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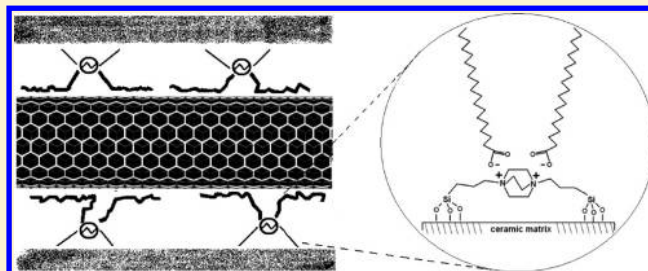
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Surfactant-Based Dispersant for Multiwall Carbon Nanotubes to Prepare Ceramic Composites by a Sol–Gel Method

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ABSTRACT: A dispersant for multiwall carbon nanotubes (MWCNTs) is proposed that fulfils the requirements of creating a uniform dispersion in the matrix and obtaining a good interface between CNTs and the matrix, and is soluble in generic nonpolar solvents. This dispersant is based on a long chain surfactant, called in this work dabcosil stearate, containing a stearate-based 18-carbon alkyl chain as an anion, and a silsesquioxane containing a bridged, positively charged 1,4-diazoniabicyclo[2.2.2]octane group. It provides not only a very good dispersion medium for the MWCNTs, but also a very good interface between MWCNTs and ceramic matrices, such as alumina and zirconia, prepared by the sol–gel method.

1. INTRODUCTION

Carbon nanotubes (CNTs), observed for the first time at 1991,[1] have attracted considerable attention, because of their unique set of extraordinary properties, which allows wide range of applications. It is well-known, however, that for any advanced applications, ranging from the medical sciences[2,3] to electronics,[4] and to composite materials,[5−9] it is required a homogeneous and stable dispersion of isolated CNTs in both organic and aqueous solutions before the preparation of the final material. Recent advances in nanomaterials, particularly, CNT/polymer[5,6] and CNT/ceramic composites,[7−9] reported that not only the dispersion is important, but also a strong interfacial bonding of the CNTs with the host matrix components is fundamental to have an efficient load transfer from host matrix to CNT. Achieving that, it is possible to obtain high performance materials with multifunctional properties.

During the past decade, ceramic matrices composites reinforced by CNTs have been extensively studied,[7] aiming to improve the intrinsic brittleness of these materials.[10−13] Among ceramics, alumina and zirconia are of great interest because of their numerous applications in several fields as guide wires in textile industry, catalyst, electric and dielectric materials, refractory materials, and others.[14,15]

However, to produce these composites, the CNTs must be processed in such a way to ensure that a homogeneous dispersion is obtained within the matrix, while developing an appropriate degree of interfacial bonding. It is worth to mention that in the case of poor or absent interfacial bondings, CNTs may even act as a source of microcracks, leading to failure.[7]

A fair amount of research has been conducted on dispersion of CNTs based on both physical and chemical approaches.[16−23] Chemical functionalization was proposed as a promising method to improve the dispersion of CNTs in organic solvents as well as in aqueous media. However, this method showed that covalent surface functionalization can affect inherent electrical, mechanical, and optical properties of CNTs.[17,18,22] Hence, several studies were concentrated on noncovalent modifications, and the use of surfactants to stabilize CNTs suspension becomes an efficient approach. Different kinds of surfactants, classified as anionic, cationic, nonionic or zwitterionic, depending on their head groups, have been investigated.[18−20]

The surfactant choice basically depends on the kind of solvent that is used to disperse the CNTs, the type of matrix (polymeric or ceramic) the CNTs will be incorporated, and what properties you want to improve. The most used anionic surfactant for the preparation of dispersed single wall carbon nanotubes is the sodium dodecyl sulfate (SDS) and the simulation described by Xu et al[23] provides comprehensive direct evidence for SDS self-assembly structures on carbon nanotube surfaces, which can help to clarify the relevant debate over the exact adsorption structure. In general, surfactants can interact with CNTs through several types of interactions, for example, hydrophobic interaction between hydrophobic chain of surfactant and sidewalls of CNTs, or π−π interaction of benzene rings on surfactants with the surface of CNTs. Such interactions lead to noncovalent adsorption of surfactants onto CNTs, providing a net positive or negative charge on the tube

