and Raven M) and from Cabot Corporation (Black Pearls L). Dispersion of these carbons was aided by the addition of surfactants; several types of surfactants were tested, including ionic (anionic) and non-ionic. The results were compared against several types of surface-modified carbons developed by Cabot Corporation using diazonium salts [8]. A demonstration kit of carbon black samples modified with various surface groups was obtained from Cabot Corporation. It included the unmodified carbon (sample A), an oxidized counterpart (sample B), and carbons modified with aliphatic amino groups (sample E), carboxyl groups (sample F), and sodium sulfonate functions (sample G).

The surface properties of several carbon black samples selected for this study were characterized by N_2 adsorption at 77 K using the Autosorb-1 instrument (Quantachrome Instruments). The BET surface area [9] and the statistical thickness surface area were measured according to a procedure following closely the ASTM method D 6556-04 for surface area characterization of carbon black [10]. The statistical thickness (or *t*-method) surface area represents the external area, not included in the micropore system [11]. The distribution of surface area by pore widths, and the cumulative pore volume were calculated using the non-local density functional theory (NLDFT) software available with the Quantachrome instrument (version 1.51).

The volatile content of carbon blacks was measured thermogravimetrically using the Hiden Analytical IGA-1 gravimetric analyzer. Carbon samples were first degassed in dynamic vacuum (<10 Pa) at room temperature for 2 h, and then heated under vacuum at 3 °C/min to 800 °C. Percentage weight losses were calculated relative to the weight of the sample after initial degassing.

X-ray photoelectron spectroscopy (XPS) analysis spectra were collected at the Evans Analytical Group laboratory in New Jersey, using a Physical Electronics 570 LSci instrument with monochromatic aluminium source. The approximate escape depth for carbon 1s electrons was 7 nm. The quantification of elements was accomplished by using atomic sensitivity factors from Physical Electronics MultiPak software (version 6.1 A).

An automatic titration station (Titrino 798 from Brinkmann Instruments Inc.) was used for potentiometric titration; it was equipped with a Brinkman pH-sensitive glass electrode and the system was controlled by the Vezuv 3.0 software (Brinkmann Instruments, Inc.). All solutions were made using ultra-pure deionised water ($0.2\ \mu S\ cm^{-1}$). In a typical run, 0.5 g carbon black was added to 50 mL electrolyte solution ($NaNO_3$ 0.1 N) in a 100 mL thermostated jacketed titration vessel. Argon bubbling was used continuously to remove CO_2 traces. A carefully measured volume of either 0.1 N HNO_3 or 0.1 N NaOH was used to shift the pH to either acidic or basic range; the pH window where accurate measurements were possible was between 3.5 and 10.5. After equilibration for at least 6 h, a monotonic equivalent point (MET) titration run was started, where 0.020 mL increments of either 0.1 N NaOH or 0.1 N HNO_3 were added with the highest delivery rate allowed by the system. The equilibration time for each titrant addition was 300 s or shorter if stable pH was achieved sooner. The most restrictive pH equilibration condition allowed by the Titrino system was used (drift smaller than 0.5 mV/min or 0.0085 pH/min). A complete run lasted between 12 and 20 h, depending on sample. Stirring and argon bubbling continued during all data collection.

Fourier-transformed infrared (FTIR) spectra were recorded in the transmission mode using a BioRad FTIR spectrometer. Carbon samples dried overnight were mixed with large amounts of spectroscopic pure KBr and pressed as thin tablets.

The particle size distribution of selected carbon black dispersions in water was measured using a Horiba 700 LA laser particle analyzer operating with a 632.8 nm He–Ne laser. The dispersions were obtained in the measuring cell of the instrument using the vortex stirrer (1 min) and/or the mild sonicator (up to 15 min) furnished with the instrument.

4. Results

4.1. Surface properties

The results in Table 1 shows the total BET surface area, the external (or statistical thickness) surface area, the surface area in the micropores, the micropore volume, and the cumulative DFT pore volume. Carbon blacks are non-porous carbons, as shown by all data in Table 1. Only Black Pearls L showed internal porosity (though very small), most likely a result of post-treatment oxidation by the manufacturer. Density functional theory (DFT) calculations (Fig. 1) showed that about 80 m^2/g of this carbon's surface is contained in pores smaller than 2 nm. In contrast, for carbon blacks in the Raven series, only about

Table 1
Selected properties of carbon black materials evaluated by various techniques

	BET total surface area (m^2/g)	External surface area (*t*-method) (m^2/g)	Surface area in micropores (*t*-method) (m^2/g)	Cumulative pore volume (NLDFT method) (cm^3/g)	Micropores volume (*t*-method) (cm^3/g)	Results of elemental analysis (%)		Volatile content (weight losses to 800 °C) (%)
						O	N	
Black Pearls L	141	114	27	0.10	0.02	n/a	n/a	4.8
Raven 1000	106	106	0	0.13	0	3.1	0.1	4.1
Raven 1040	97	95	0	0.07	0	n/a	n/a	3.8
Raven M	81	79	0	0.06	0.01	2.4	0.2	2.3
Cabot sample A (pristine)	104	104	0	0.08	0	n/a	n/a	n/a
Cabot sample B (oxidized)	123	123	0	0.09	0	n/a	n/a	n/a
Cabot sample E (amino)	n/a	n/a	n/a	n/a	n/a	5.8	0.4	n/a
Cabot sample F (carboxyl)	80	80	0	0.06	0	5.8	0.9	n/a
Cabot sample G (sulfonate)	85	84	1	0.06	0	5.5	0.2	5.9

