J Mater Sci (2009) 44:2851–2857
DOI 10.1007/s10853-009-3377-z

Electrical and mechanical properties of aluminosilicate inorganic polymer composites with carbon nanotubes

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Received: 2 December 2008 / Accepted: 27 February 2009 / Published online: 25 March 2009

Abstract The DC electrical conductance of potassium aluminosilicate inorganic polymers (geopolymers) containing up to 6 wt% single-wall carbon nanotubes has been determined as a function of temperature up to 340 °C. After removal of the processing water during the first heating cycle, the conductance in subsequent heating cycles increases as a function of carbon nanotube content and temperature from 9.75×10^{-4} to 1.87×10^{-3} S m^{-1} in the composites containing 0 and 0.2 wt% carbon nanotubes, respectively, at 290 °C. By comparison, the electrical conductance of potassium inorganic polymer composites containing graphite was generally lower. The conductance activation energies of the carbon nanotube and graphite composites were similar, and decreased from about 55 to 5 kJ $mole^{-1}$ with increasing carbon content. The tensile strengths of carbon nanotube and graphite-containing potassium geopolymer composites, determined by the Brazil method on 10–12 replicates, were about 2 MPa, and showed little change with increasing carbon nanotube content up to 0.3 wt%. By contrast, the tensile strengths of an analogous set of sodium composites were up to four times greater, possibly reflecting the necessity for less processing water in the synthesis of the sodium samples.

Introduction

Aluminosilicate inorganic polymers, also called geopolymers, were first described by Davidovits [1] as being formed under highly alkaline conditions from a solid aluminosilicate (typically thermally dehydroxylated kaolinitic clay) and an alkali silicate solution. The product, which hardens at ambient temperatures, is amorphous to X-rays and contains a random tetrahedral network of silicon and aluminium atoms, with charge neutrality being achieved by the presence of the alkali cations [2]. These products rapidly attain strength and are heat-resistant, making them potential substitutes for Portland cement-based building materials and for fireproof panels in buildings and vehicles. For these structural applications, additional strength can be imparted by the use of fibre reinforcement, employing a variety of fibres including carbon, graphite, basalt, aramide, or glass [1, 3].

Aluminosilicate inorganic polymers would be expected to display both thermal and electrical properties typical of more conventional aluminosilicate ceramics, but few detailed studies have been reported of the electrical properties of these materials apart from an observation [4] that the electrical resistivity of several sodium aluminosilicate geopolymers ranges from 10^5 to 10^{12} Ω cm and depends on the moisture content of the material; samples pre-heated at 300 °C and left in the air were observed gradually to pick up surface moisture in a 90% RH atmosphere, with a concomitant decrease in their electrical resistivity from 10^{12} to about 10^{10} Ω cm. over a period of 230 min [4].

Carbon nanotubes are known to possess interesting electrical properties, showing a wide spectrum of both metallic and non-metallic properties depending on their diameter and the helicity of their carbon atoms [5]. Typical resistivities of individual carbon nanotubes fall in the range 10^{-4}–10^{-6} Ω cm, but show abrupt jumps as the temperature is varied [5]. The electrical behaviour of single-wall carbon nanotubes (SWCNTs) differs from that of multiwall nanotubes, the former showing a metallic–non metallic

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transition at 280 K and the temperature dependence of the latter along the tube axis similar to a graphene sheet [6]. Multi-wall nanotubes prepared by spark plasma sintering (SPS) show anisotropic electrical conductance at high temperatures [7], and the electrical behaviour of thin films of nanotubes above room temperature has been explained in terms of randomly disordered nanotube networks [8]. The effect of electron-beam irradiation on the DC electrical conductivity of single-wall and multi-wall carbon nanotubes has also been reported [9].

In view of these interesting electrical properties, a number of studies have been reported of the electrical properties of composites containing carbon nanotubes. These include nanocomposites with polyester [10] and polythiophene conducting polymer [11]. The electrical properties have also been reported of composites of carbon nanotubes with inorganic systems including titanium nitride [12], silica [13] and stabilized zirconia [14].

