ANALYSIS BY ATOMIC FORCE MICROSCOPY OF THE EFFECTS ON THE NANOINDENTATION HARDNESS OF CEMENT PASTES BY THE INTRODUCTION OF NANOTUBE DISPERSIONS

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Since their discovery in 1991 by Iijima [1], carbon nanotubes (CNTs) have probably become the most promising nanomaterials due to their unique properties. The aim of this work is to improve the mechanical properties of cement pastes by the addition of CNTs, giving rise to a new and higher-performance composite material. However, due to the interaction between the graphene sheets of the nanotubes, these tubes aggregate to form bundles or "ropes" that are very difficult to disperse. Ropes are even entangled with one another. Therefore, they must be disentangled, although it is extremely difficult to achieve a uniform dispersion at the single tube level, above all in aqueous media such as that for cement composites. Furthermore, due to their graphitic nature, there is not a proper adhesion between the nanotube and the matrix causing what it is called sliding. Both the non homogeneous dispersion of the nanotubes and the lack of interaction with the matrix prevent nanotubes from exhibiting their outstanding mechanical properties in nanocomposites. The main challenges in the search for efficient carbon nanotube reinforced composites are to obtain a good dispersion and load transfer.
First attempts to produce carbon nanotube reinforced cementitious composites have been recently reported [2] and [3]. In Ref. [4] the average compressive strength was discussed for reinforced cement paste matrices with SWNTs and MWNTs. In the present work a preliminary nanoindentation study to measure the Young modulus and hardness of the carbon nanotube reinforced cement paste matrices is presented.

The pastes used for the study were made from cem I 52.5 R. This type of cement has been selected because it presents the finest granulometry of all the commercial cements, which suits best for the inclusion of nanomaterials. A reference sample, C0 (w/c=0.34) was first prepared in order to study the impact of the addition of the nanotubes. Both single and multi walled carbon nanotubes were dispersed in the mix. The nanotube dispersions were carried out in plain distilled water (CM1, 0.2 wt % of mwnts; CM2 , 0.1 wt % of mwnts; CS1, 0.1 wt % of swnts, and CS2, 0.05 wt % of swnts) and in water with gum arabic (GA) powder (CGM1, 0.2 wt % of mwnts and 2 wt % of GA, and CGS1, 0.1 wt % of swnts and 1 wt % of GA) to improve the dispersion of the nanotubes as proved in Refs. [5] and [6]. After mixing, different amounts were moulded into prism-shaped specimens ($1 \times 1 \times 6$ cm^3) and compacted by vibration.

These samples were scanned with a Digital Instruments Nanoscope III Dimension 3100 atomic force microsope. With this type of microscope the surface topography can be characterized, as well as the mechanical, electrical and thermal properties of samples, with the appropriate probes. In our experiment, tapping-mode AFM imaging was used to characterize the surface structures of the polished CNT/Cement composites. The mechanical properties of the samples were measured using the nanoindentation module of the AFM. The elastic modulus was evaluated, based on the measured parameters, by using the approach of Sneddon [7], [8].

The calculated Young modulus and hardness were plotted versus their frequency of appearance in order to obtain their corresponding distributions. Our results for the plain cement are in good agreement with those reported in Ref. [9] for the values of the Young modulus (between 20 and 30 GPa). The results of the plain cement paste will be taken as reference to study the impact of the addition of the carbon nanotubes in the different samples.

Overall, the samples containing nanotubes but without gum arabic (CM1, CM2, CS1 and CS2) have worse mechanical properties than the plain cement paste. This behaviour stems from the afore-mentioned difficulties in the dispersion of the nanotubes in aqueous media due to their intrinsic hydrophobicity. Another result that supports this discussion is the fact that the samples with lower concentration of nanotubes get better mechanical properties in both cases (with SWNTs and MWNTs).

In the case of the samples with the nanotubes pre-dispersed with gum arabic (CGM1 and CGS1), a different trend is observed: both the Young's modulus and the hardness increase with respect to the same samples without the gum arabic (CM1 and CS1). The sample with SWNTs (CGS1) shows a considerable enhancement of the mechanical properties, whereas the enhancement is not so high for the MWNTs.

References:

[1] S. Iijima, Nature, **354** (1991) 56-58.
[2] I. Campillo, J. S. Dolado and A. Porro, Nanotechnology in construction, The Royal Society of Chemistry, Cambridge, UK (2004) 215**.**
[3] J. M. Makar and J. J. Beaudoin, Nanotechnology in construction, The Royal Society of Chemistry, Cambridge, UK (2004) 331.
[4] J. S. Dolado, I. Campillo, A. Porro and Y. Sáez de Ibarra, EUROMAT, Lausanne, Suiza (2003).
[5] R. Bandyopadhyaya, O. Nativ-Roth, O. Regev and Y. Rozen, Nano Letters, **2** (*1*) (2002): 25-28.
[6] Y. Sáez de Ibarra, I. Campillo, J. S. Dolado, E. Erkizia, Y. de Miguel and A. Porro**,** III Reunión Nacional de Física del Estado Sólido, San Sebastián (2004).
[7] I. N. Sneddon, International Journal of Science Engineering, **3** (1965): 47-57.
[8] J. W. Harding, and I. N. Sneddon, In: Proc. Cambridge Philos. Soc., **41** (1945) 16-26.
[9] G. Constantinides and F.-J. Ulm, Cement and concrete research, **34** (2004) 67-80.