surface and resulting in an enhanced solubility of the CNTs in aqueous solution. The development of a surfactant that can enhance the CNTs solubility in generic nonpolar organic solvent is of great interest, especially for the composite fabrication using the sol−gel processing method. This method provides an alternative route to creating an intimate dispersion of the CNTs in inorganic matrices, as well as a good adhesion of the host matrix to CNT, as far as a proper surfactant is used. Particularly, in the case of alumina (Al_2O_3) and zirconia (ZrO_2), matrices produced by the sol−gel method, the right choice of surfactant is critical.

Recently a silica-based hybrid xerogel was synthesized that contains the double-charged group diazoniabicyclo[2.2.2]-octane chloride, bonded to the silica moiety in a bridged way.[24] This charged silica-based hybrid material showed interesting properties, such as thermal stability and an anisotropic self-organization that induced optical birefringence when the organic content was above 60%. Additionally, this material can act as an anion-exchanger that allowed its use as adsorbent and in electrochemical devices.[25−27] An important characteristic of this material is that it has a specific affinity for aluminum, possibly forming a Si−O−Al bond, and it was already used as protective coating for aluminum surfaces.[28] Based on this specific affinity, we propose a preparation and application of a new ionic surfactant as a dispersant for MWCNTs in ceramic matrices. It contains a stearate-based 18-carbon alkyl chain as anion (octadecanoic acid), which makes hydrophobic interaction with side walls of CNTs, and a silsesquioxane containing a bridged, positively charged 1,4-diazoniabicyclo[2.2.2]octane group, which presents high affinity for aluminum. This surfactant was called dabcosil stearate (Db-St) in this work.

2. EXPERIMENTAL SECTION

The surfactant Db-St was prepared by ionic exchange of an ionic silsesquioxane containing positively charged 1,4-diazoniabicyclo[2.2.2]octane group and having chloride as counterion (Db−Cl), showed in Scheme 1. This silsesquioxane was prepared

Scheme 1. Representation of Ionic Silsesquioxane Containing Positively Charged 1,4-Diazoniabicyclo[2.2.2]octane Group, Having Chloride as Counter Ion
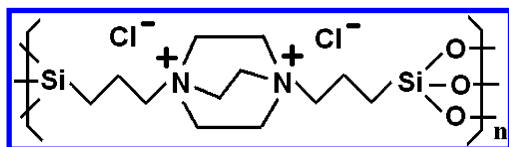
according to the experimental procedures described in Arenas et al.[24] To perform the ionic exchange it was used a solution of 4.0 mmol of sodium stearate [$CH_3(CH_2)_{16}COONa$], in 50 mL of water at 70 °C. Sodium stearate was obtained by hydrolyses with NaOH of purified fat, washed with ethanol (C_2H_5OH), and dried. Db−Cl (2 mmol) was added to the sodium stearate solution under stirring for 15 min, obtaining a suspension, which was cooled and filtered. The solid was washed with cold water (2 °C) until no chloride was detected by $AgNO_3$ reaction, and then the solid was dried at 60 °C.

The CNTs used were multiwalled (MWCNTs) with purity higher than 95% and with agglomerate sizes higher than 100 μm (Bayer Baytubes) and were used directly out of the box, without additional purification or treatment. The dispersion of the MWCNTs for the two ceramic matrices (alumina-Al_2O_3 and zirconia-ZrO_2) was performed as follows. It was prepared a solution with a ratio of 1.00 g of Db-St for

100 mL of solvent, butyl alcohol ($C_4H_{10}O$) and 1-propanol (C_3H_8O), for alumina and zirconia, respectively. It was added 2 mL of aluminum trisec-butoxide [$Al(O\text{-}s\text{-}C_4H_{10})_3$] for alumina and 2 mL of Zr n-propoxide [$Zr(O\text{-}n\text{-}C_3H_8)_4$] for zirconia. Each mixture was stirred for 3 h at 50 °C. After this step, the surfactant is completely dissolved and 0.0074 g of MWCNTs was added for alumina and 0.0215 g of MWCNT was added for zirconia. These suspensions were sonicated and stirred for approximately 35 h and after that we obtained a very good dispersion of the MWCNTs, in both suspensions, as seen by the naked eye. The sonication was performed using a standard sonicator with a frequency of 40 kHz, at room temperature.

