An analysis of carbon nanotube structure wettability before and after oxidation treatment

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Abstract

In this work contact angle measurements have been carried out on different carbon nanotube-based materials. Thin layers of entangled carbon nanotubes have been considered, together with thick mats of vertically aligned carbon nanotubes. Pressed single-walled carbon nanotubes and graphite have also been considered, for comparison.

In particular, the properties of the as-grown thick carpets have been compared to those of the oxidized material. Oxidation treatments have been performed either by chemical oxidation with a nitric/sulfuric acid mixture or by applying a bias voltage of 10 V on the material. Tests have been performed using three liquids with differing polarity (water, dimethylsulfoxide and diiodomethane). Very high hydrophobicity was observed for the top surface of the aligned carbon nanotube mats, but after oxidation a dramatic reduction in the contact angle was observed, bringing about a hydrophilic behaviour. Theoretical calculations of the bulk pore distribution of the material have been made to estimate the liquid percolation through the oxidized carpet's surface.

1. Introduction

Even though the first known direct observations of the tubular nature of some nano-sized carbon filaments were published in 1952 [1] and 1976 [2], the scientific community started to seriously focus its attention on carbon nanotube (CNT) structures only after the observation of multi-walled carbon nanotubes (MWCNTs) in 1991 [3] and of single-walled CNTs (SWCNTs) in 1993 [4, 5]. Aside from the controversy surrounding their discovery [6], their remarkable mechanical and electronic properties destine them to play a major role in all kinds of nanotechnologies and molecular electronics [7–9].

Although, the major issue of how to fine-tune the various properties of the material to suit particular applications has to be resolved in order to fulfil this potential. Thus, a synergic effect in nanotube properties can be obtained by adding together the ability to grow high purity CNTs in a controlled manner directly on different substrates using various chemical vapour deposition (CVD) techniques, and the ability to tailor the surface properties by means of functionalization techniques [10].

For example, the wettability of the CNTs' surface is an important property, governed both by chemical composition and by the geometrical microstructure of the contact surface, which can play a key role in the CNTs' performance during their applications as reinforcements in polymer composites [11], as sensors [12] or as highly selective molecular membranes [13]. In fact, when dispersing carbon nanotubes into a solvent or a monomer/polymer compound, the as-grown material shows a non-reactive and very amphiphobic nature. Whereas on the microscopic level [14, 15] the interaction of a single CNT with solvents has been studied extensively, the challenge is to understand the

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wetting behaviour at a macroscopic level, when nanotubes are grouped into aligned configurations and the chemical/physical manipulation of the properties can greatly facilitate some applications and can also result in some new properties.

In the light of these topics, different samples of CNTs produced by CVD from a gas mixture evaporated from camphor and ferrocene have been studied. Camphor is an unconventional precursor, successfully used for the first time in CNT deposition by Kumar and Ando [16, 17]. Since then several works have been devoted to studying and developing such a simple and efficient technique [18–21].

Thin layers of entangled CNTs have been considered, together with thick mats of vertically aligned carbon nanotubes (VACNTs). In particular, modification of wettability properties due to chemical oxidation has been studied on the thick carpets of VACNTs.

Theoretical calculations have been performed, to estimate the effect of the morphology of the carpets on both the wetting properties and the percolation rate of the liquid through the surface.

Contact angle tests, performed using three liquids with different polarities, have been compared with those resulting from graphite and pressed pellets of SWCNTs.

2. Experimental details

Contact angle and percolation measurements have been performed on different kinds of nanotube structures. Multi-wall carbon nanotubes (MWCNTs) have been grown by CVD, using camphor as carbon precursor and ferrocene as catalyst. The reagents were brought to the boil and carried in an N_2 stream into a tubular furnace kept at high temperature (700–850 °C), where the deposition took place. Details about the procedure have been previously reported [19].

