Borosilicate glass matrix composites containing multi-wall carbon nanotubes

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Abstract

Carbon nanotubes (CNTs) are in the range of the most promising reinforcing materials for structural composites, since they possess extraordinary Young's modulus and mechanical strength. In this study, multi-wall CNTs are considered for the first time as reinforcing elements in a borosilicate glass matrix. The densification behaviour and the microstructure characterisation of composites containing 10 wt.% multi-wall CNTs are presented. The coating of CNTs with silica by a sol–gel process is effective in promoting the homogenisation and the densification of the CNTs/glass powder mixtures. Cold pressing and pressureless sintering or hot pressing at moderate temperatures were employed to fabricate the composites. Pressureless sintering did not lead to well densified composites. The compaction degree achieved by hot pressing (85% theoretical density), on the contrary, is found to be promising for the development of structural composites, although optimisation of the hot-pressing parameters is required to achieve higher densities.
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1. Introduction

Carbon nanotubes (CNTs) are some of the most innovative materials developed in the recent years. Since their discovery,[1] several studies have been performed on their production, properties and structure characterization. Due to their molecular assembly, made from rolled graphene sheets, CNTs possess extraordinary electric, thermal, optical and mechanical properties. A single-wall CNT consists of a perfect closed cylinder, with a diameter of a few nanometers. Several concentric cylinders assembled together yield the so-called multi-wall CNTs. Both single- and multi-wall CNTs exhibit a very large aspect ratio, i.e. their length is 1000 to 10,000 times their diameter. CNTs are extremely rigid; their elastic modulus has been measured to be higher than 1 TPa

(1000 GPa) and strong; their tensile strength being in the order of 10 GPa.[2–4] Such extraordinary and unusual mechanical properties are due to the fact that the graphene sheets are closed, while in the classic graphitic structure, which could be found in the commonly produced carbon fibres,[5] especially in the so-called high-modulus fibres,[6] the graphene sheets are open, planar and linked with each other by a weak bond. The extraordinary stiffness of the graphite structure along its basal planes is therefore made available in CNTs for tubular three-dimensional morphology. The CNTs can be consequently treated as the ultimate evolution of the carbon fibre.[2]

Despite other important properties, like their excellent electronic conductivity, CNTs may find extensive applications in replacing carbon fibres as the reinforcement of several materials, such as polymers, metals or ceramics,[4,7–10] thus forming innovative (nano-)composite materials. Unlike metal and polymer matrix composites, the obtainment of

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high strength and high stiffness materials is not the unique aim in ceramic matrix composites, including glass matrix composites.[11,12] In such composites the reinforcing phase is intended to enhance the fracture toughness and decrease the inherent high flaw sensitivity of the matrix. Although they generally possess a high elastic modulus and a good mechanical resistance, particularly when related to the density, monolithic ceramics cannot be employed in several structural applications mainly due to their brittleness. Such a situation is particularly notable with glasses, since the amorphous structure does not provide any obstacle to the fracture propagation. The reinforcement of glasses with carbon fibres has been found to be successful since the late 1960s.[13] Carbon fibres are particularly effective since the interface is not extremely strong, but still enough for the load transfer between the phases, thus allowing a notable amount of energy to be dissipated during fracture propagation, due to debonding and pullout of the fibres. The fracture toughness of carbon fibre reinforced glass matrix composites may reach excellent values (sometimes over 30 MPa m$^{0.5}$).[14]

In recent times, a significant research activity has been conducted on exploiting the toughening ability of carbon nanotubes in ceramic matrices. CNTs are thought to be promising since their dimensions and their aspect ratio provide a huge interfacial area, so that the energy dissipation during fracture propagation due to pullout could be highly enhanced.

The most significant results are those with SiC,[15] MgO, MgAl$_2$O$_4$[16–18] and Al$_2$O$_3$[16–20] matrices. Zhan et al.[20] achieved nearly fully dense nanocomposites of single-wall carbon NTs (10% volume fraction) in a nanocrystalline alumina matrix. Such composites exhibited a fracture toughness of about three times that of un-reinforced nanocrystalline alumina, thus confirming the toughening ability of CNTs towards ceramics. Moreover, the wear behaviour of alumina ceramics was found to be greatly improved by the addition of CNTs.[19] The wear behaviour of such composites is enhanced, since the lubricating ability of the carbon inclusion depends not only on the sliding of the concentric graphene layers but also on the rolling motion of the CNTs.