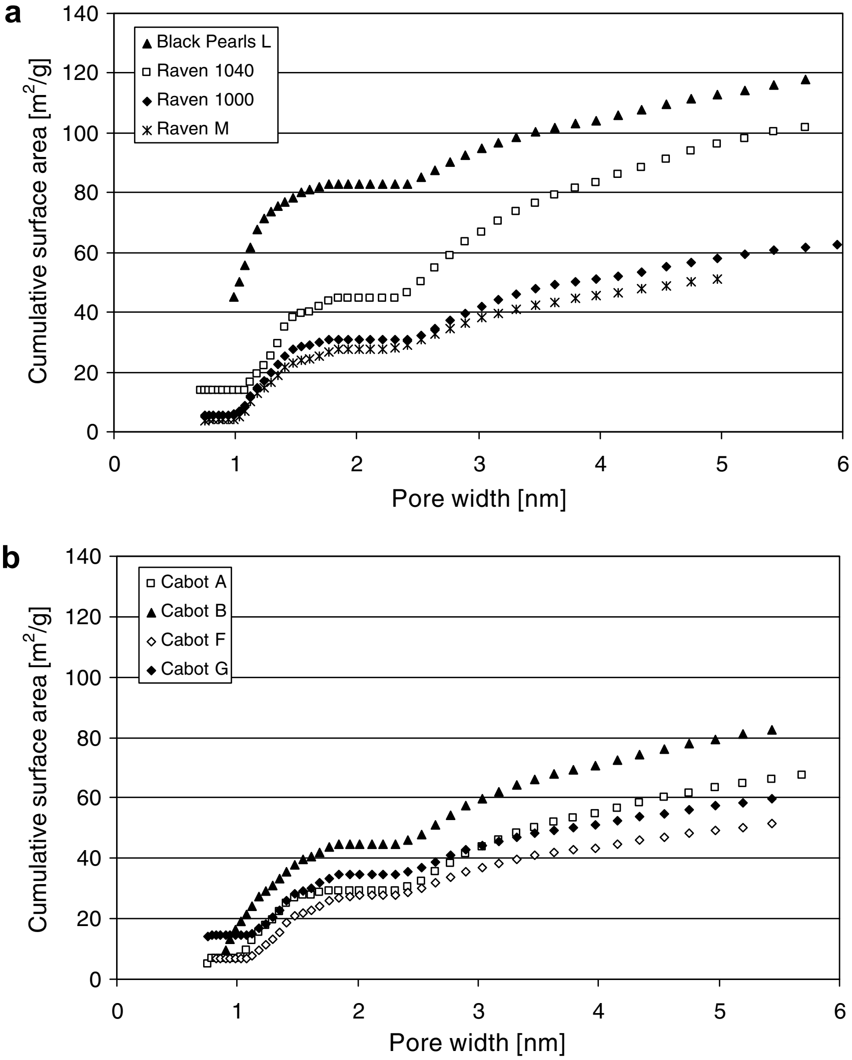

Fig. 1. Cumulative surface area versus pore width measured by nitrogen adsorption at 77 K. The slit pore model was used for density functional theory calculations: (a) commercially available carbon black samples; (b) surface-modified carbons from Cabot samples kit.

20–40 m^2/g of total surface area is contained in ‘pores’ <2 nm in size, which were most probably located at contact points between primary particles having sizes in the 20–30 nm range (based on electron microscopy results). Some of the surface-modified carbons (i.e. Cabot sample E) could not be characterized by nitrogen sorption because of the low thermal stability of surface modifying groups.

4.2. Volatile content

The results on volatile content shown in Table 1 and Fig. 2 confirmed the information from vendors, according to which Black Pearls L and Raven 1000 are surface-oxidized carbons, while Raven M is not. In addition to water loss peaks at about 100 °C, the differential weight loss curves by thermogravimetric analysis (Fig. 2) show two more desorption peaks for the oxidized carbons Black Pearls L and Raven 1000. Based on literature data [12], the latter were assigned to decomposition of carboxylic groups (at 300–350 °C) and of phenols or lactones (at about 600 °C) that may be present on the carbon surface. Fig. 2 also shows that the decomposition of surface groups grafted on Cabot sample G occurs at about 500 °C.

4.3. Surface chemical analysis

XPS analysis was used for additional characterization of elemental surface composition of selected samples. Both survey spectra (for elemental identification) and high resolution spectra (for characterization of chemical bonding states) were collected for an oxidized carbon black (Raven 1000), a non-oxidized carbon black (Raven M), and a surface-modified carbon black (Cabot sample G). Overlay high resolution spectra in Fig. 3 show the main differences between these samples in the energy range corresponding to carbon, nitrogen, oxygen, sodium, and sulphur, as well as for the vacant 3p states in the valence band (V 3p).

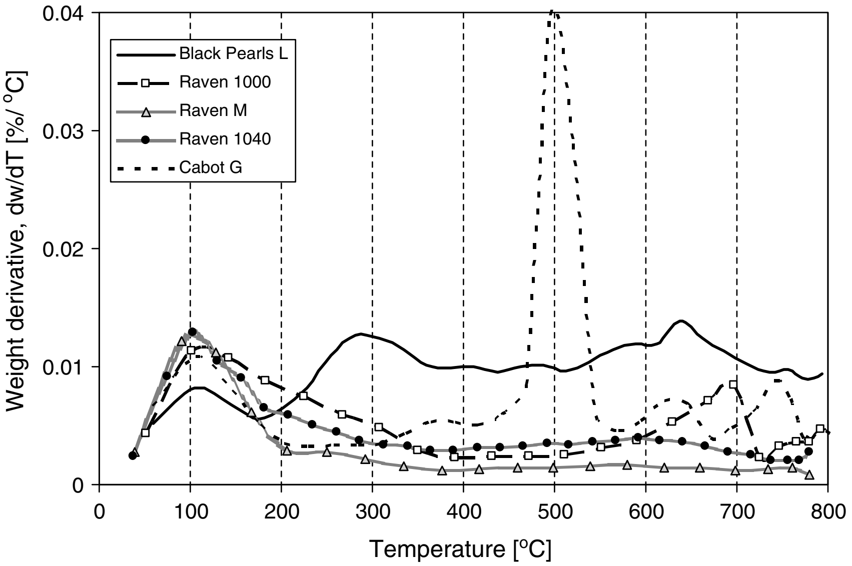

Fig. 2. Differential weight loss curves for selected carbon black samples upon thermal treatment under vacuum.

The analysis of XPS spectra did not reveal significant differences between samples Raven 1000 and Raven M. For both samples, the main peak at 284.6 eV (C 1s) indicates the predominance of C–C and C–H bonds. A continuous feature was apparent at high energies, which could be assigned either to various surface oxides (Table 2), or could be interpreted as a continuous energy loss specific to graphitized materials. Oxygen was more abundant on the surface of Raven 1000 (1.4 at.%) than on Raven M (0.4 at.%), and the O 1s peak (532.5 eV) indicates that oxygen is bonded to carbon. The oxygen peak in surface-modified Cabot sample G has a component at 536.3 eV, indicating oxygen bonded to sulphur. For this sample, XPS revealed a larger concentration of sulphur (2 at.%) and oxygen (7.2 at.%) on the surface. The sulphur peak (S 2p) was deconvoluted into components assigned to organic sulphur (S–C,H) at 163.9 eV and S^{4+} (sulfates, sulfonates) at >168 eV; the latter peak is very evident on Cabot sample G. The sodium peak found on this sample was assigned to Na^+. The valence band region of sample Cabot G showed distinct peaks corresponding to Na 2p (29.3 eV) and O 2s (22.9 eV) electron levels, besides a broad feature below 20 eV which originates from C 2s (12–22 eV) and C 2p (5–12 eV) electron levels and is common to all three carbon black samples. Collectively, this information confirms that sample G was modified with $-SO_3Na$ (sodium sulfonate) functional groups.