With this deposition technique, thick carpets of VACNTs (up to some mm) on a silicon substrate have been achieved. Carpets with thicknesses of approximately 2 mm (figure 1(a)) came from long depositions (1.5 h), working with a deposition temperature of 850 °C. A laminar nitrogen flux of about 400 cm^3 min^{-1} has been used as carrier for the transport of the precursors into the deposition chamber (with a camphor/ferrocene mass ratio of 20). The resulting diameter of the well aligned MWCNTs ranges between 30 and 80 nm, with an average distance between the tubes of approximately 100–150 nm. A detailed report on characterizations of such material can be found in [20].

Using the same deposition technique, by properly changing the deposition parameters [22], thin layers of entangled carbon nanotubes have also been obtained on silicon substrates. The parameters were: deposition temperature 700 °C, nitrogen flux 1500 cm^3 min^{-1}, camphor/ferrocene mass ratio 30, deposition time 20 min. In such a way, thin layers of entangled nanotubes of 5–20 μm thickness have been produced (figure 1(b)). In this case the average diameter of the tubes, as shown by FESEM images, ranges between 10 and 40 nm.

The VACNTs carpets obtained by the massive growth have been delaminated by the substrate, obtaining self-standing

Table 1. Properties of the solvents [25–27].

Properties @ 20 °C	Water [25]	Dimethyl sulfoxide [26]	Diiodomethane [27]
Density (g cm^{-3})	0.9982	1.1014	3.3254
Dynamic viscosity (cP)	1.001	2.15	2.76
Cinematic viscosity (cSt)	1	1.95	0.83
Surface tension (mN m^{-1})	72.80	44.00	50.80
	Dispersive: 29.10 Polar: 43.70	Dispersive: 36.00 Polar: 8.00	Dispersive: 50.42 Polar: 0.38

mats which have been used for both the contact angle and percolation measurements. The analyses have been performed on the carpet surface which had previously been in contact with the substrate, especially because it appears more uniform and smooth than the top side and there is a lower concentration of impurities (e.g. mainly amorphous carbon and iron particles). On the other hand, the thin layers of entangled nanotubes have been maintained stuck on silicon, because the very thin layer does not form a self-standing mat.

In order to tune the surface properties of the material, the thick carbon nanotube carpet was oxidized using two different techniques. In the first procedure, an acid mixture of nitric and sulfuric acid was used. The surface of the mat was wetted with the HNO_3/H_2SO_4 (25 vol% HNO_3) solution for 16 h at room temperature. The acid treatment allows the formation of oxygen-containing functional groups on the nanotube surface, such as carboxyl (–COOH) and sulfonic (–SO$_3$H) acid groups, as recently reported [23]. Although, the treatment was less drastic than reported, in order to preserve the shape of the CNTs mat for the subsequent contact angle and percolation measurements.

An alternative way to functionalize the VACNTs has been followed by applying a bias voltage across the material. The application of an external potential is known to modify the surface wettability of carbon nanotube forest, moving from a hydrophobic to a hydrophilic behaviour [24].

In our experiments a positive dc bias up to 15 V and currents up to 2 A were applied to a 5 mm × 5 mm VACNTs carpet by placing its two sides in contact with copper wire electrodes for a time ranging from 1 to 30 s. The best oxidation conditions were found for 10 V, 1 A and 5 s. At higher currents or voltages a progressive burning of the samples was observed, with the formation of an iron oxide residue.

Optical contact angle (OCA) and percolation measurements were performed using the OCAH200 set-up (Dataphysics). Interaction between the carbon-based surfaces and three kinds of liquids with different polarities was studied. In our experiments we used (going toward lower polarity) water, dimethyl sulfoxide (DMSO, $(CH_3)_2SO$) and diiodomethane (CH_2I_2). The main properties of the liquids are listed in table 1.