MWCNT/alumina and MWCNT/zirconia composites were prepared by the sol−gel method. Alumina sol−gel (Al-gel) was prepared using the precursor aluminum trisec-butoxide (Fluka, 95%) in the presence of acetic acid (Nuclear, 99,5%) and iso-butyl alcohol (Sigma-Aldrich, 99%) at a mass rate of 2:1:6.[29,30] In volume, the quantities used were 2.7 mL of Al(O s-Bu), 7.3 mL of i-BuOH, and 1.2 mL of AcOH. The precursor was dissolved with isobutyl alcohol under continuous mixing, and drops of acetic acid were added to this mixture at room temperature. After that, 7.3 mL of the suspension of MWCNTs was added and stirred. This solution then undergoes a condensation reaction to generate a composite of MWCNT/alumina. The gel was let to dry at room temperature and ambient pressure, without any heat treatment, and after seven days a dried gel was obtained.

For zirconia sol−gel (Zr-gel), it was used 5 mL of zirconium(IV) propoxide (Sigma-Aldrich, 70 wt % in 1-propanol), 0.8 mL of acetylacetone (Sigma Aldrich, 99+%), and 2.8 mL of distilled water.[31] This solution was kept in magnetic stirring, where 2.3 mL of the suspension of MWCNTs was added. This final solution was vigorously stirred at room temperature and the gelation occurred in 30 min. A homogeneous slightly yellow-gray colored gel nanocomposite of MWCNT/zirconia was obtained.

The resulting monoliths of the composites of MWCNT/alumina and MWCNT/zirconia were comminuted, and the powder obtained was heat treated at 500 °C for 3 h in air for both cases. The concentration of MWCNTs for Al-gel and Zr-gel was about 10^{-2} wt % MWCNTs. The temperature of the heat treatment was determined by thermogravimetric analysis (TGA). These measurements were carried out on a Shimadzu TGA-50 system from room temperature to 800 °C at a heating rate of 20 °C/min in air or nitrogen flux.

In order to determine the phases of alumina and zirconia powders, before and after heat treatment, we performed X-ray diffraction (XRD) studies carried out using Siemens D-500 powder diffractometer equipped with Soller slits and a graphite monochromator in the secondary beam. Data were collected with Cu Kα radiation, with a wavelength of 0.15418 nm, in the angular range from 10° to 100° (2θ).

The morphological studies were performed by transmission electron microscopy (TEM) using JEOL equipments operating at 120 kV (JEM 1200ExII) and 200 kV (JEM 2010). An energy dispersive spectrometer (EDS) coupled to JEM 2010, capable of detecting elements between B and U was used to determine the coating of CNTs. The fine powder samples were initially dispersed in isopropyl alcohol by ultrasonication for 10 min. Afterward, a drop of the suspension was transferred onto a carbon coated copper grid for analysis.

3. RESULTS AND DISCUSSION

Figure 1 shows photographs of the dispersion of MWCNTs in a solution of Db-St with butyl alcohol containing 2 mL of aluminum trisec-butoxide (Figure 1a), and MWCNTs dispersed only in butyl alcohol (Figure 1b). Some transmission electron microscopy (TEM) images of these suspensions are shown as well (Figure 1c−f).