In addition to their electrical properties, carbon nanotubes combine high stiffness with resilience and the ability to buckle and collapse reversibly [15], and both single-wall and multi-wall carbon nanotubes are reported to show tensile strengths of 50–60 GPa and Young's moduli of about 1 TPa [16]. The addition of carbon nanotubes to inorganic polymer systems may therefore bestow both interesting and useful electrical and mechanical properties on the resulting composite. The incorporation of 0.5–1.0 wt% of carbon nanotubes into Portland cement pastes has been reported [17] to result in slight increases in strength (8.7–13.1% increase in compressive strength and 1.8–2.1% increase in flexural strength). The incorporation of SWCNTs into nanocrystalline alumina by SPS at 1,150 °C is reported to result in a nearly three-fold increase in the fracture toughness of the composite [18].

Despite these promising results in other inorganic systems, the electrical and mechanical properties of aluminosilicate inorganic polymers containing carbon nanotubes have not been reported. The aim of the present study was therefore to investigate the effect of incorporating up to 6 wt% SWCNTs on the electrical and mechanical properties of aluminosilicate inorganic polymers. Since the sample sizes were limited by the amount of SWCNTs available, the tensile strengths were determined by the Brazil method, in which small cylindrical samples are broken across their diameter, and the carbon content of these samples was limited to 0.3 wt%. The DC electrical conductivities of similar-sized samples were determined as a function of temperature up to 340 °C. For comparison, a series of composites containing graphite was also investigated, and the effect on the mechanical strength of changing the alkali metal from potassium to sodium was studied.

Experimental

The potassium inorganic polymer matrix was synthesized from New Zealand halloysite clay (Imerys Premium Grade) dehydroxylated at 600 °C for 12 h, mixed with a solution of potassium silicate (Ineos Silicas, UK, Type 66), reagent-grade potassium hydroxide and water in proportions giving a composition with the following molar ratios: $SiO_2:Al_2O_3 = 3.16$, $H_2O:K_2O = 16.2$, $K_2O:SiO_2 = 0.34$. For the purpose of the strength tests, a corresponding set of sodium-based composites was prepared using O-type sodium silicate solution (Fernz Chemical Co., NZ, $SiO_2:Na_2O = 3.2$, 40.0 wt% solids) and reagent-grade NaOH (Scharlau, Australia) in proportions giving the following composition: $SiO_2:Al_2O_3 = 3.18$, $H_2O:Na_2O = 11.1$, $Na_2O:SiO_2 = 0.29$. The uncured mixtures were blended with 0.2–6 wt% SWCNTs (approximately 90% single-walled, kindly supplied by Sigmar Roth, Max Planck Institut, Stuttgart). The limited availability of these high-quality SWCNTs restricted the upper limit of their addition to 6 wt% in the samples for electrical measurements, and to 0.3% in the samples for Brazil tensile strength testing, for which 10–12 replicate samples were used to provide acceptable statistics. The samples were cast into 15 mm diameter circular plastic moulds, vibrated to remove entrapped air bubbles, wrapped in plastic film, hardened overnight in an oven at 60 °C then unwrapped and dried at 60 °C. The samples for strength measurements were 7-mm thick but the conductivity measurements were made on 3-mm thick samples. For comparison, an analogous series of samples containing 0.2–6 wt% graphite (BDH reagent grade) was prepared for testing. Samples of good homogeneity were obtained by thoroughly blending the dry components (clay and carbon) before adding the silicate solution and water and all the composites cured and hardened to form mechanically stable pellets.

Samples of the resulting products were powdered and examined by XRD (Philips PW 1700 computer-controlled goniometer with Co Kα radiation and a graphite monochromator) and solid-state ^{27}Al and ^{29}Si MAS NMR (Varian Unity 500 spectrometer at a field of 11.7T using 4 mm and 5 mm Doty MAS probes spun at 10–12 kHz for ^{27}Al and 5–6 kHz for ^{29}Si under the following conditions:

> ^{27}Al: spectrometer frequency 130.224 MHz with a 1 µs pulse and a 1 s delay, the spectra referenced to $Al(H_2O)_6^{3+}$.
> ^{29}Si: spectrometer frequency 99.296 MHz with a 6 µs pulse and a 60 s delay, the spectra referenced to TMS.

Scanning electron microscopy was carried out on Au-coated samples using a JEOL JSM-6500F microscope operated at 15.0 kV. Elemental analysis was carried out using an EX23000BU energy dispersive X-ray analyzer.