Liquids have been dispensed (in the form of drops of 1–8 μl) through a micro-syringe. The interaction with the surface
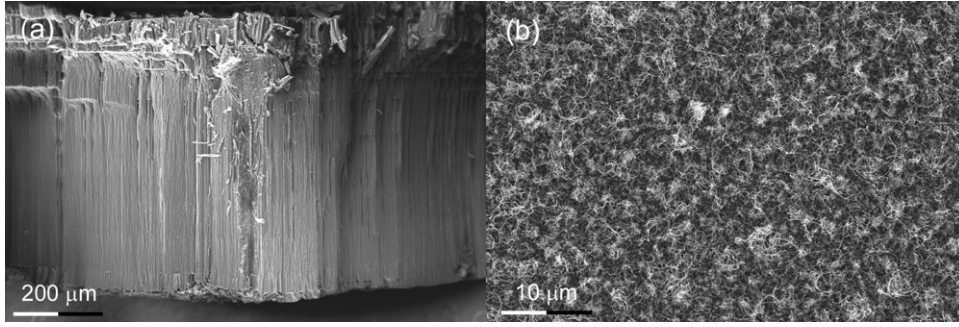
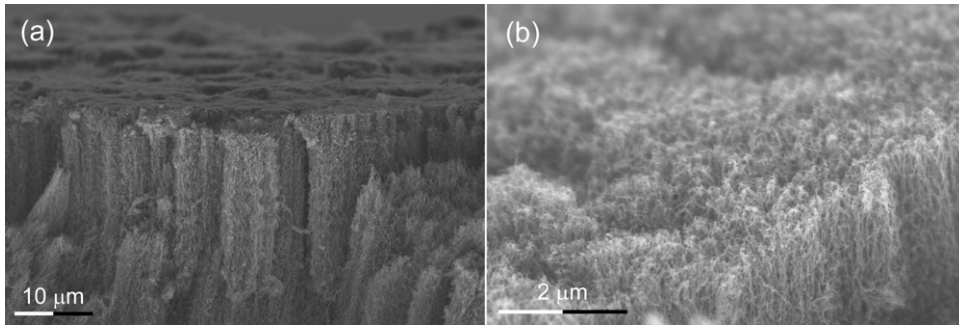**Figure 1.** SEM images of (a) VACNTs (side view); (b) thin layer of entangled CNTs (top view).

Figure 2. Image of the surface of a VACNTs carpet showing a significant surface roughness.

has been monitored with a CCD camera, with a time step of 40 ms between two successive acquisitions (25 frames s^{-1}). The contact angle was evaluated both by fitting the drop profile with a Young/Laplace model and by using the tangent calculation method, while percolations were monitored by evaluating frame by frame the behaviour of the drop on the material surface.

Contact angle or percolation measurements have been performed on VACNTs mats both on the as-grown materials and after the two kinds of oxidation procedure. For comparison, contact angle was also evaluated on the thin layer of entangled nanotubes and on a commercial graphite substrate. Furthermore, percolation measurements have been performed on pressed pellets of single wall carbon nanotubes (SWCNTs), with an average diameter <2 nm and a length of a few microns, provided by Thomas Swan and Co (UK).

3. Theoretical considerations

3.1. Contact angle

A drop on a rough surface displays an equivalent contact angle ϑ_{eq}, different from the intrinsic one ϑ_{i} (related to the corresponding flat surface). Two states are possible: the Wenzel state, in which the drop is conformal to the topology of the surface and the Fakir state, in which it is protruding on the carbon nanotube roughness [28]. In the Wenzel state we expect:

$$\cos \vartheta_{\mathrm{eq,W}} = w \cos \vartheta_{\mathrm{i}} \qquad (1)$$

where w is the roughness (actual surface area over apparent one), whereas in the Fakir state we expect:

$$\cos \vartheta_{\mathrm{eq,F}} = \varphi \left(\cos \vartheta_{\mathrm{i}} + 1 \right) - 1 \qquad (2)$$

where φ is the area fraction of nanotubes in the forest. The drop will stay in the state corresponding to the minimum of the energy, i.e. in the state with the smaller contact angle (metastability is here neglected), namely:

$$\vartheta_{\mathrm{eq}} = \min \left(\vartheta_{\mathrm{eq,W}}, \vartheta_{\mathrm{eq,F}} \right). \qquad (3)$$