In Figure 1a, we can observe a stable black suspension of the MWCNTs in the surfactant solution of Db-St, in a concentration of 0.0074 g of MWCNT to 100 mL of butyl alcohol, whereas in Figure 1b we clearly see that the MWCNTs
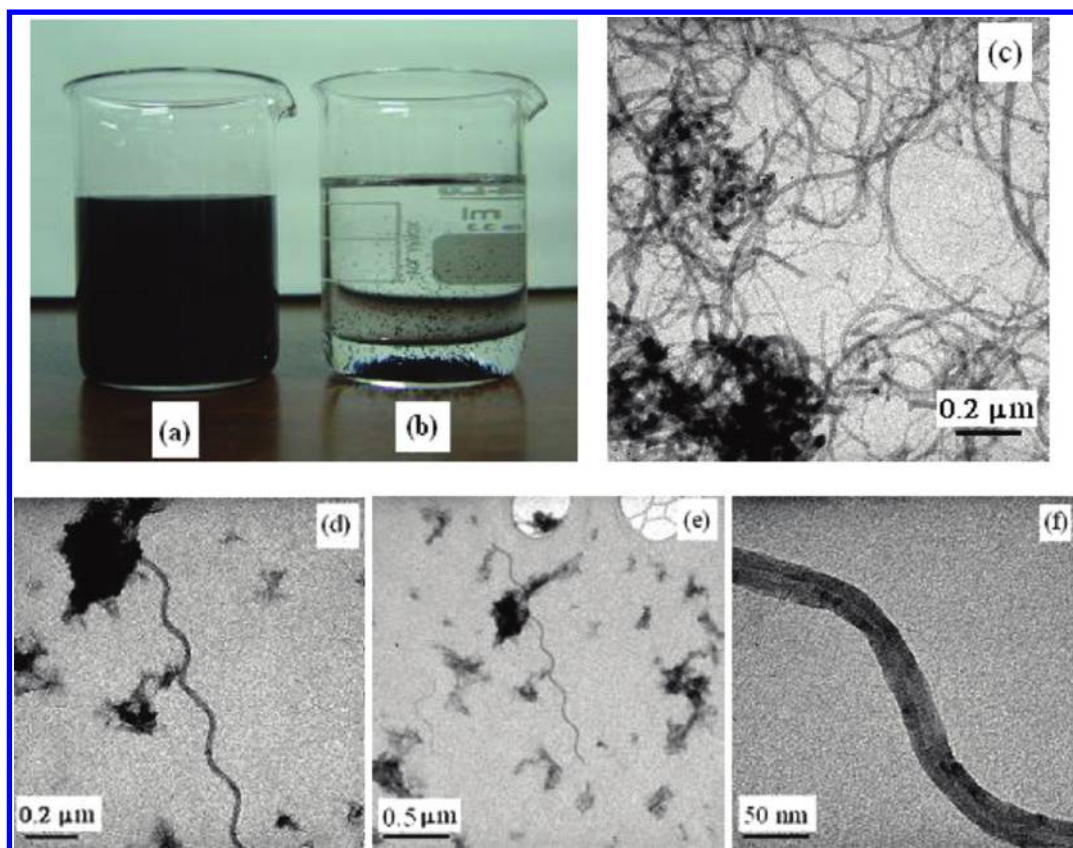
Figure 1. Photographs of suspensions of (a) MWCNTs dispersed in Db-St solution (7.4 mg MWCNT/100 mL butyl alcohol/2 mL of aluminum trisec butoxide) and in (b) the same concentration of MWCNTs, but only in butyl alcohol. TEM images obtained from these suspensions: (c) a tangle of MWCNTs and (d) individually dispersed MWCNT, at the same magnification; (e) lower magnification of the same region showed in (d); (f) higher magnification of the MWCNT.

are precipitating to the bottom, using the same concentration of MWCNTs, but only in butyl alcohol. In Figure 1c, the TEM image shows a tangle of MWCNTs and the diameter of the pristine MWCNTs was estimated to be between 10 and 40 nm. In Figure 1d, at the same magnification, we see an individually dispersed MWCNT. It is important to point out that these two TEM images are representative of all regions we investigated indicating that effectively it was possible to isolate one MWCNT using this surfactant. Figure 1e shows a TEM image with a lower magnification of the same region showed in Figure 1e, and it is possible to observe that there is another MWCNT, also isolated in that region. Figure 1f shows a higher magnification, where we can estimate the diameter of the MWCNT as about 30 nm, in the same diameter range of the pristine MWCNTs. Also we can observe that the MWCNT is not damaged, maintaining its integrity. Several TEM images were taken in different regions, and with different magnifications, being similar to the ones that are showed here.