The flat faces of the pellets on which the electrical measurements were made were smoothed with 1,000 grit silicon carbide paper and coated with platinum paint (Gwent Electronic Materials Ltd., UK) to give good contact with the platinum electrodes of the measurement cell, which was enclosed in an infrared furnace (Delta Model 9023). The DC conductivity measurements were made using a Keithley Model 230 programmable voltage source and a Keithley Model 485 picoammeter. The furnace was heated at a linear heating rate of 2 °C min^{-1} to a maximum temperature of 340 °C, determined by thermal analysis experiments in air (TA Instruments TGA/DSC Model Q600), which indicated the onset of thermal breakdown of the SWCNTs in the composites was about 400 °C (by contrast, the graphite-containing composites were thermally stable to >1,000 °C). The conductance results reported here were made during a second heating cycle, an initial heating cycle of the as-synthesized samples to 340 °C having been made to eliminate the effect of the absorbed moisture and hydration water.

The tensile strength measurements were made by breaking the pellets across their diameter using an Instron 25 tonne TTKM universal testing machine at a crosshead speed of 1 mm/min. Ten to twelve replicates of each sample were tested and their tensile strengths were calculated according to the equation [19]:

$$\sigma = 2P/(\pi D t) \qquad (1)$$

where P is the breaking load, t and D the thickness and diameter of the pellet, respectively, measured using digital vernier calipers.

Results and discussion

Figure 1 shows typical XRD traces and ^{29}Si NMR and ^{27}Al spectra of the SWCNT and graphite-containing geopolymers. All samples show the characteristic X-ray amorphous XRD trace (Fig. 1a) expected for a well-cured geopolymer [2], with small sharp peaks corresponding to the SiO_2 polymorphs quartz (PDF file no. 33-1161) and cristobalite (PDF file no. 11-695), both present as impurities in the clay starting material. The strong, superimposed sharp graphite reflection (PDF file no. 12-212) seen in the graphite-containing composites has its major reflection coincident with the major quartz reflection (Fig. 1a). The ^{29}Si NMR spectra of the K-geopolymer composites (Fig. 1b) show single broad resonances at about −87 to −88 ppm, in the chemical shift range of metakaolin-based geopolymers [2], with similar spectra being recorded for the corresponding Na-geopolymer composites (not shown here). The ^{27}Al NMR spectra of all the geopolymer composites (Fig. 1c) indicate Al in solely tetrahedral coordination as expected, with only slight traces of octahedral Al at about 2 ppm. SEM micrographs (Fig. 2a) show a homogeneous distribution of carbon nanotubes twisting randomly throughout the samples. SEM micrographs of the samples containing graphite (Fig. 2b) show irregularly shaped carbon grains in a range of sizes up to 800 µm. The homogeneity of carbon distribution in both the SWCNT and graphite-containing samples was confirmed by elemental mapping of carbon. The individual SWCNTs are difficult to image, but a few associated multi-wall nanotubes can be seen to be distributed throughout the nanotube-containing composites (Fig. 2c).

Electric conductance measurements

As expected, the initial electrical conductance of all the as-synthesized samples increases sharply with temperature up to about 40 °C (Fig. 3), thereafter dropping rapidly as the hydration water is lost from the sample. The depletion of the mobile charge-carrying hydrous species is complete at about 80 °C, whereupon other charge-carrying mechanisms become significant, especially in the samples containing carbon (Fig. 3a). Since the primary object of this study was to determine the effect of the carbon allotropes on the conductance, the effect of water on the low-temperature conductance behaviour was eliminated during