Thus the activation of the Fakir state is expected for:
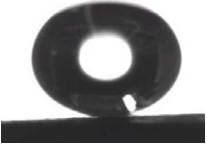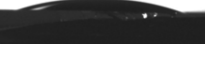
$$\vartheta_{\mathrm{i}} > \vartheta_{\mathrm{WF}} \qquad \text{where } \cos \vartheta_{\mathrm{WF}} = -(1 - \varphi)/(w - \varphi). \quad (4)$$

Note that since $w > 1 > \varphi$, $\vartheta_{\mathrm{WF}} > 90°$, suggesting that super-oleophobic surfaces are hard to be realized. However, considering in addition to the roughness and area fraction also a new key parameter, that is the re-entrant surface curvature, could help in producing such surfaces [29]. Moreover we expect also hierarchy as a key parameter [30].

3.2. Percolation

Let us model the percolation of the liquid drop along the functionalized nanotube forest as a Torricelli-like liquid flow, in which the driving pressure Δp is given not only by gravity, i.e. $\Delta p = \rho g H$, where ρ is the fluid density, H is the height of the fluid column and g is the gravitational acceleration, but also by surface tension and capillarity. The liquid drop has a nearly

Table 2. Contact angle for different carbon materials with different solvents.

Material	Water		Dimethyl sulfoxide		Diiodomethane	
VACNTs	176°		23° [a]		24° [a]	
Entangled CNTs	144°		17° [a]		20° [a]	
Graphite	97°		24°		15°	
SWCNT	<55° [a]		—		—	

[a] Percolation observed.

spherical shape, of radius R, suggesting a positive internal pressure $\Delta p = 2\gamma/R$, developed thanks to the non-negligible liquid surface tension γ. An additional pressure is imposed by the capillary flow inside the interstices, let say having characteristic radius r, in the nanotube forest, namely $\Delta p = f 2\gamma \cos\vartheta/r$ (positive for $\vartheta > 0$), where ϑ is the contact angle of the liquid in the interstices and f is a parameter smaller than one introduced to take into account friction. Thus the total driving pressure is $\Delta P \approx \rho g H + 2\gamma/R + f 2\gamma \cos\vartheta/r$ and equivalent gravitational acceleration is $g_{eq} \approx g + 2\gamma/(\rho H R) + f 2\gamma \cos\vartheta/(\rho H r)$. This term, even if it depends on H, can be considered roughly constant. As a matter of fact, in the second term, while the drop is percolating H decreases but R increases, since the drop flattens on the surface. In the third term, corresponding to the capillarity effect, when the liquid begins to fill the pores of the carpet, friction arises, that reduces the parameter f and thus the percolation. Globally, as a first approximation, we can thus consider g_{eq} constant.

Accordingly, the fluid velocity $\dot{h}$ in the interstices is $\dot{h} = \eta\sqrt{2g_{eq}H}$, where the coefficient η takes into account the resistance of the nanotube forest against the liquid flow (if in air, as in the Torricelli's case, $\eta = 1$, and $g_{eq} = g$). Due to mass conservation $V_{drop} \equiv \pi R^2 H_{max} = \pi R^2 H + n\pi r^2 h$, where n is the number of interstices present under the drop and h is the height of liquid inside the interstices. Accordingly $V = n\pi r^2 h$ represents the percolated volume. Rearranging the previous equations yield $V/V_{drop} = 1 - H/H_{max}$ and $(1-\varphi)\dot{h} = -\dot{H}$, where $\varphi = 1 - n\pi r^2/(\pi R^2)$ is the area fraction of nanotubes in the forest. Since $\varphi \approx d^2/(d+r)^2$, where d is the nanotube diameter, the radius of the equivalent interstices can be estimated as $r \approx d(1-\sqrt{\varphi})/\sqrt{\varphi}$, where $\varphi \approx \rho_{bulk}/\rho_{CNT}$ can be calculated as the ratio between the bulk and the carbon nanotube densities.