The preparation of the composites of MWCNT/alumina and MWCNT/zirconia was performed by the sol−gel method and we obtained a powder of both composites. These powders have to be heat treated in order to eliminate the surfactant that it is known to hinder the process of compaction, if we desire to produce some ceramic compacts with improved properties.[7,8] The temperature of the heat treatment was determined by thermogravimetric analysis (TGA). Figure 2 shows TGA measurements for the Db-St and the pristine MWCNTs.

The Db-St starts to degrade around 200 °C and the organic moiety is eliminated around 500 °C, as we can see in Figure 2a.

The MWCNTs initiate the degradation around 600 °C (Figure 2b).[32] Hence, we have a limit on the temperature of the heat treatment, which we stipulate according to TGA, as 500 °C in air for 3 h, for both composites.

It is important to notice that we need to eliminate the surfactant and also the organic material that remained from the sol−gel process, and at the same time we should provide that the interface between the MWCNTs and the matrix is good enough to preserve the good incorporation and dispersion of the MWCNTs within the matrix. To determine if we eliminate the Db-St and the organic material after the heat treatment at 500 °C, we performed XRD measurements and the results are shown in Figure 3 for MWCNT/alumina and in Figure 4 for MWCNT/zirconia.

Figure 3a shows the diffractogram of a commercial gamma alumina for comparison. Figure 3b−d shows, respectively, the diffractograms for Al-gel, MWCNT/alumina, both before heat treatment, and for MWCNT/alumina after heat treatment. Figure 3e shows a diffractogram of pristine MWCNTs for comparison. In Figure 3b and c, the peaks that are seen for 2θ between 20° and 40° are from the organic material that remains in the synthesis. The diffractogram in Figure 3d shows that the heat treatment eliminates these peaks, indicating that the organic material was significantly reduced. These results were confirmed by CHN elemental analysis, showing less than 1.0 wt % of carbon in these samples. In Figure 3d, the MWCNT/alumina remained amorphous with an onset of crystallization to the gamma phase, which can be observed by a peak that starts to appear around $2\theta = 67°$. The crystallization of the gamma
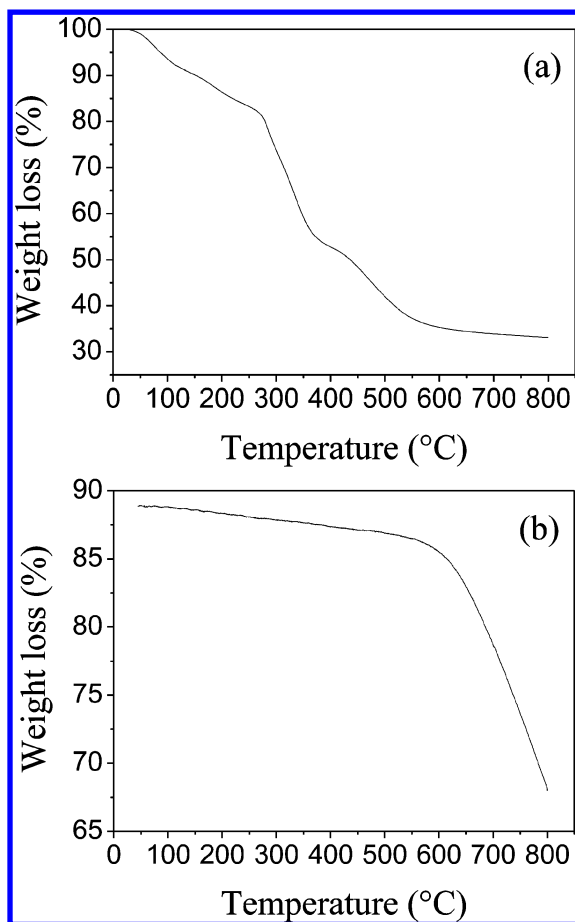
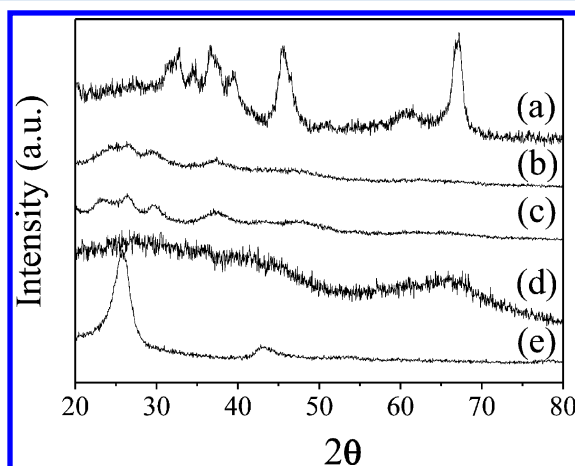**Figure 2.** TGA measurements performed in nitrogen flux for (a) Db-St and (b) pristine MWCNTs.