4.4. Acid–base properties and pH effects

More specific information on the pH effect on surface chemical groups on carbon black samples was obtained by direct characterization of acid–base properties by potentiometric titration. Oxygen, which is by far the most common heteroatom present on most carbon surfaces, participates in a broad spectrum of surface groups that may potentially exist on carbons (Fig. 4). Of these groups, some have acid–base properties (such as carboxylic groups, which are weak acids, or phenolic groups, which are very weak acids), some others have redox properties (like the quinone–phenol couple), and others are neutral or not active in normal conditions (ketones, esters). The basicity of carbons is usually associated with the presence of Brönsted basic groups (pyrones), Lewis basic sites (π electrons on basal planes of micrographitic structures), or the effect of oxidation followed by proton binding at several redox-active sites (chromene, phenoxide) [13].

The acidic strength of various functional groups that decorate the carbon surface is characterized in terms of acidity constants (pK_a), which are derived from the mass action law of the acid–base equilibrium:

$$\equiv \mathrm{S-H} \leftrightarrow \equiv \mathrm{S}^- + \mathrm{H}^+$$
$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a} = -\log[\{\equiv \mathrm{S}^-\}[\mathrm{H}^+]/\{\equiv \mathrm{S-H}\}], \qquad (1)$$

where ≡S represents a surface site on carbon and { } and [ ] symbols are used for surface concentrations and solution concentrations, respectively.

The potentiometric titration method for identification of surface groups with acid–base properties is based on measuring the pH response of carbon dispersions in an aqueous electrolyte upon controlled additions of strong acid or strong base. A proton balance is calculated by comparing the equilibrium pH after addition of titrant with the pH expected for blank conditions (either calculated or measured). The result is a proton binding isotherm, which shows the amounts (millimoles) of protons bound or released per gram of carbon sample as a function of solution pH. This experimental proton binding isotherm is an average property of all proton binding equilibria on surface groups, each with its own acidity constant. Assuming that the distribution of acidity constants pK_a is continuous, the distribution function $F(pK)$ can be calculated from the

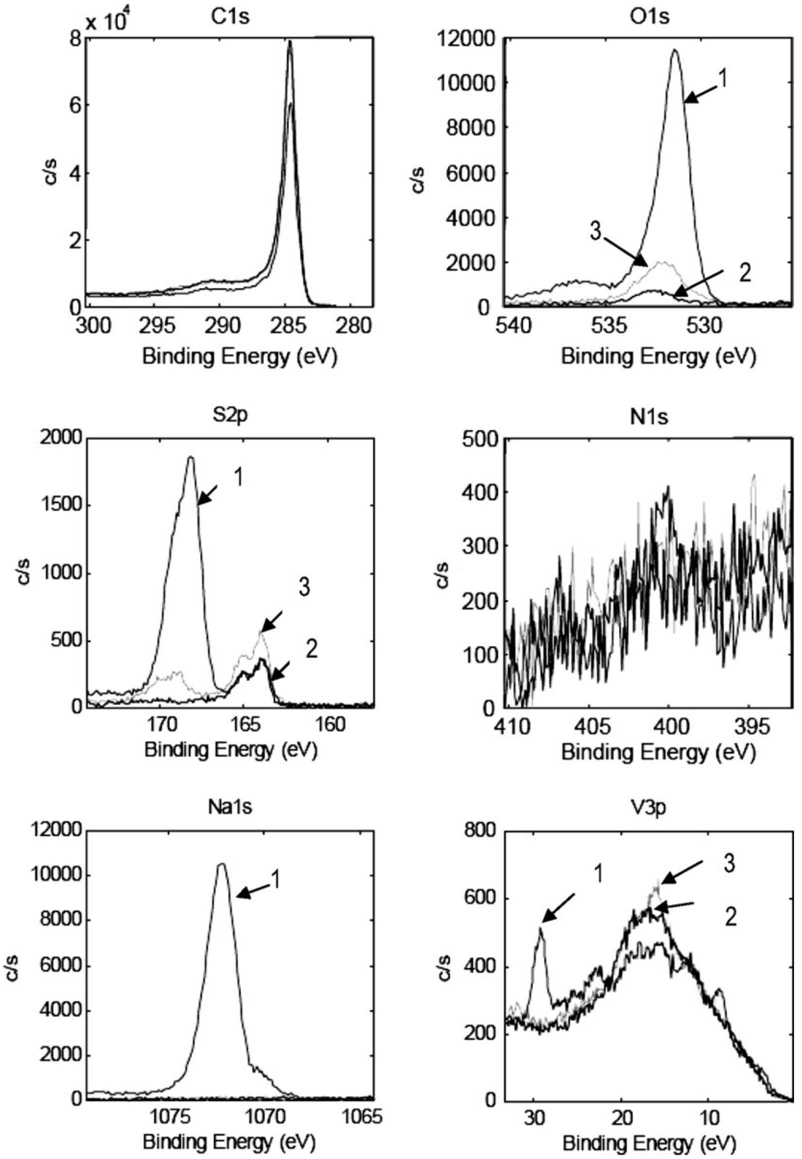

Fig. 3. Overlaid high resolution XPS spectra of representative elements (C, O, N, S, Na) and of the valence band (V) region for selected carbon black samples: 1 – Raven Cabot sample G; 2 – Raven M; 3 – Raven 1000.

Table 2
Effects of surfactants, medium composition and pH on the viscosity values of typical carbon black dispersions obtained with various carbons

Test no.	Carbon Black	Surfactant	Medium	Sonication (min)	pH	Viscosity (cP)	Notes
1	Black Pearls L	Tamol SN	HMTA–Urea	30	10	18.5	
2		Tamol SN	HMTA–Urea–ADUN	90	4.7	49	Optimal DAR[a]
3	Raven 1000	Tamol SN	HMTA–Urea	30	10	19.2	
4		Tamol SN	HMTA–Urea–ADUN	30	4.5	53	Optimal DAR
5		BorchiGen12	HMTA–Urea	30	10.5	>100	
6		Tergitol XD	HMTA–Urea	30	10.5	>100	
7	Raven M	Tamol SN	HMTA–Urea	30	10.5	19.6	
8	Sample E	None	HMTA–Urea	0	10	18	
9		None	HMTA–Urea–ADUN	0	4.7	9.6	Gelation problem
10	Sample F	None	HMTA–Urea	0	10	22	
11		None	HMTA–Urea–ADUN	0	4.7	11.6	Gelation problem
12	Sample G	None	HMTA–Urea	0	10	18.1	
13		None	HMTA–Urea–ADUN	0	4.6	32	Recommended

[a] DAR = 'dispersant agent requirement,' a measure of the amount of dispersing agent that produces the optimal dispersion results.