Although the reinforcing of crystalline ceramics with CNTs is a reasonably well-established field of research, very few works have been done considering amorphous glass matrices. Very recent works demonstrated the feasibility of the coating of CNTs with a silica matrix, mainly by the sol–gel method.[21–23] In one of the studies,[23] the silica/CNTs composites were prepared for non-linear optical applications and the CNTs content was very low (0.25 wt.%). To the authors' knowledge, only the recent work of Ning et al.[24] has focussed on the application of CNTs as reinforcement in glass matrices with the aim of exploring the possible toughening ability of the CNTs. They focussed on a silica matrix and found an increase of both bending strength and fracture toughness with addition of 5 vol.% CNTs. In this work, we present the results of a preliminary study on the manufacturing of CNT reinforced borosilicate glass matrix composites containing a significant amount of multi-wall CNTs (10 wt.%). Although

multi-wall CNTs are not best choice in terms of mechanical properties, they were selected for this preliminary study due to their lower cost in relation to single-wall CNTs. The goal is to produce inorganic composites with improved fracture toughness as well as enhanced electrical conductivity and, possibly, optical properties. The method for dispersing CNTs in the glass matrix is presented. The composites were developed by two routes: (i) cold pressing, followed by pressureless sintering, and (ii) hot pressing at moderate temperatures. The densification behaviour and the microstructure of the composites are discussed.

2. Experimental procedure

2.1. Starting materials

The matrix in the present investigation consists of powdered Duran® borosilicate glass (Schott-Glas, Mainz, Germany), with a particle size between 10 and 40 μm. Duran® is a relatively low thermal expansion coefficient glass; it is very resistant to corrosion and it is consequently employed extensively in the field of the chemical industry. The chemical composition and the physical properties of Duran® glass are shown in Table 1.[25] This glass has been used extensively as matrix in ceramic platelet[26,27] and fibre reinforced composites.[28,29]

As shown in Table 1 there is alumina in the chemical composition of Duran® glass: such addition is favourable since it should prevent the glass from crystallization (with cristobalite precipitation), which may occur when sintering or other heat-treatments are performed.

The CNTs employed as reinforcing phase were multi-wall CNTs (Yorkpoint New Energy Sci. & Tech. Department Co. Ltd., Guangzhon, China), with a distribution of diameters between 10 and 40 nm. Fig. 1 reports a TEM micrograph of the CNTs used, showing that the CNTs are tangled together.

2.2. CNT/glass powder mixtures

Two different Duran® glass/CNTs mixtures were prepared. The CNT content was 10 wt.% in both mixtures. In

Table 1
Characteristics of the Duran® glass[25]

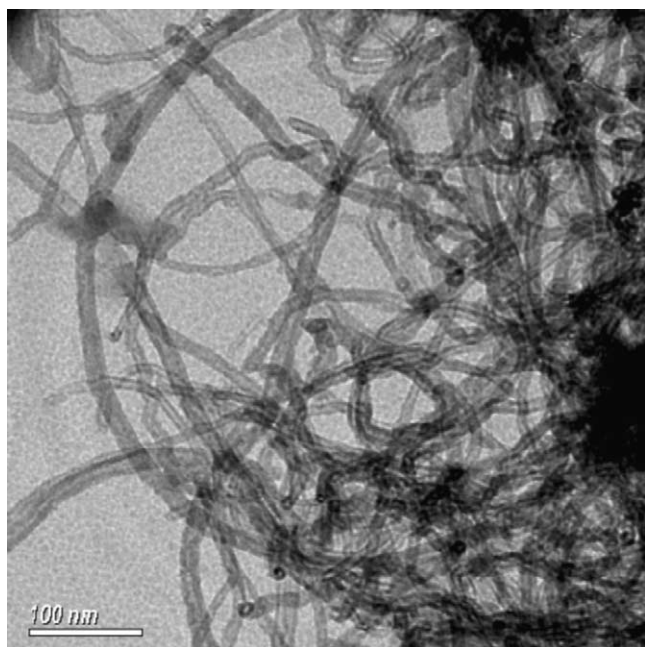| Chemical composition (wt.%)	
SiO$_2$	81
B$_2$O$_3$	13
Na$_2$O + K$_2$O	4
Al$_2$O$_3$	2
Physical properties	
Density (g cm^{-3})	2.23
Modulus of rupture (MPa)	60
Elastic modulus (GPa)	64
Coefficient of thermal expansion (°C^{-1})	3.3 × 10^{-6}
Refractive index	1.473

Fig. 1. TEM micrograph of the carbon nanotubes in as-received condition.