Figure 3. Diffractograms for (a) commercial gamma alumina, (b) Al-gel and (c) MWCNT/alumina, both before heat treatment, (d) MWCNT/alumina after heat treatment, and (e) pristine MWCNTs.

phase was not complete because it is well-known that it occurs at ambient pressure only above 750 °C and the samples were treated at 500 °C. Since alumina matrix remains amorphous, it is impossible to determine the grain size.

Figure 4a and b shows the diffractograms for MWCNT/zirconia, after and before heat treatment, respectively. In this case, it was not observed any peak related to the organic material, probably because the quantities that remained from
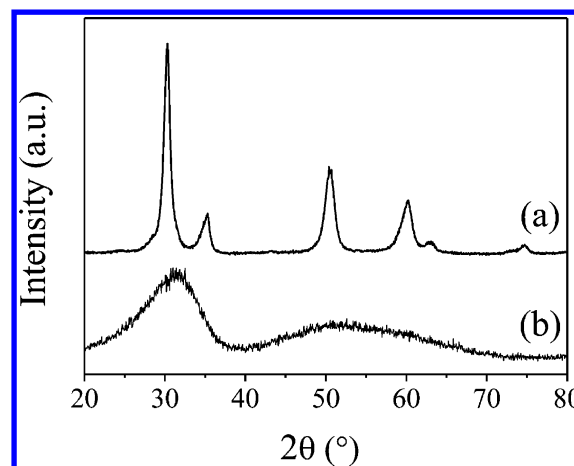

Figure 4. Diffractograms for MWCNT/zirconia (a) after heat treatment and (b) before heat treatment.

the synthesis are very low, not detectable by XRD. However, after the heat treatment, there is a phase transformation from amorphous to the tetragonal phase. It is known that the temperature of the different phase transformations for zirconia powders decreases with decreasing grain size.[30,33] The phase transformation obtained at 500 °C indicates that the crystallites of MWCNT/zirconia powder are in the nanoscale range, as already observed by other authors for nanocrystalline zirconia produced by the sol−gel method.[34,35] The grain size of the tetragonal phase of zirconia was determined by the Scherrer equation, using the more intense peak (around 30°) showed in the diffractogram of Figure 4a. The average grain size was estimated as 25 ± 5 nm, confirming that we have a nanostructured composite. It should be pointed out here that we could not determine the peaks for MWCNTs (Figure 3e) in MWCNT/alumina and MWCNT/zirconia powders by XRD measurements, because of the low concentration of the MWCNTs in the matrices ($\sim10^{-2}$ wt %). Only by TEM images it was possible to confirm their presence in the matrices, before and after the heat treatment. The surfactant used in this work has an important characteristic that is, a specific affinity for aluminum forming possibly Si−O−Al bond, according to ref 28. During the sol−gel drying process, before the heat treatment, this kind of bonding should occur. When we perform the heat treatment the excess of organics will be removed, however the CNTS were already dispersed and covered with the alumina matrix in intimate contact. TEM images shown in Figures 5−7 display the morphology and
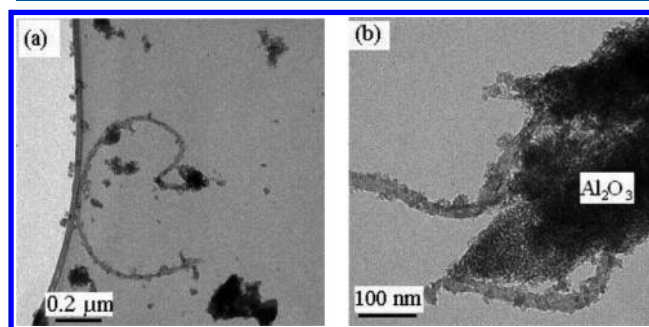