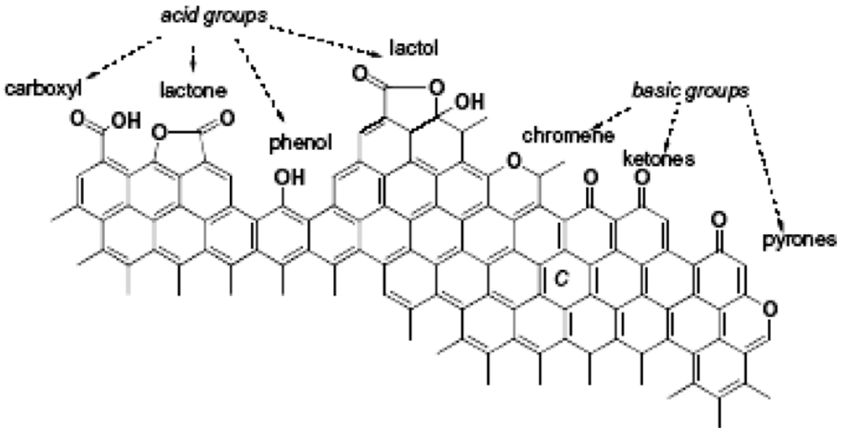

Fig. 4. Schematic representation of oxygen-containing functional group on edge sites of graphene layers in carbon [13].

experimental proton binding isotherm, $Q(\mathrm{pH})$, by solving the following integral equation [14]:

$$Q(\mathrm{pH}) = \int_{\mathrm{p}K_{\min}}^{\mathrm{p}K_{\max}} q(\mathrm{pH}, \mathrm{p}K_\mathrm{a}) F(\mathrm{p}K_\mathrm{a}) \mathrm{dp}K_\mathrm{a} + Q_0, \tag{2}$$

where $q(\mathrm{pH}, \mathrm{p}K_\mathrm{a})$ is the local binding isotherm for the acid–base sites with acidity strength pK_a, and Q_0 is a constant background term. The proton affinity distribution function $F(\mathrm{p}K_\mathrm{a})$ is in fact the pK_a spectrum of the carbon surface. It describes the distribution of surface groups (mmoles/g) as a function of their acid strength (or pK_a). Developed first for characterization of surface hydroxyls on oxide materials [14], the potentiometric method for calculation of pK_a spectra was later extended to characterization of acid–base properties of carbon materials [15–17], and evolved as a powerful alternative [18,19] of the classical Boehm titration method [20] for characterization of surface functional groups on carbon.

Fig. 5 shows proton binding isotherms measured in separate titrations with acid or base. Negative values of $Q(\mathrm{pH})$ indicate development of negative surface charges by dissociation of protons from weak or very weak acidic groups. The pK_a spectra calculated from these data using a regularization method (SAIEUS code [21]) are shown in Fig. 6.

The results show an interesting correlation between the volatile content reported above and the acid–base response of surface chemical groups. The most oxidized carbons (Raven 1040 and Black Pearls L) with the highest volatile content (Table 1) have acidic immersion pH and develop the largest amount of negative surface charge in basic solutions (Fig. 5); this is indicative of a large concentration of acidic surface groups. In contrast, the carbons with low volatile content (Raven M and Raven 1000) have amphoteric properties and a small concentration of surface groups.

The pK_a spectra of Fig. 6 were further used for identification of functional groups on various carbons, based on typical pK_a values for organic functions [22]. The dominant groups on all carbons are phenols (pK_a 9–10.5) and lactones (pK_a 7–8); carboxyl groups (pK_a 4–5) are also present on all commercial carbons, though in very low concentration (Fig. 6(a)). The Black Pearls L carbon, with the highest volatile content of all commercial carbons, exhibits the most complex pK_a spectrum, with a large population of phenolic groups along with functions of lower pK_a, presumably carboxyls and lactones. In the group of surface-modified carbons (Fig. 6(b)), only the unmodified carbon (sample A) and the carbon modified with $-\mathrm{SO_3Na}$ groups (sample G) have neutral immersion pH; all other carbons are acidic. The pK_a spectrum of the unmodified Cabot sample A has a striking resemblance with that of the commercial sample Raven 1000; both carbons have neutral immersion pH, characteristic to a low degree of surface oxidation and low concentration of surface groups. The fact that the pK_a spectrum of sample G, which contained $-\mathrm{SO_3Na}$ groups, is also almost featureless is not surprising (Fig. 6(b)). Sodium sulfonate is a derivative of a very strong acid (sulfonic acid, p$K_\mathrm{a} = -6.5$) and a very strong base (sodium hydroxide, p$K_\mathrm{a} = 15.7$); although in large concentration on sample G, neither one of these groups has acid–base reactions in the experimental pH window of the potentiometric titration ($4 < \mathrm{pH} < 10$). The pK_a spectra of the remaining surface-modified samples in Fig. 6(b) show a gradual increase in number of peaks in the pH range between 4 and 10. However, further assignment of these peaks was not attempted because the titration technique cannot distinguish between genuine reactions of carbon surface groups and the solution reactions of associated counter-ions, which may be present in large amounts on some surface-modified carbons.

4.5. Infrared spectra

Because of the low surface area and the low number of functional groups on carbon black, the quality of FTIR spectra was poor (Fig. 7). However, several qualitative conclusions could be drawn, which were in line with other characterization techniques. In the group of commercial carbon blacks, distinct features were identified at 3430–3460 cm^{-1} and 1000–1200 cm^{-1}, confirming the presence