Thus, from $(1-\varphi)\eta\sqrt{2g_{eq}H} = -\dot{H}$ by integration we obtain the following simple percolation law:

$$\sqrt{1 - V/V_{end}} = 1 - t/t_{end} \qquad (5)$$

where $V_{end} = V_{drop} - V_{residual}$ takes into account the occurrence of a residual, i.e. not percolated, volume $V_{residual}$, t is the time and $t_{end} = \sqrt{2H_{max}/g_{eq}}/[\eta(1-\varphi)]$ is the percolation time.

We note that in the percolation time the parameter η is *a priori* unknown as f. Treating the nanotube forest as a mechanical filter we would roughly (assuming a constant percolation velocity) deduce $t_{end} \approx H_{max}\mu/(r^2\rho g i)$, where μ is the dynamic viscosity of the liquid and i is the piezometric pressure loss, thus an information about η. But a nanotube forest is not just a mechanical filter and i too is not defined *a priori*. In spite of this, equation (5) can be easily and successfully applied, ignoring the details, as we are going to show.

4. Results and discussion

4.1. Contact angle before oxidation

Contact angle was measured for VACNTs carpets, thin entangled CNTs layers, graphite and a pressed SWCNTs disc, and the results are presented in table 2.

With DMSO and CH_2I_2 solvents the contact angles are quite low for all materials, showing, as expected, a positive interaction between the low polarity solvents and the carbon surface of graphite or of carbon nanotubes. Since carbon nanotubes structures are porous and the contact angle is low, percolation is observed for these materials. In this case the definition of a contact angle is not fully correct, since no equilibrium condition is observed.

On vertically aligned carbon nanotubes super-hydrophobic behaviour is observed, with a contact angle of 176°. Similar behaviour was already observed for instance by Wang and co-workers [24] and Lau and co-workers [31]. The former found a contact angle of 163° for water over a nanotubes forest similar to our. The latter observed an angle of 161° for a water droplet over a regular forest of a few micrometres long carbon nanotubes, however, after a few minutes, the drop seeped in the forest. This phenomenon occurred due to bundling of carbon

Table 3. Wenzel w and Fakir φ parameters calculated for VACNTs and entangles CNTs in the case of water drops.

Material	$\vartheta_{contact}$ (deg)	w (Wenzel)	φ (Fakir)
VACNTs	176	9.9	0.0027
Entangled CNTs	144	8.0	0.21

nanotubes, that bent to form clusters at the top, while the roots remained attached to the substrate. In our case we observe neither seeping of the drop into the nanotubes nor bundling of the nanotubes under the drop. This is probably due to a denser microstructure and greater height of our carpet, with respect to those used in [31].

In order to explain this very high contact angle for water on the VACNTs carpet, some considerations can be made using Wenzel and Fakir theory.

Experimentally we observed for water on graphite a contact angle of 97°, slightly higher than that observed in the literature [31]. The used graphite has a low surface roughness, suggesting values of w (equation (1)) and ϕ (equation (2)) close to unity. With low w ($w < 1.5$) and high φ values ($\varphi > 0.8$) the calculated ϑ_{WF} angles are comprised between 100° and 130°, suggesting that Wenzel mode is active. Applying Wenzel theory, the obtained theoretical contact angle is close to the experimental value, and was calculated to be $\vartheta_i = 95.5 \pm 1°$.