Figure 5. TEM image for MWCNT/alumina powder: (a) with a magnification of 0.2 μm and (b) a larger magnification in another region.
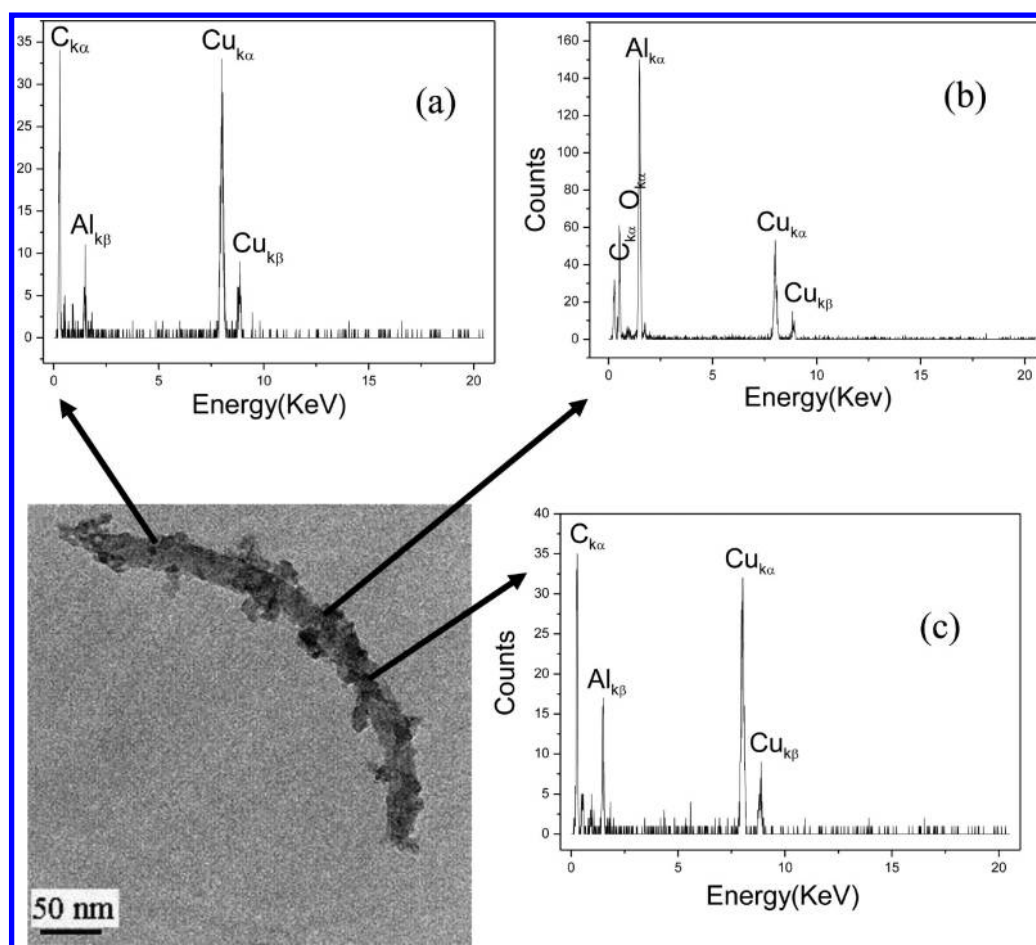
Figure 6. EDS measurements were made in three different regions on an isolated MWCNT: (a) and (c) in an internal region and (b) in the external surface.

surface features of the MWCNTs incorporated in the matrices, after the heat treatment. Figure 5a shows the TEM image for MWCNT/alumina powder, where we can observe a very large MWCNT in length (about 2.0 μm) coming from inside the alumina matrix. It can also be seen that there is a coating on the surface of the MWCNT, if compared to Figure 1d, where we have only the MWCNT dispersed on the Db-St. Figure 5b shows, at a larger magnification, that effectively the MWCNTs are incorporated in the matrix and its surface is well coated.