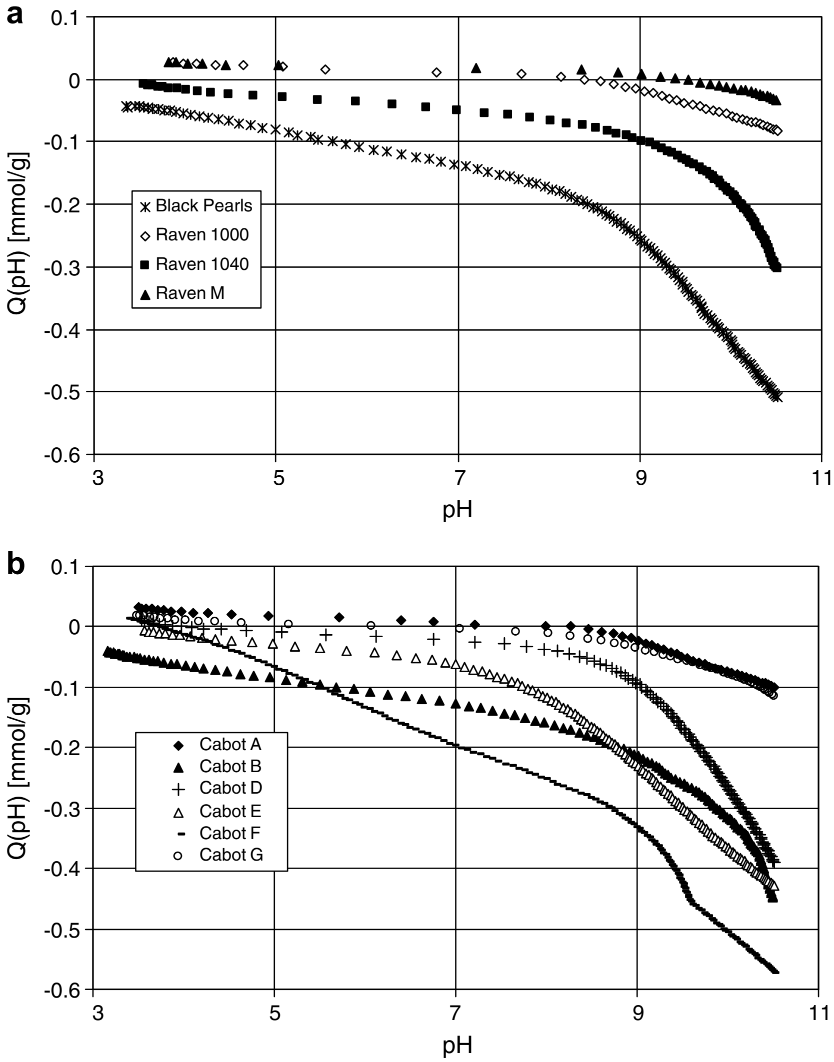

Fig. 5. Proton binding isotherms measured by separate potentiometric titrations with either 0.1 N HNO_3 or 0.1 N NaOH. The electrolyte (0.1 N $NaNO_3$) was continuously bubbled with argon in order to remove dissolved CO_2.

of phenolic hydroxyl groups on all samples. Phenolic groups were also found by potentiometric titration and identified with the dominant peaks of most pK_a spectra in Fig. 6. In the group of surface-modified carbons, the presence of sulfonate groups (not revealed by pK_a spectra) was confirmed on sample Cabot G (broad bands at 1117 and 1179 cm^{-1}). The carboxyl groups on sample F could not be identified in FTIR spectra because of the overlap with features caused by residual water traces at 1660–1769 cm^{-1}, but these groups were clearly demonstrated by the peaks at pK_a 4–5 in the proton affinity distribution spectra in Fig. 6. The amino groups on sample E were identified through the pair of bands at 1050 and 1213 cm^{-1}.

4.6. Dispersions characterization

The viscosity of selected compositions was measured in conditions simulating the dispersion of carbon black, either in the basic component (urea–HMTA aqueous solution) or in the acidified broth (after addition of ADUN), under conditions comparable to the pH and temperature of the gelation process. A Brookfield DV-III rheometer was used and the sample temperature was closely controlled at 5 °C. All solutions were non-Newtonian; i.e., the measured viscosities varied with the shear rate in the rheometer. The viscosity values reported in Table 2 were measured at a constant shear rate of 5 rpm.

5. Discussion

Historically, an anionic dispersing agent (Tamol SN) was used to disperse Raven 1000 at the basic pH of aqueous HMTA/urea solutions. Tamol SN (from Rohm and Haas) is the sodium salt of a naphthylmethane sulfonate condensate. The mechanism of its dispersing action is a two-fold: bulky, hydrophobic naphthalene rings are dynamically adsorbed on non-polar patches of the carbon surface, and the anionic sulfonate groups induce strong

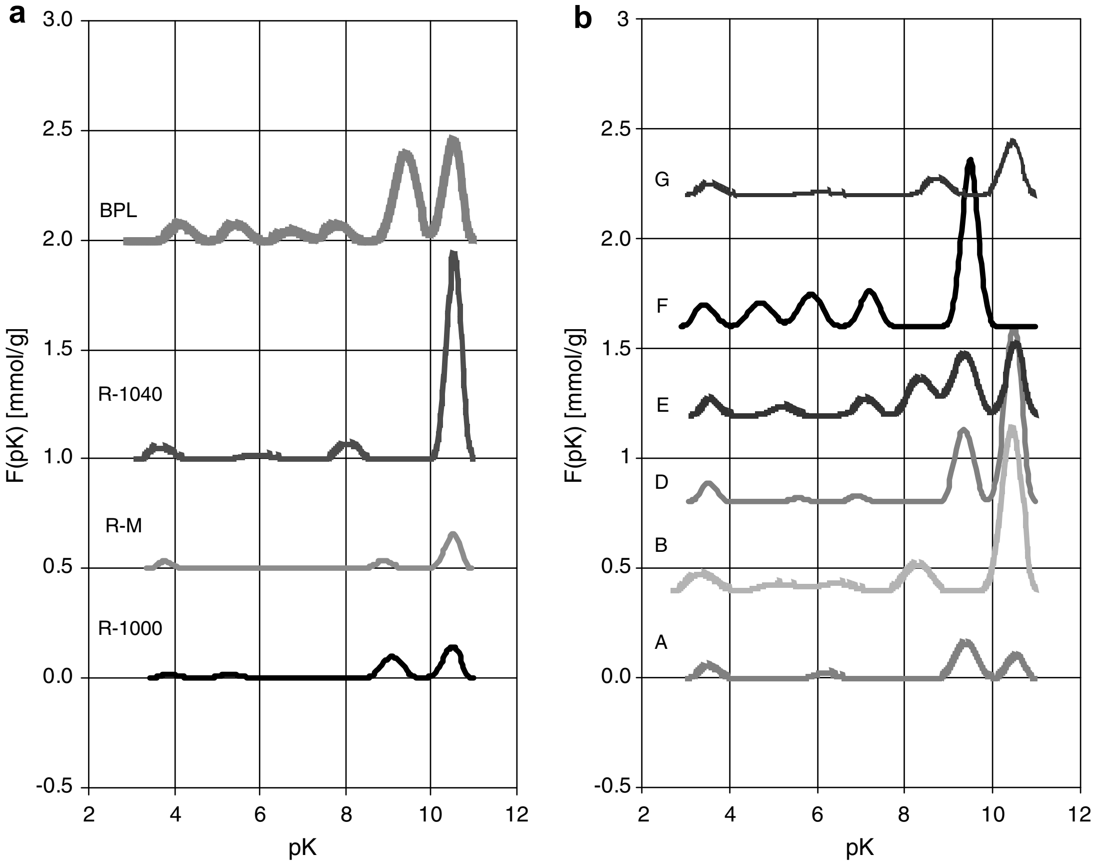

Fig. 6. Proton affinity distribution (pK_a spectra) of functional groups identified on carbon black surface by analysis of potentiometric titration data. The curves are shifted arbitrarily on the vertical axis for convenience. (a) Commercial carbon blacks: Raven 1000 (R-1000), Raven M (R-M), Raven 1040 (R-1040), and Black Pearls L (BPL); (b) selected surface-modified carbons (samples A, B, D, E, F, and G) from the Cabot sample kit.