By assuming that the theoretical contact angle on the graphite and on the CNT surface is the same, from equations (1) and (2) is possible to derive the following expressions:

$$w_{CNT} = \frac{\cos\left(\vartheta_{eq}^{CNT}\right)}{\cos(\vartheta_i)} = \frac{\cos\left(\vartheta_{eq}^{CNT}\right)}{\cos\left(\vartheta_{eq}^{graph}\right)} w_{graph};$$

$$\varphi_{CNT} = \frac{\cos\left(\vartheta_{eq}^{CNT}\right) + 1}{\cos(\vartheta_i) + 1} = \frac{\cos\left(\vartheta_{eq}^{CNT}\right) + 1}{\cos\left(\vartheta_{eq}^{graph}\right) + 1} \varphi_{graph}$$

(6)

from which it is possible to calculate the parameters w and φ for the VACNTs carpet.

The results are shown in table 3. In the case of Fakir theory, the φ value is very low, 0.0027. By the definition of the parameter φ, that is the fraction of solid contacting the liquid [28], we can assume that the super-hydrophobic behaviour is due to the fact that the actual contact surface between the drop and the nanotubes is extremely small, i.e. 0.27% of the actual surface.

If considering instead the Wenzel approach we can calculate $w = 9.9$, that means that the drop should be in contact with a surface ten times higher than that under the drop, suggesting the percolation of the drop inside the first nanometres of the carpet.

In the case of the thin entangled CNTs layer, the experimental contact angle is lower (144°), and consequently a higher $\varphi = 0.21$ is calculated by Fakir theory; this means that 21% of the surface is in contact with the drop. This is reasonable since in this case the nanotubes are horizontally aligned, so that the drop touches their lateral surface and not

their tip. In the Wenzel approach $w = 8$, suggesting that also in this case the drop wets a much larger surface of nanotubes than that under the drop.

It is impossible to determine whether Wenzel or Fakir mode is active, since it is not possible to calculate w and φ for the carbon nanotubes structures. Actually, from its definition, it is possible to see that φ is the ratio between bulk and theoretical density:

$$\varphi = \frac{\rho_{bulk}}{\rho_{carbon}}$$

(7)

so that it could be possible to calculate it from density measurements. The bulk density of the VACNTs carpet was measured to be 0.30 g cm^{-3}, and considering a theoretical value of 2.3–2.6 g cm^{-3} for CNTs [32] it results that $\varphi = 0.12$–0.13. The difference between this value and the calculated 0.0027 value can however be ascribed to the difference between surface density and bulk density, as observed also by SEM observation (figure 2). The number of carbon nanotubes protruding from the surface is much lower than the number of nanotubes in the bulk. Thus, the reason why in our experiments the contact angle is extremely high can be found in the irregular surface morphology of the samples, that bring to a large roughness. On the entangled carbon nanotubes, where the surface is more flat, a significantly lower contact angle is observed.

4.2. Contact angle after oxidation

Contact angle measurements were also realized after two different oxidation treatments, and the results are shown in table 4. Also in this case it must be considered that with angles lower than 90° percolation through the CNT carpet is observed.

Oxidation performed by applying a difference of potential to the VACNTs carpet (bias oxidation on the table) resulted in a non-uniform distribution of polar groups on the surface of the carpet. Thus, it was found a wide distribution of contact angles for water, ranging from 50° to 100°, according to the position on the surface. No regular pattern was observed for the measured different angles.

Conversely, after the acid oxidation treatment the contact angle was constant on the whole surface of the carpet. Its value was very low, showing that a transition from a hydrophobic to hydrophilic behaviour occurred.
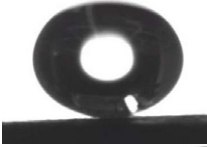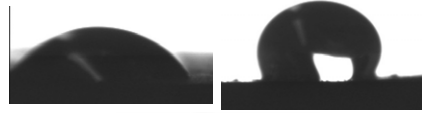
The measurement of contact angle for DMSO and CH$_2$I$_2$ showed very similar values with respect to those observed on the unoxidized carpet. This suggests that the oxidation forms a sufficient number of polar groups on the surface to allow an hydrophilic behaviour, without however altering substantially the surface properties toward low polarity solvents.

4.3. Percolation

On all samples that showed solvophilic behaviour, percolation of the solvent through the carpet was observed. The percolation rate of the solvent was measured in order to derive information on the structure of the carpet from the analysis of the percolation data.