the first case, CNTs were dispersed in a water solution containing 10 wt.% of a surfactant (Triton100, Sigma-Aldrich) and the dispersion was ultrasonicated for 2 h. Duran® glass powder was added and the final mixture, called mixture A, was sonicated for other 2 h. In the second case, CNTs were dispersed in a water/ethanol solution containing 10 wt.% of Triton, tetraethoxysilane (TEOS) and NaOH (the molar ratio TEOS/H_2O/NaOH was 1/5/0.01) and the dispersion was ultrasonicated for 2 h. Duran® glass powder was added and the final mixture, called mixture B, was ultrasonicated for other 2 h. The mixtures were calcined at 200 °C in air to evaporate water, ethanol and triton. Scanning electron microscopy (SEM) (JEOL LV 5610) was used to assess the homogeneity of the CNTs/glass powder mixtures. It was not possible to determine the density of the mixtures by gas pycnometry due to considerable adsorption on the CNTs leading to inaccurate results. The theoretical density of the mixtures was therefore estimated from the rule of mixtures and data for the density of the glass matrix (Table 1) and of CNTs. The density (volumetric weight) of multi-wall CNTs was assumed, in a first approximation, to be 2.16 g cm^{-3}, an average value from data reported in the literature, which are in the range 2.09–2.25 g cm^{-3}, the latter being the density of graphite.[30] The density of carbon nanotubes is in fact a function of both their diameter and their number of shells.[20]

2.3. Composites manufacturing

Different processing routes were used for the manufacturing of the CNT reinforced glass matrix composites. The first two routes start from the cold pressing and viscous flow pressureless sintering of glass powders. The powder mixtures were compacted into cylindrical shaped pellets (about 8 mm diameter and 3 mm height) at room temperature, by applying a pressure of about 10 MPa. In the first case the samples were directly sintered in an argon atmosphere at a temperature varying from 750 to 770 °C, with a heating rate of 3 °C/min and a holding time varying between 2 and 6 h. In the second case, a two-step method was employed. The samples were firstly heated up to a holding temperature (varying between 400 and 500 °C) in an oxidizing atmosphere, in order to burn out the organic residues from the preparation stage. TGA analysis performed in flowing air showed that these temperatures are not high enough to cause an extensive oxidation of the used CNTs (~0.3% weight loss at 500 °C; ~10% weight loss at 600 °C). Subsequently, a vacuum was created in the furnace, argon was introduced and the samples were heated up to 750 °C, with a holding time of 3 h. The argon flow was about 0.2 l/min for all inert atmosphere stages.

The third fabrication route consisted in hot pressing of samples in vacuum at 750 °C, with a slow heating rate of about 1.5 °C/min and a holding time of 2 h. The compaction pressure was 10 MPa. The cooling rate was 3 °C/min. No further heat-treatment (e.g. annealing) was performed on the samples after fabrication.

2.4. Samples characterization

In order to investigate the sintering behaviour of the CNTs/glass mixtures, density measurements were conducted by the geometric and Archimedes' methods. The reference theoretical density for the glass matrix composites (with 10 wt.% CNTs) was $\rho_c = 2.22$ g cm^{-3}, calculated from the rule of mixtures. X-ray diffraction (XRD) analyses were conducted on all samples in order to detect any crystallization of the glass occurred during sintering. SEM was conducted on fracture surfaces of selected samples in order to confirm the integrity of CNTs after the thermal treatments, to identify residual porosity and other microstructural defects, and to infer the occurring of possible toughening events (crack-CNTs interactions), essential to understand the potential of CNTs in reinforcing glass matrices.

3. Results and discussion

SEM images showing the starting CNTs/glass mixtures are shown in Fig. 2a–d. The micrographs show that the maximum dimension of particles in Duran® glass powder is about 40 μm. At low magnifications (Fig. 2a and b) agglomerates of glass powder and CNTs are clearly visible, together with some glass powder that is not in contact with CNTs. The agglomerates in mixture B (Fig. 2b) seem to be smaller than those in mixture A (Fig. 2a), but they are more numerous. At high magnification CNTs are clearly visible in both mixtures (Fig. 2c and d). In the agglomerates of the mixture B, probably due to the introduction of a SiO_2 interface between the CNTs and the glass, a rather homogeneous mixing was
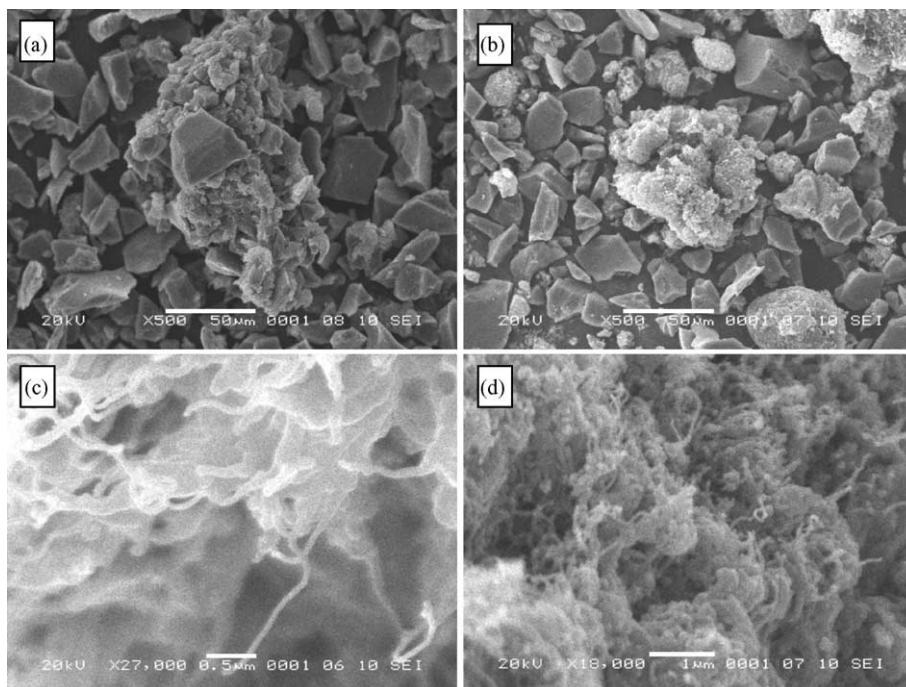
Fig. 2. SEM micrographs of the starting CNTs/Duran® glass mixtures: (a) mixture A at low magnification; (b) mixture B at low magnification; (c) mixture A at high magnification; and (d) mixture B at high magnification.