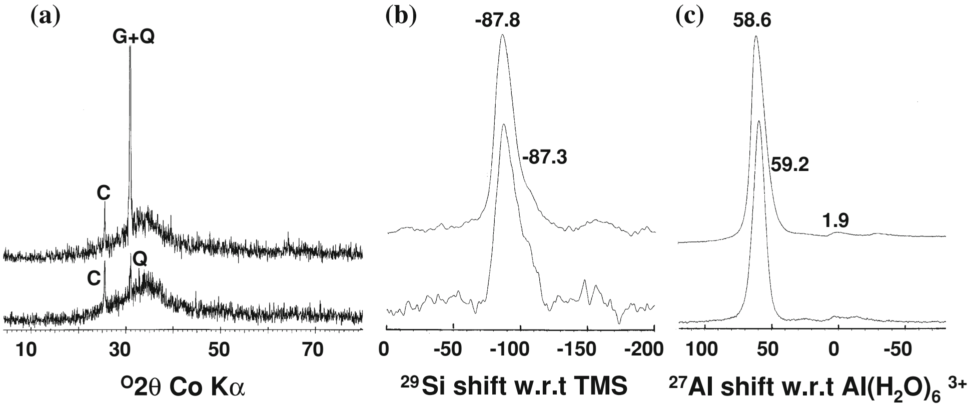

Fig. 1 XRD, ^{29}Si and ^{27}Al solid-state NMR characteristics of potassium geopolymer composites containing SWCNTs (*lower*) and graphite (*upper*). Key to the XRD peaks: *C* cristobalite (PDF no. 11-695), *Q* quartz (PDF no. 33-1161), *G* graphite (PDF no. 12-212)

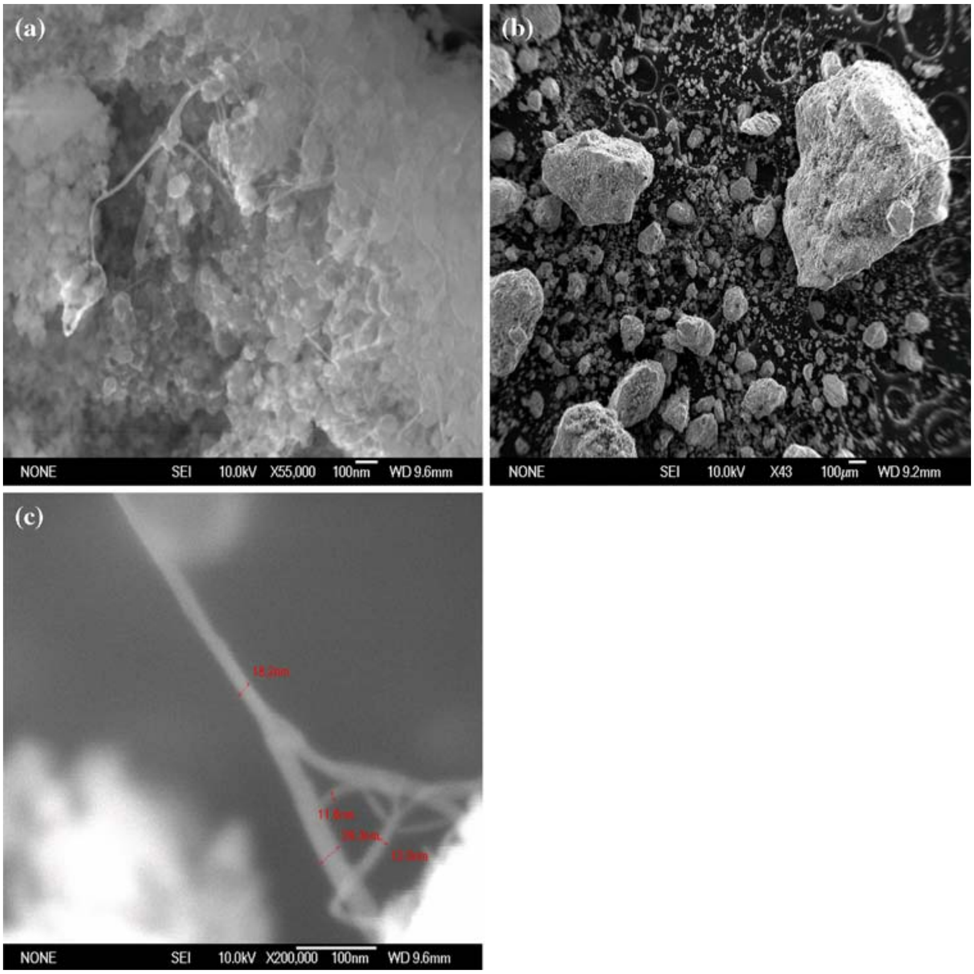

Fig. 2 Scanning electron micrographs of potassium geopolymer composites containing: **a** SWCNTs, **b** graphite, **c** close-up of a multiwall CNT associated with the SWCNTs in micrograph **a**