A typical percolation experiment is observed in figure 3 for a VACNT carpet oxidized by applying a difference of

Table 4. Effect of oxidation on contact angle of different solvents on VACNTs.

Material	Water		Dimethyl sulfoxide	Diiodomethane
As grown	176°		23° [a]	24° [a]
After bias oxidation	50° [a]–100°		—	—
After acid oxidation	25° [a]		21° [a]	33° [a]

[a] Percolation observed.

Figure 3. Percolation of a water drop into the bias oxidized VACNTs carpet.

Figure 4. Fit of the percolation of a water drop into the bias oxidized VACNTs carpet.
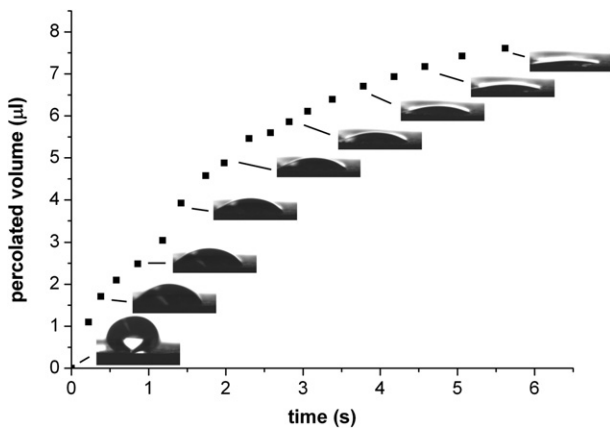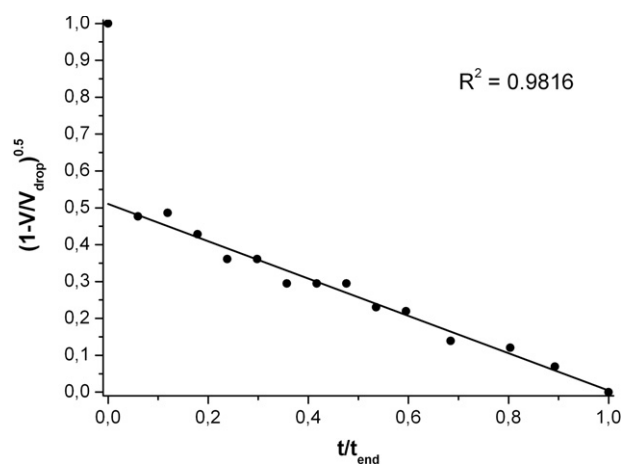

Figure 5. Fit of the percolation of a water drop into the acid oxidized VACNTs carpet.

potential. In a few seconds the drop percolates through the carpet, and some frames were extracted from the movie of the percolation to show the percolation of the drop.

The fitting of the percolation curve with equation (5) results in a very good fit, as shown as example for water in figures 4 and 5. The first point of the percolation curve, for the cases with low contact angle, results higher than the fitting curve (figure 5); this is due to the fact that during the wetting/percolation experiment the drop falls down from a small height onto the sample. Thus the first observed point is vitiated by the energy of the fall, that pushed the solvent into the carpet. Apart from the first point of the curve however, the fitting is always very good, resulting in R^2 values close to 0.99.