found, as shown in Fig. 3. In addition, it seems, at least by qualitative assessment, that the use of TEOS helped disentangling CNTs in mixture B (Fig. 3). The surface modification of CNTs is thus found to be useful, even though not sufficient to ensure a complete homogenisation of the CNT/glass powder mixture. This result agrees with literature reports considering the need to modify the surface of CNTs in order to improve their dispersion in ceramic matrices.[31]

All sintered samples were black and opaque. The data from the density measurements of the glass matrix composites fabricated by the different routes are summarized in Table 2. Cold pressing and pressureless sintering techniques were tried first because they constitute the most cost-effective method to produce glass matrix composites offering also the highest versatility in terms of shape of components that can be fabricated. For the present CNT containing composites, one-step pressureless sintering was found to be unsuitable, since the densities achieved were very low and the samples
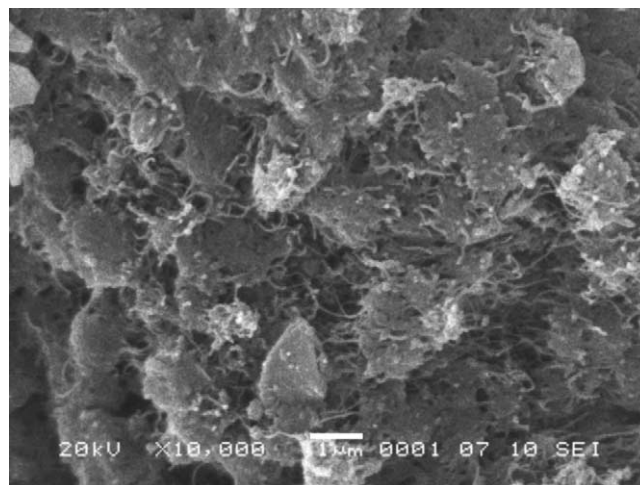

Fig. 3. SEM micrograph at high magnification of CNTs/glass in the mixture B revealing mixture homogeneity.

Table 2
Density and porosity values of one-step sintered, two-step sintered and hot-pressed samples

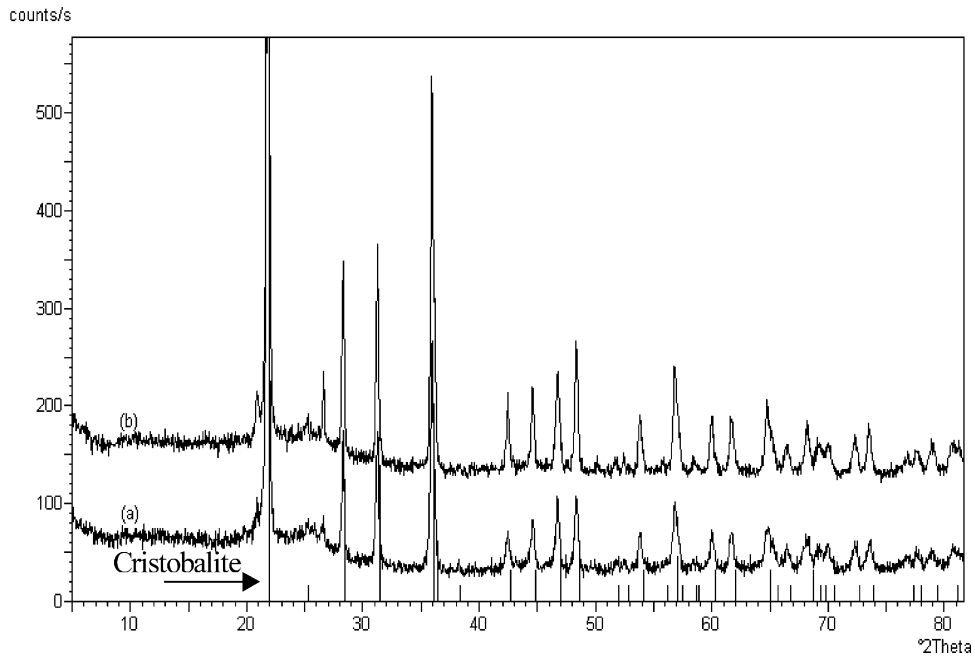| Powder type	Thermal treatment	Density (± 0.02 g cm^{-3})	Average estimated porosity % ($\pm 2\%$)
A	One-step sintering at 750 °C	1.02	54
B	One-step sintering at 750 °C	1.11	50
A	Two-step sintering (intermediate at 500 °C)	1.98	11
A	Two-step sintering (intermediate at 400 °C)	1.14	49
B	Two-step sintering (intermediate at 500 °C)	1.94	13
A	Hot pressing at 750 °C (10 MPa)	1.66	25
B	Hot pressing at 750 °C (10 MPa)	1.81	18