Figure 6 presents EDS measurements in three different regions on an isolated MWCNT and it is possible to observe that aluminum is present in all regions. Figure 6b shows an EDS in a region, where the peaks for aluminum are much more intense than for carbon. In Figure 6a and c, the EDS, the peaks for carbon are more intense than for aluminum. The peaks ascribed to copper are due to a carbon coated copper grid used for support the samples. The diameter of the MWCNT also increased, due to the coating, if compared to Figure 1f. This coating is not very homogeneous in thickness, but in some regions the coated MWCNT has a diameter of about 50 nm.

Figure 7 shows TEM images for MWCNT/zirconia. Figure 7a shows a MWCNT about 2.5 μm in length, crossing the zirconia matrix, a magnification of this image is seen in Figure 7b. It is impressive how homogeneous is the coating thickness if we compare to the coating obtained in the alumina matrix. It is possible also to estimate the diameter for the coated MWCNT as about 50 nm, almost in all length. It is noteworthy to mention that when we make a heat treatment at 300 °C in
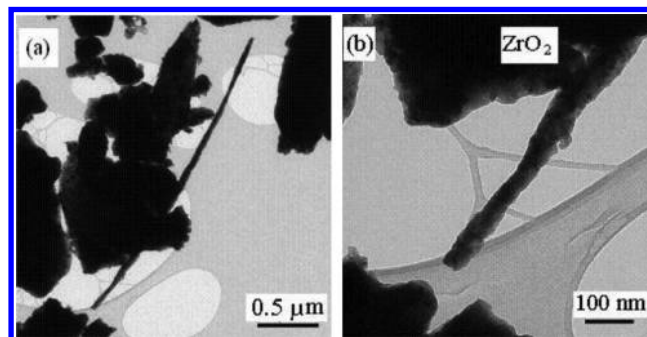

Figure 7. TEM images for MWCNT/zirconia: (a) a MWCNT crossing the zirconia matrix and (b) a magnification of this area showing a coated MWCNT with a zirconia matrix.

MWCNTs/zirconia, we still have amorphous phase and the TEM images in this case are much like the ones obtained with amorphous alumina. The differences between the two matrices could be related to differences in crystallinity.

Figure 8 shows a schematic view suggesting how the surfactant may adsorb onto the MWCNT surface and how the Db-St molecules may interact with the ceramic matrix. Studies are underway to describe and understand better these interactions, particularly how the Db-St interacts with the ceramic matrix. It has been reported in literature that most of the surfactants with long alkyl chains lies flat along the
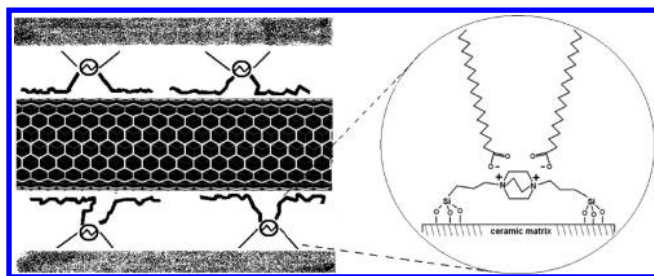
Figure 8. Schematic representation of the possible interaction of Db-St with the MWCNT surface and the ceramic matrix.

nanotube surface rather than to bend around the circumference. Energetically this situation seems to be more favorable.[36]

4. CONCLUSION

A new dispersant for MWCNTs called dabcosil stearate, based on an 18-carbon alkyl chain as anion, and a silsesquioxane containing a bridged, positively charged 1,4-diazoniabicyclo[2.2.2]octane group. It is soluble in generic nonpolar solvents and can be used for the preparation of reinforced ceramic composites such as MWCNT/zirconia and MWCNT/alumina by a sol−gel method. It was possible, using this new surfactant, to unbundle MWCNTs, creating a uniform dispersion of CNTs in the ceramic matrix and to obtain a good interface between CNTs and the matrix. In this way, we open the possibility to prepare new CNT/ceramic composites.

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■ ACKNOWLEDGMENTS

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