electrostatic repulsions between carbon black aggregates. Because sulfonate groups carry a negative charge at any solution pH, the amount of surfactant required to stabilize the dispersion depends on the amount of dispersing agent that is actually adsorbed on the hydrophobic sites of carbon black aggregates. The latter depends on the surface chemistry of carbon black: the more oxidized (or more hydrophilic) the carbon, the lower is the number of hydrophobic sites available for adsorption of the surfactant. As a consequence, more surfactant is needed in solution in order to build a large enough surface density of negative charges able to produce a stable dispersion at a given pH. However, this is opposed by the fact that, even in the absence of a surfactant, oxidized carbons develop negative surface charges through dissociation of their acidic surface groups (i.e. carboxyls, phenols, etc.). On the other hand, deprotonation of weakly acidic groups is strongly dependent on solution pH, as shown, for example, by the proton binding isotherms in Fig. 5. The balance of these two opposite trends determines a complex effect: in general, it is considered that oxidized carbon blacks require less dispersing agent to form stable dispersions than their unmodified counterparts, but the dispersing agent requirement for particular conditions is strongly dependent on pH. For anionic surfactants (Tamol SN) and an oxidized carbon (such as Black Pearls L), the dispersing agent requirement increases abruptly in the acidic range [23]. This fact explains why early attempts to disperse carbon black (Raven 1000 and Black Pearls L) using the anionic dispersant Tamol SN rendered the dispersions unstable as the pH was shifted from basic to acidic, even if excessively large amounts of surfactant were used. The destabilizing effect of acidulation was easily detected as a sudden increase in the viscosity when ADUN was added to apparently stable dispersions prepared in HMTA-urea solutions (compare lines 1, 2, 3, and 4 of Table 2).

Non-ionic surfactants are insensitive to pH changes. Most non-ionic surfactants consist of hydrophilic ether groups grafted onto a hydrophobic backbone. Their dispersion action results from the competition between the hydrophobic and hydrophilic characteristics of various molecular segments. However, the hydrophilizing effect of ether polar groups is lower than that of ionized functions; consequently, most non-ionic surfactants must be large molecules, with numerous polar groups, in order to develop effective dispersing properties. They are more efficient at much higher solution concentrations than ionic surfactants. However, these facts lead to undesired consequences in that, at equal carbon black loading, dispersions prepared with non-ionic surfactants have higher

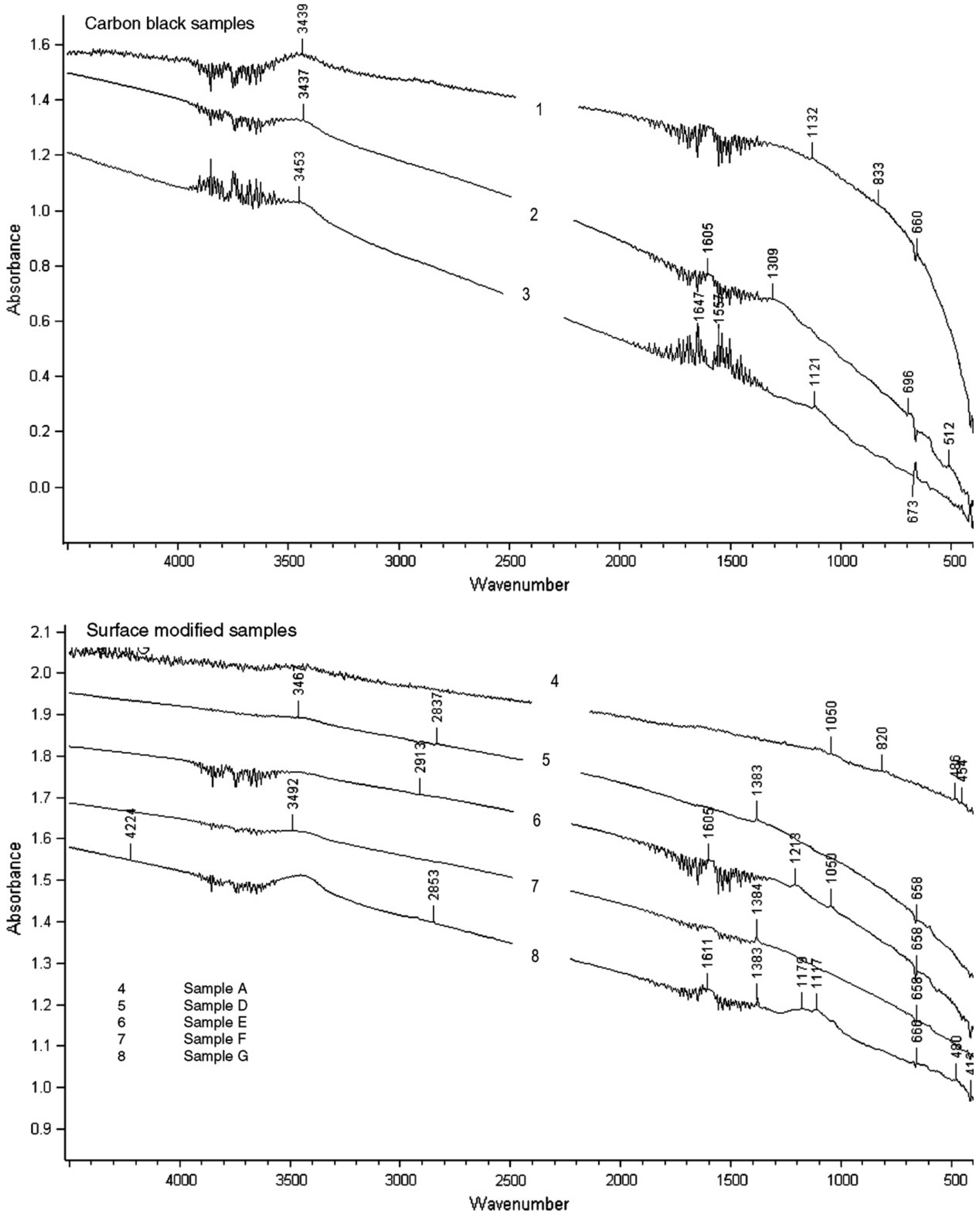

Fig. 7. FTIR spectra of selected commercial carbon black samples (1 – Black Pearls L; 2 – Raven 1040; 3 – Raven 1000) and of surface-modified carbons from the Cabot sample kit (4 – sample A; 5 – sample D; 6 – sample E; 7 – sample F; 8 – sample G).

viscosities caused by the high polymer concentration. This was confirmed in tests with Raven 1000 and two non-ionic dispersants, Tergitol XD (Dow Chemicals Corp.) and BorchiGen 0451 (Lanxess Corporation); the former is an ethylene oxide – propylene oxide copolymer with a molecular weight of 2990, and the latter is a non-ionic polyurethane oligomer. Although a pH variation from 10 to 2.5 had no apparent effect on the stability of dispersions made with Tergitol XD and Raven 1000, the viscosity exceeded the acceptable limits for production of UO_2 microspheres in the sol–gel process (see lines 5 and 6 in Table 2).