Fig. 4. X-ray diffraction (XRD) patterns of samples made from (a) mixture A and (b) mixture B by two-step sintering method (first step at 500 °C) showing cristobalite formation.

were weak. The estimated porosity in the samples was about 50%. The two-step pressureless sintering process led to notably higher density for samples with an intermediate treatment at 500 °C. For an intermediate step at 400 °C, the samples showed a sintering behaviour comparable to that of the one-step sintered samples.

XRD and SEM analyses were performed to explain the observed sintering behaviour. Consistently with the literature,[17]
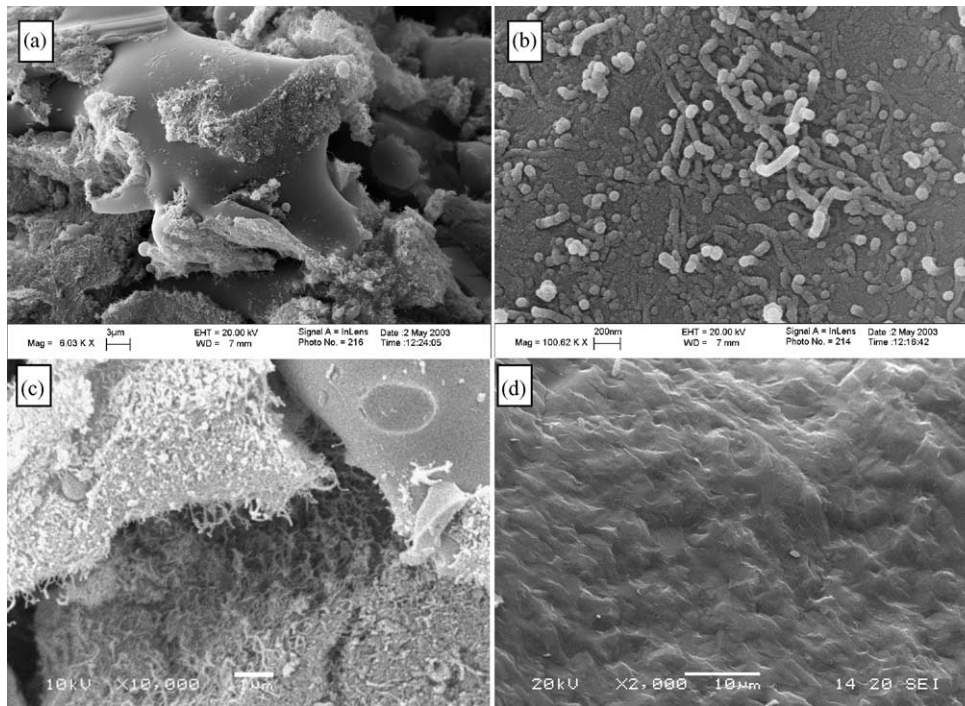

Fig. 5. SEM micrographs of the fracture surface of pressureless sintered samples: (a) one-step sintered sample (mixture B) showing CNT agglomerates around not fully sintered glass grains; (b) slight pullout of CNTs from a one-step sintered sample (mixture B); (c) two-step sintered sample (mixture A) with first step at 400 °C, showing CNTs; and (d) two-step sintered sample (mixture A) with first step at 500 °C, showing the absence of CNTs.