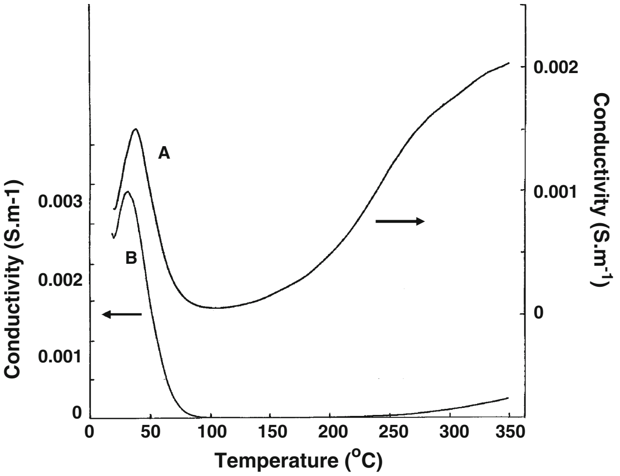

Fig. 3 DC conductivity of as-synthesized potassium geopolymers as a function of temperature during the first heating cycle. **a** Geopolymer composite containing SWCNTs and **b** carbon-free control sample

the first heating cycle up to the maximum measurement temperature (340 °C) and making the measurements during a second heating cycle.

The conductivities on a logarithmic scale of the resulting thermally pre-treated potassium inorganic polymer samples containing carbon nanotubes are shown in Fig. 4, with the corresponding plots for graphite-containing composites shown in Fig. 5. The conductivities of all samples (apart from that containing 0.2% graphite) are higher than the carbon-free control sample, and that in general the conductivities increase as expected with increasing carbon content, except for the samples containing higher concentrations of SWCNTs, of which the 0.6% and 1.5% SWCNT samples cross over at about 275 °C, and the trend in the 3% and 6% SWCNT samples is reversed over the whole temperature range (Fig. 4). The conductivities of the samples containing SWCNTs are generally greater than those containing the same content of graphite; at 290 °C, the conductivities of samples containing 0.2 wt% carbon are 1.87×10^{-3} S m^{-1} for SWCNTs and 7.81×10^{-5} S m^{-1} for graphite. At this temperature, the conductivity of the control sample without carbon is 9.75×10^{-4} S m^{-1}.

The conductivity behaviour of the sample containing SWCNTs is as would be expected for a material composed of conducting a conducting phase in a relatively less-

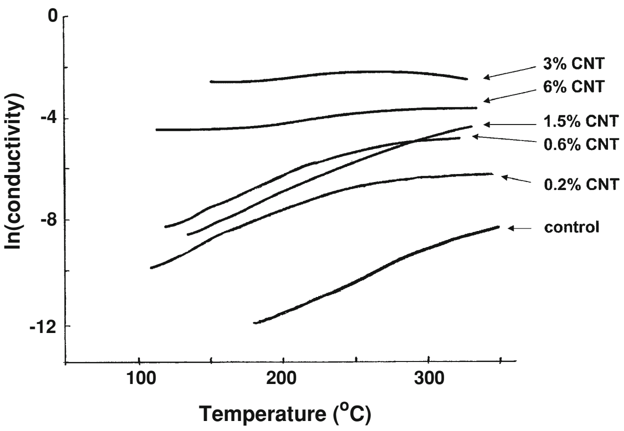

Fig. 4 DC conductivity (on a logarithmic scale) as a function of temperature for the second heating cycle of potassium geopolymer composites with varying SWCNT contents

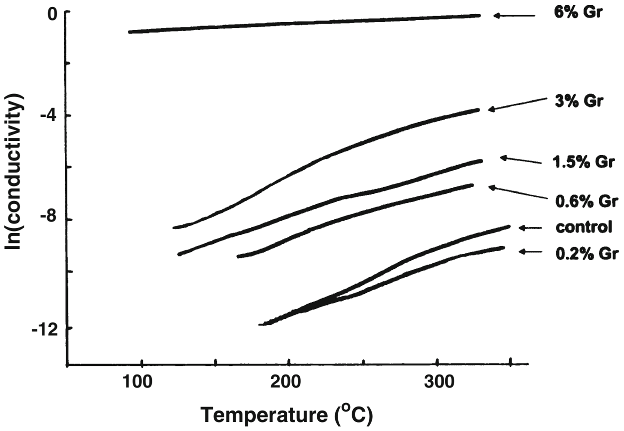

Fig. 5 DC conductivity (on a logarithmic scale) as a function of temperature for the second heating cycle of potassium geopolymer composites with varying graphite contents