In table 5 are reported the data for the various percolation experiments realized. On the sample of VACNTs oxidized by the application of a difference on potential, the time needed for a complete percolation of the water into the carpet was measured to be $t_{end} = 5.6$ s, while, on the sample oxidized by the nitric–sulfuric acid mixture, the time was $t_{end} = 0.67$ s. This difference was probably due to the different polarity of the functionalized carbon nanotube surfaces. In the case of acid oxidation the obtained contact angle was very low (25°) and the oxidation was uniform on the surface (and presumably in the bulk) of the sample. In the case of oxidation via a difference of potential the contact angle was higher and less uniform,
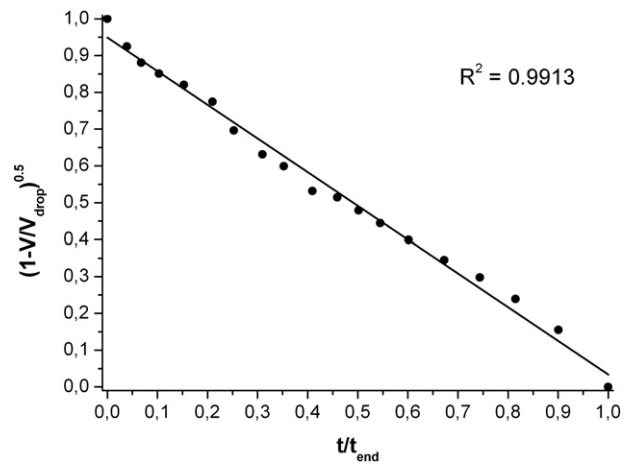
varying from 50° to 100°; in some zones a hydrophobic behaviour was observed, and a contact angle lower than 90° is needed in order to have percolation. Low percolation times have been observed also for DMSO and CH_2I_2.

The modified Torricelli law suggested in section 3.2 has been considered, and the parameter η has been calculated

Table 5. Percolation data for different solvents and CNTs structures.

Material	Solvent	V_{drop} (μl)	d_{drop} (mm)	$\vartheta_{contact}$ (deg)	R^2	t_{end} (s)	η
VACNTs after acid oxidation	CH$_2$I$_2$	1.29	1.35	24	0.9890	0.2	6×10^{-6}
VACNTs	DMSO	6.8	2.35	23	0.9893	1.1	3×10^{-6}
VACNTs after acid oxidation	Water	2.07	1.58	25	0.9816	0.67	1×10^{-6}
VACNTs after bias oxidation	Water	7.7	2.45	50	0.9913	5.6	3×10^{-6}
SWCNT	Water	7.8	2.46	55	0.9965	5.8	4×10^{-6}

to fit the t_{end} parameter, considering $f = 1$, the results being presented in table 5; the value of φ was chosen to be 0.12, following density measurements. The calculated surface value of 0.0027 was not considered since in this case the bulk properties have to be considered. Even if the predicted percolation law of equation (5) is clearly observed in our experiments, with a statistical correlation close to 0.99, the suggested values for the parameter η are of the order of 10^{-6}. It can be observed that slightly higher values are observed for the less polar solvents, meaning that the resistance to the flow is lower. With VACNTs, the stronger oxidation route brings to slightly higher η values, but the flow mechanism inside the carpet must in all cases be very similar.

5. Conclusions

Contact angle measurements were performed with water, dimethylsulfoxide and diiodomethane on two different carbon nanotubes structures: carpets of vertically aligned CNTs, with a height in the millimetric range; thin layers (5–20 μm) of entangled CNTs. On both structures the less polar solvents had a low contact angle, while a hydrophobic behaviour was observed, depending on the nanotubes orientation. Over the VACNTs the contact angle was exceptionally high (176°), while over the horizontally aligned entangled CNTs an angle of 144° was observed. The results have been explained in terms of Fakir effect: since the surface of the VACNTs carpet is irregular, presenting a very small number of protruding CNTs, the angle is very high. When the surface is more flat, the effect is smaller and the contact angle too.

After oxidation of the VACNTs a transition toward a hydrophilic behaviour was observed. On solvophilic samples, percolation experiments were also performed and the results were well fitted with our proposed percolation law, showing a very high quality of the fit for all solvents and structures.

These results seem interesting in view of the application of CNTs carpets as filters. On one side it was confirmed that oxidation, either acid or obtained by applying a bias voltage, lowers the contact angle of water on carbon nanotube carpets, thus switching from a super-hydrophobic state to a hydrophilic one. On the other side this work hints at the possibility of applying these materials for the separation of mixtures of water and non-polar substances.

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