X-ray diffraction analysis was not effective in revealing the presence of CNTs; however XRD revealed that cristobalite crystallization occurred in samples made using both mixtures and during all heat treatments. This behaviour is shown in Fig. 4a and b for samples of mixture A and mixture B, respectively, which were sintered by the two-step heat treatment. Although the chemical composition of Duran® glass renders this glass to be rather stable against cristobalite formation, crystallization occurred in the present composites accordingly to the fact that the heat-treatments were rather long and CNTs may have acted as nucleation centres. In fact, crystallisation of Duran® glass powders free of inclusions does not occur under heat-treatments similar to those used here.[26] It is well known that crystallization hinders the densification of glasses, since any crystal will act like a rigid inclusion, thus enhancing the effective viscosity of the sintering mass.[32] In fact CNTs themselves are thought to be responsible for the observed poor sintering behaviour: it has been widely shown that inclusions with a high aspect ratio (fibre-like inclusions, like CNTs, being the most critical) dramatically enhance the viscosity of glass,[33] and thus they should impair viscous flow densification.[34,35]

The presence of CNTs in sintered samples was assessed by means of SEM, as shown in Fig. 5. In the one-step samples, the CNTs are clearly visible (Fig. 5a), together with not completely sintered glass grains. Micrographs at high magnification reveal a slight pullout of the nanotubes (Fig. 5b). The CNTs are still visible in the two-step sintered samples with an intermediate step at 400 °C (Fig. 5c), while they are not visible with an intermediate step at 500 °C (Fig. 5d). The treatment at 500 °C caused, in practice, the combustion of the CNTs. This fact is consistent with the observed sintering behaviour: the two-step sintered composites with intermediate stage at 500 °C are the samples with highest density since the number of inclusions hindering the densification has been drastically lowered.

The hot pressing treatment led to samples with a density notably higher than those obtained by the one-step pressureless sintering treatments. The estimated porosity content is about 25% for mixture A and 15% for mixture B. The coating of CNTs with silica in the mixture B is found to favour the densification. This may also be due to more uniform distribution of CNTs in these samples, as discussed below. Low magnification micrographs of polished and fracture surfaces for samples made from mixture A, as shown in Fig. 6a and b, are consistent with the lower level of porosity. The agglomerates of CNTs and glass are still present, leading to tangles of CNTs surrounded by glass (Fig. 6c), together with areas free of nanotubes. High magnification images of fracture surfaces, as shown in Fig. 7, demonstrate the feasibility of pullout of the CNTs in the hot-pressed samples made from mixture A. However, some areas of the samples seem to indicate limited infiltration of the glass matrix inside the CNT tangles (Fig. 7b). The fracture surfaces of hot-pressed samples made from mixture B are shown in Fig. 8. The CNTs are more visible and homogeneously distributed (Fig. 8a) than in
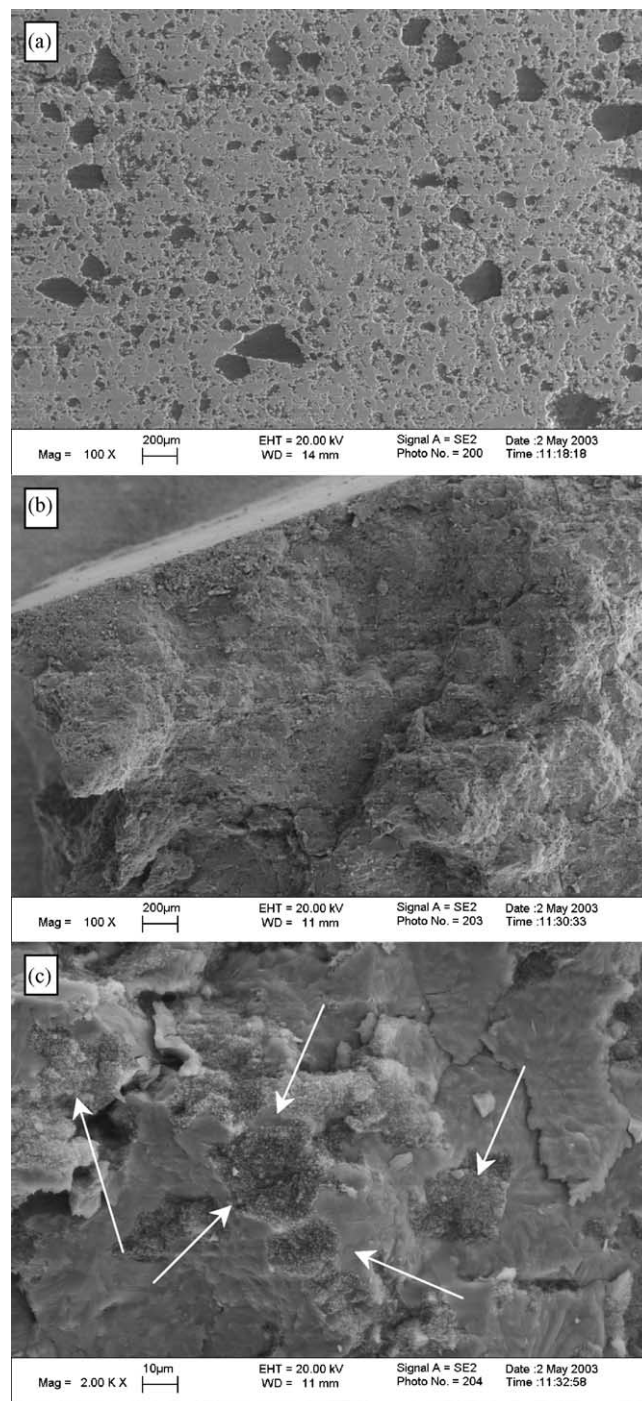