conducting matrix (the inorganic polymer). The temperature dependence of the conduction processes in the two phases may be different, particularly if one of the components is behaving as a metallic conductor and the other is a semi-conductor, but at a given temperature an increase in the proportion of the more conducting component will result in an overall increase in conductivity with increasing contact between the conducting grains. This leads to the interesting question whether these results reflect anisotropic conduction behaviour in the carbon component. As noted above, the conductivity of SWCNTs is anisotropic, and ranges from 10^6 to 10^8 S m^{-1} [5], but graphite particles are also reported to exhibit anisotropy [20, 21], the conductance in the plane of their hexagonal layers (3.7×10^2 S m^{-1}) being much greater than perpendicular to this plane (1.7×10^{-1} S m^{-1}). The degree of anisotropy is reported to vary with the degree of perfection and twinning of the graphite crystals, the *c*-axis conductivity being more variable than that of the *a*-axis [21]. The conductance of the present composites containing graphite might be expected to reflect the behaviour of graphite perpendicular to the hexagonal layers due to a degree of preferred orientation during sample preparation, whereas the anisotropy in the conductance of SWCNTs may be offset by their more random orientation in the composites. This could explain the generally higher conductivity of the SWCNT-containing composites, although the relative conductance of these materials could be complicated by the possible presence of other factors with different temperature dependences. An example of one possible complicating factor in the graphite composites is the intercalation of alkali metal compounds into the graphite under the highly alkaline synthesis conditions [22]. The occurrence of this reaction to even a very limited extent would produce a significant increase in the conductivity of the graphite-containing samples, since the reported room temperature conductivities of these intercalation compounds are 1.38×10^7 S m^{-1} and 2.6×10^7 S m^{-1} in the *a* and *c* directions, respectively [22]. An example of a factor that may affect the conductance of the SWCNT-composites is the ability of the nanotube components to take up water into their inner space, leading to an increase in their electrical conductivity [23]. Although the present experimental data provide no evidence for the operation of these mechanisms, they illustrate the difficulty of deriving precise conduction mechanisms in these systems.

The activation energies for conductance in the various samples are shown in Fig. 6 as a function of carbon content. Although the points corresponding to nanotubes and graphite cross over at various carbon contents, both groups

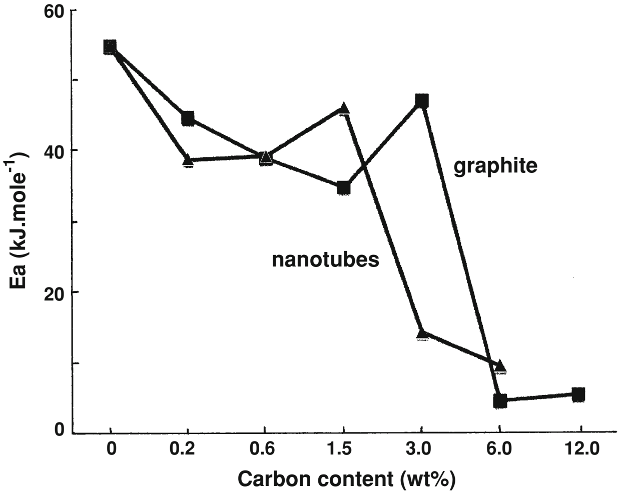

Fig. 6 Conduction activation energies for potassium geopolymer composites with SWCNTs and graphite as a function of carbon content

of samples follow the expected general trend for the activation energy to decrease with increasing carbon content, reflecting the difference in the temperature dependence of the conduction mechanism in the more highly conducting species and that of the aluminosilicate matrix.

Tensile strength measurements

Figure 7 shows the tensile strengths, derived from Brazil test measurements on a minimum of 12 replicates, as a function of carbon content, for both SWCNT and graphite-containing samples. Results for both K- and Na- geopolymer composites are shown.

The considerably higher strengths of the Na-geopolymer series are probably due to the need for less water in the processing of these samples. In addition, the water demand in the synthesis step of both the SWCNT and graphite composites increases with increasing carbon content, especially in the case of the SWCNTs, which are approximately 16 times less dense than the graphite. This militated against the use of a standardized water content, and necessitated the addition of a minimum amount of additional water to make the raw mixtures workable and secure a homogeneous distribution of the carbon through the samples. Although the presence of this additional processing water had no effect on the electrical measurements, which were made on pre-heated samples, it is expected to influence the strength measurements.