At this time it became clear that classical solutions, based on dynamic adsorption of dispersing agents on carbon black surfaces followed by electrostatic or steric repulsions, cannot produce dispersions that would remain stable and not increase the viscosity under large pH variations. The reason is that the concentration of dispersing agents adsorbed on the surface (through hydrophobic interactions) cannot be controlled while the surface charge (and the hydrophilic properties) varies strongly with the solution pH.

The advantage of surface-modified carbons is that they have a constant (and well controlled) concentration of ionisable groups grafted on their surface through stable chemical bonds [24]. This feature produces a predictable behavior under pH variations. For example, the carbons modified with amino groups carry positive surface charges and produce stable dispersions at all pH values lower than the characteristic pK_a values of amino groups (pK_a 10–11); those modified with weak carboxylic acid functions develop negative charges and stay dispersed at all pH values higher than the typical pK_a range of carboxylic acid groups (pK_a 4–5). In contrast, samples modified with alcohol functions should not be affected by solution pH as these groups do not normally participate in acid–base reactions; they disperse with difficulty. Most importantly, the sample modified with sodium sulfonate functions, which are always dissociated (and negatively charged) at all solution pH, should remain dispersed over large variation in pH.

The above statements were confirmed through vial tests with surface-modified carbons from Cabot Corporation. Without the addition of any surfactant and simply by immersion of 0.1 g of the respective carbons in 20 mL deionized water, sample E (modified with $-C_6H_4-(CH_2)_2-NH_2$ groups in protonated form), sample F (modified with

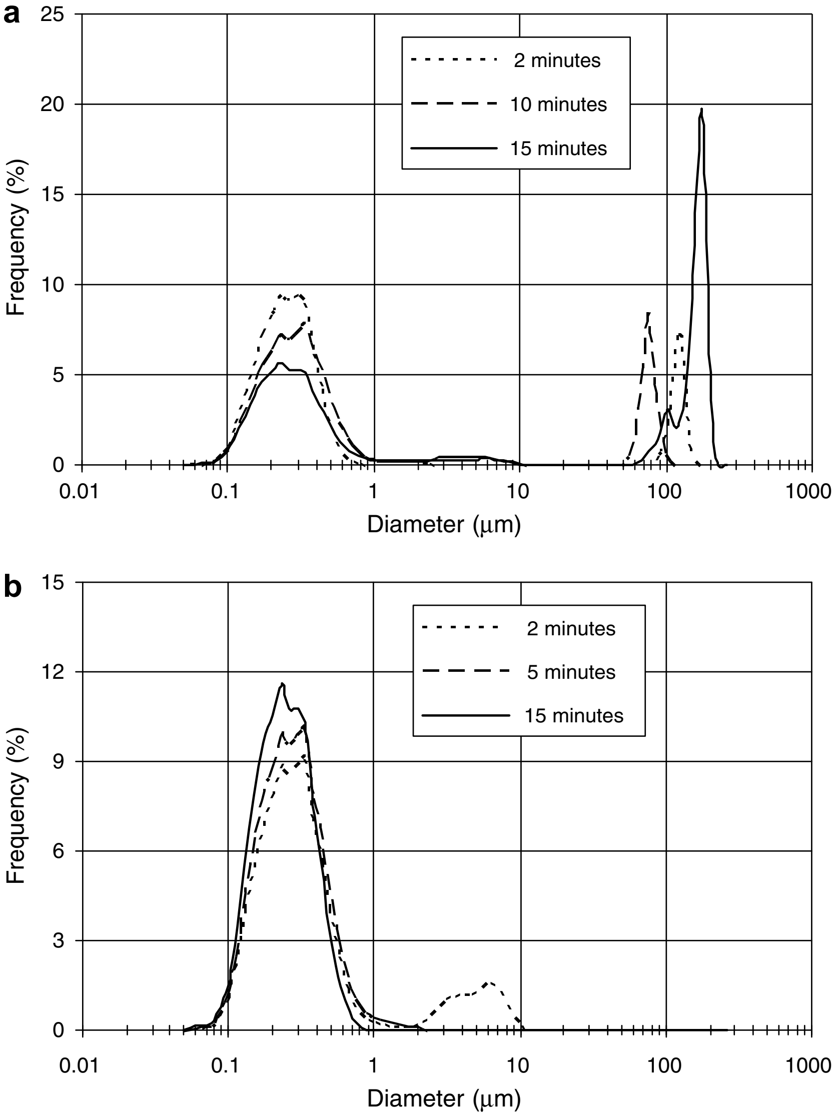

Fig. 8. Particle size distribution of carbon black agglomerates in water dispersions of surface-modified carbons: (a) sample E; (b) sample F; (c) sample G; (d) sample G dispersed in HMTA/urea aqueous solutions. The sonication times are shown for each test.