Fig. 6. SEM micrographs of a hot pressed sample from mixture A: (a) polished surface revealing a relatively low porosity; (b) fracture surface (low magnification) revealing the absence of large pores; and (c) fracture surface (high magnification) showing dense sample but relative inhomogeneous distribution of CNTs (marked by arrows).

the sample made from mixture A, consistently with the lower porosity content of the sample. High magnification images (e.g. in Fig. 8b) show the feasibility of CNT pullout in these samples.

In this study CNT/glass matrix composites have been prepared following the two traditional procedures for the manu-
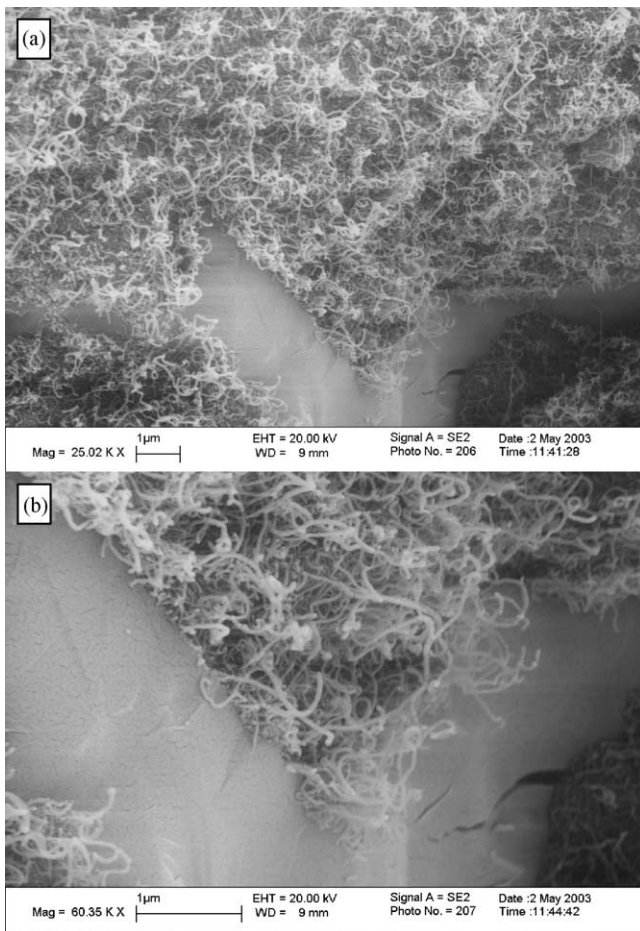
Fig. 7. SEM micrographs of the fracture surface of a hot pressed sample made from mixture A: (a) general view and (b) particular view revealing the possibility of pullout of carbon nanotubes from the glass matrix, which could be favourable for the toughness of the composite.
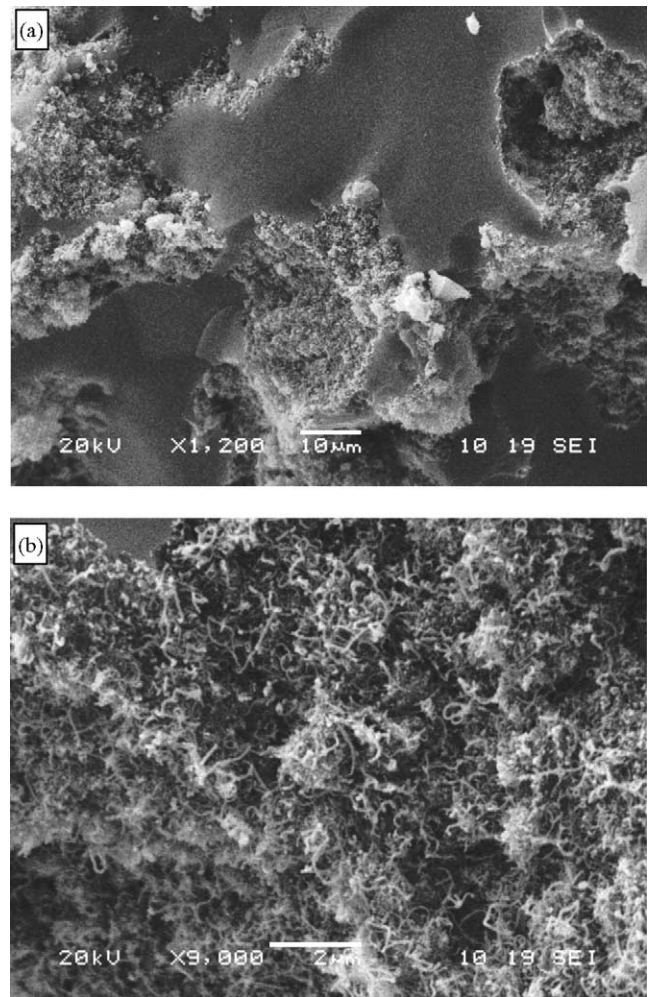