Figure 7 shows that for the K-geopolymer series, the tensile strength is not significantly improved by presence of either SWCNTs or graphite up to 0.3 wt% carbon addition. The Na-geopolymer series shows more variation, with additions of up to 0.25 wt% SWCNTs imparting greater strength than graphite. These disappointing results may be related to the amount of added carbon, which was limited by the availability of the SWCNTs; any additional strength that may be gained by increasing the content of added carbon may, however, be limited by its acting as a filler or diluent, or by its introduction of voids or imperfections from which cracks could form or propagate.

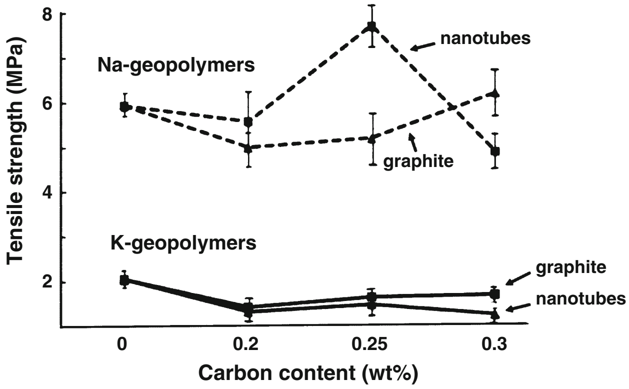

Fig. 7 Tensile strengths of potassium geopolymer composites with SWCNTs and graphite (*lower*) and the corresponding sodium geopolymer composites (*upper*) as a function of carbon content

The small size of the present samples, dictated by the quantity of SWCNTs available, made it necessary to measure tensile strengths rather than compressive strengths more frequently quoted. However, the following linear relationship between the tensile strength σ_t and the compressive strength σ_c can be derived from data for conventional porcelain ceramics [24]:

$$\sigma_t = 0.091\sigma_c - 4.4. \tag{2}$$

This relationship, derived for a material consisting of a glassy matrix in which crystalline phases are embedded, may also approximate to the present geopolymer composites, suggesting that their compressive strengths could be approximately 11 times larger than their tensile strengths. On this basis, the tensile strengths of the present composites containing SWCNTs would approximate to compressive strengths of 22 and 88 MPa for the potassium- and sodium-nanotube composites, respectively. Thus, the compressive strength values for the Na-series are very good, but the relatively poorer results for the K-series may be due to the effect of the additional processing water, as discussed above.

Conclusions

Composites of potassium aluminosilicate inorganic polymers (geopolymers) with up to 6 wt% SWCNTs have been synthesized and their DC electrical conductance measured as a function of temperature to below the decomposition temperature of the nanotubes (340 °C), with the following results.

1. During the initial heating, the conductance increases, then decreases rapidly due to the depletion of water.
2. During subsequent heating cycles, the conductivities of the SWCNT-containing samples are all greater than the control sample without nanotubes, and generally increase with increasing nanotube content. By comparison, the electrical conductivities of potassium composites containing the same amounts of graphite were generally lower that those of the SWCNT-containing samples.
3. The conduction activation energies are similar for both the nanotube and graphite-containing potassium geopolymer samples, and decrease with increasing carbon content.
4. The tensile strengths of potassium samples containing up to 0.3 wt% nanotubes are not significantly different from samples without carbon (2 MPa) and slightly less than samples containing the same content of graphite.

By contrast, a series of sodium-geopolymers containing SWCNTs have much higher tensile strengths (8 MPa at 0.25 wt% carbon content), possibly reflecting the lower water content needed in the synthesis of these samples. On the basis of known strength relationships for other ceramic materials, these tensile strengths would approximate to compressive strengths of 22 and 88 MPa for the potassium- and sodium-nanotube composites, respectively.

Acknowledgements We are indebted to Thomas Borrmann and Sigmar Roth for kindly supplying the high-quality SWCNTs, to David Flynn for assistance with the electron microscopy, to Ross Fletcher for assistance with the strength measurements and to Jeremie Barrel for advice on the electrical measurements. This work was supported by financial assistance from the MacDiarmid Institute for Advanced Materials and Nanotechnology.

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