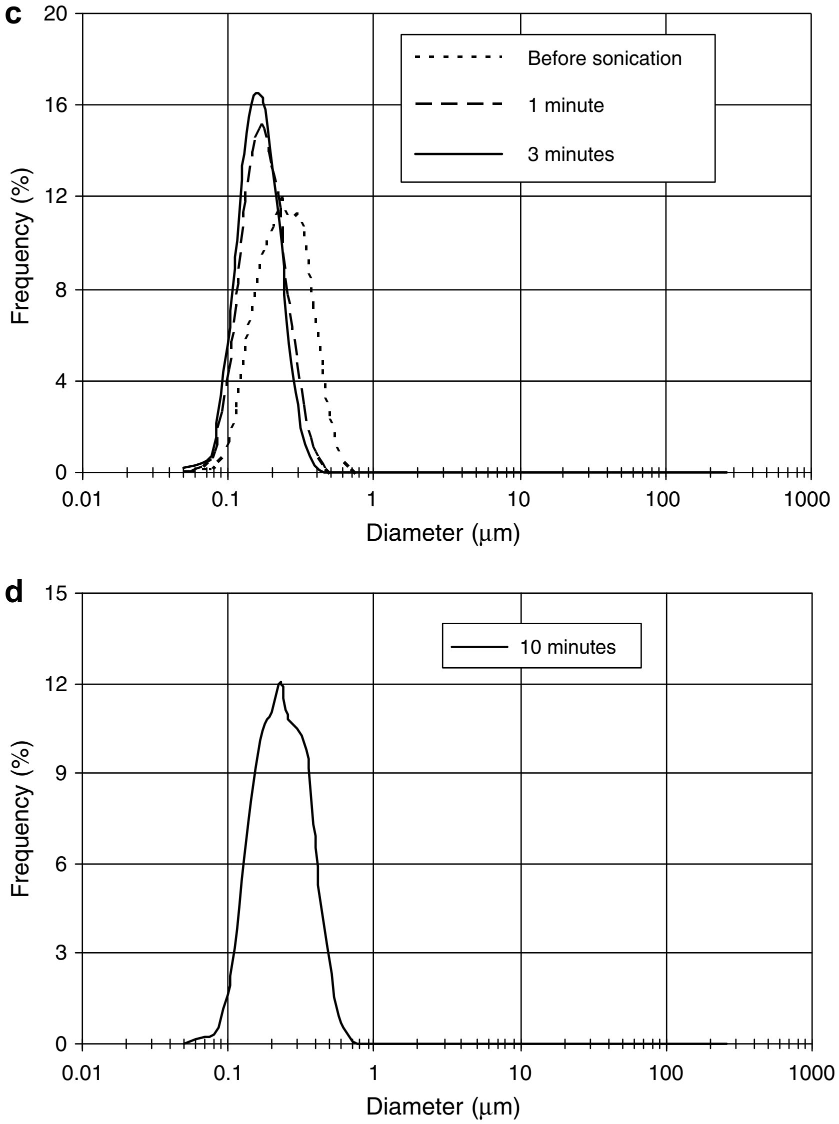

Fig 8. (*continued*)

weakly acidic –C_6H_4–COOH groups), and sample G (modified with ionized $-C_6H_4-SO_3^-Na^+$ groups) produced dispersions that remained stable for several days at equilibrium pHs of 3.5 (sample E), 4.2 (sample F), and 6.7 (sample G), respectively. In contrast, sample D (modified with nonpolar –C_6H_4–$(CH_2)_2$–OH groups) was only partially dispersed, and samples A (unmodified carbon) and B (oxidized carbon) did not disperse at all. The dispersions made with samples E and F remained stable for at least 3 days, and that made from sample G was still stable after 2 months.

Samples E, F, and G could be easily dispersed in aqueous HMTA-urea solution (pH 10) with the aid of gentle mechanical stirring only. This contrasted with the conditions required for dispersing other carbon blacks with anionic surfactants; e.g., 20 min of sonication was required to obtain dispersions of Raven 1000 in the presence of Tamol SN. In addition to their easy dispersability, surface-modified carbons E, F, and G produced dispersions with very low viscosity compared with the best dispersions stabilized by Tamol SN (compare lines 8, 10, and 12 with lines 1, 3, and 7 in Table 2). This emphasizes yet again the advantage of preparing dispersions using surface-modified carbons containing properly chosen functional groups.

Addition of acid to simulate the pH conditions of the sol–gel process had distinct effects on the stability of dispersions obtained with surface-modified carbons. In these tests, care was taken to simulate as closely as possible the conditions of pH, temperature, ionic strength, and organic content of the broth mixtures (ADUN and HMTA/urea with dispersed carbon) at the sol–gel point. The only notable difference was that no uranium (or other metal) salt was present. Under these conditions, it was found that dispersions obtained from sample G remained stable for at least 6 h, even after pH adjustment from 10 to 4.5. This is an important result that demonstrates the suitability of using sample G in the gelation process. In contrast, dispersions made from sample E were not stable in basic solutions, whereas sample F lost stability after one hour in acidic solutions. These changes were accompanied by slight, albeit acceptable variations in viscosity (Table 2). This behavior reflects the weakening of electrostatic stabilization effects caused by the pH response of amino groups (sample E) and carboxyl groups (sample F) grafted on the respective carbons.

To further confirm the results, dispersions made from samples E, F, and G were also characterized by measuring the particle size distribution of primary carbon black aggregates. Homogeneous dispersions were obtained through short-time stirring (~1 min) or mild sonication directly in the measuring cell of the Horiba particle analyzer. The results (Fig. 8) confirmed that, under these mild dispersing conditions, over 95% of the particles in samples F and G dispersed either in water or in HMTA/urea had sizes between 0.1 and 0.2 μm. For these carbons short sonication times in the measuring cell produced unimodal dispersions, with all particles below about 0.15–0.20 μm in size (Fig. 8(b–d)). In contrast, dispersions of sample E were bimodal, with particles under 0.2 μm but also with aggregates in the 50–200 μm range. For this sample, sonication increased the fraction of large agglomerates (Fig. 8(a)).

6. Conclusions

Based on an in-depth characterization of surface and structural properties of several commercial carbon blacks, it is concluded that classical dispersing techniques, based on dynamic adsorption of surfactants and helped by intense mechanical shear (or prolonged sonication), may not produce carbon dispersions that would satisfy the requirements for fabrication of high quality uranium oxicarbide kernels. For this process, the carbon dispersions must uniformly contain particles in the 0.5–1.0 μm range and must be able to withstand large variations in pH and ionic strength conditions during the mixing of the ADUN–HMTA/urea broth. In the classical dispersing method based on use of ionic or non-ionic surfactants, the binding of surfactants to the carbon surface is a dynamic adsorption process. Because of the dynamic character, the amounts adsorbed on carbon vary with the concentration (or availability) of surfactant in the dispersing vehicle, and are sensitive to even small changes in carbon surface properties (surface oxidation) or solution conditions (pH, ionic strength, temperature). Because of the large pH shock prior to the gelation step, electrostatic stabilization of dispersions (using ionic surfactants) is very difficult, even impossible to control. On the other hand, the use of non-ionic surfactants, which are not affected by pH variations, requires large concentrations in solution, which in turn produces impractically high viscosity levels. For these reasons, the classical method produces unstable dispersions.

The results presented in this paper demonstrate that it is possible to optimize dispersing conditions for the manufacture of uranium oxicarbide kernels by using surface-modified carbons. With a proper choice of the chemical modifier grafted on their surface, surface-modified carbons can be used without a surfactant to produce stable and uniform dispersions with minimal mechanical action or sonication. In this context, it was found that a carbon black modified with sodium sulfonate groups was dispersed quickly and with very little mechanical shear in HMTA/urea solutions. The dispersions remained stable for at least one month (at pH 10) and were stable for several hours in conditions mimicking the internal gelation step (acidification to pH 4.8–5.0). The carbon particle size distribution obtained under these conditions was unimodal and narrow, with all particles in the size range of 0.1–0.2 μm.

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