Fig. 8. SEM micrographs of the fracture surface of a hot pressed sample made from mixture B: (a) fracture surface (low magnification) showing dense sample and clearly visible tangles of CNTs and (b) particular view, revealing the pullout of carbon nanotubes from the glass matrix.

facturing of glass matrix composites, which consist of (i) cold pressing followed by pressureless sintering or (ii) hot pressing at relatively low temperatures (when compared to those temperatures required for processing polycrystalline ceramic matrix composites). These procedures have been successfully applied in previous studies to produce dense monolitic Duran® glass and Duran® matrix composites containing alumina platelets,[26] but they have not been considered so far to fabricate equivalent glass matrix composites with CNTs reinforcement.

DiMaio et al.[23] were successful in manufacturing CNT/silica matrix composites, however with a porosity content of about 20% and a very low CNTs content (0.25 wt.%). Moreover, they employed a complex chemical formulation for preparing the mixtures and an expensive thermal treatment by means of Nd:YAG laser irradiation. Seeger et al.[22] have recently reported a preliminary study on a CNT/silica glass matrix composite developed at high temperature (1150 °C), but no information has been provided about the density or the mechanical properties of their composites. The reinforcement of SiC and Al_2O_3 matrices with CNTs is

highly expensive, since the compaction must be performed at very high temperatures,[15,16–20,36] with a certain risk of damaging the CNTs. Thus, taking into consideration the few previous results published in the literature, it can be stated that the present densification results are highly promising, with a porosity content of ∼15% achieved by means of hot pressing at moderate temperature and pressure.

Since the sintering of glass-based mixtures depends essentially on the effective viscosity of the system, further work is needed for the optimisation of the operating temperature in order to counterbalance the increased viscosity effect due to the presence of extremely rigid inclusions of high aspect ratio such as CNTs.

The relatively poor homogenisation of the CNTs/glass mixtures may lead to samples with no significant improvement of the mechanical properties, especially fracture toughness and strength. The modification of the surface of CNTs with silica, consistently with the findings of Seeger et al.,[22] was found here to improve the homogenisation of the mix-

ture, thus further efforts should focus on the optimisation of the mixing of CNTs and glass powders based on "wet" techniques. Two approaches are suggested on the basis of the present results: (i) the coating of each individual glass particle with a sol–gel silica layer containing the CNTs, or (ii) the use of a sol–gel derived borosilicate glass to disperse the CNTs prior to the mixture with the Duran® glass powder. Other surface treatments proposed for CNTs, including heat-treatment in nitrogen and ammonia atmospheres as well as the use of alternative cationic or anionic dispersants,[31] should be also considered. The dimension of the starting glass powder is thought to be another key parameter: finer glass powders are suggested for future experiences, in order to achieve a better homogeneity at the stage of the powder preparation, essential for obtaining denser materials and exploiting fully the extraordinary reinforcing ability of CNTs.

4. Conclusions

The present work was essentially a study of the densification behaviour of carbon nanotubes/borosilicate glass mixtures aimed at fabricating CNTs reinforced or functional glass matrix composites. It has been shown that the presence of CNTs decreases the sintering ability of the glass matrix, which is thought to be due to the huge aspect ratio of the rigid, non-sintering inclusions causing a dramatic increase of the effective viscosity of the system at the sintering temperature. Such effect was also found in hot-pressing experiments. The relatively poor homogenisation of the CNTs/glass mixtures used probably hinders significant improvement of the mechanical properties of the composites, especially fracture toughness, despite the possibility of CNT pullout from the glass matrix. The coating of the surface of CNTs with silica, developed by the sol–gel method, was found to be promising to increase the homogeneity of CNT/glass powder mixtures and the density of composites made from them.

Acknowledgements

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