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Electromagnetic characterization and shielding effectiveness of concrete composite reinforced with carbon nanotubes in the mobile phones frequency band

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1. Introduction

With the development of the nanotechnologies, the use of nanomaterials as reinforcement in traditional composites has become a research topic in many fields. The mechanical and electromagnetic (EM) properties of polymeric composite materials [1–5] are highly enhanced by the inclusion of carbon nanoparticles within the matrix. In particular, as far as the EM properties are concerned, the main advantage in dispersing carbon nanopowders within a polymeric resin is the increase of the composite electric conductivity [6], which in turn allows to tune the EM shielding at certain frequencies [7–10]. Recently, some research works have analyzed the thermo-mechanical properties and the durability of concrete composites reinforced by carbon nanomaterial [11-18]. On the contrary, in the scientific literature only few studies on dielectric and EM shielding properties of concrete composites reinforced with carbon nanomaterials are available [19-22]. Such subject is addressed by the present work, where concrete composite materials, made of commercial sand of river, pozzolana and cement, are reinforced by commercial carbon nanotube (CNT) powder. The

ABSTRACT

The electromagnetic properties of carbon nanotube powder reinforced concretes are numerically and experimentally characterized. This typology of composite material is built by following the simple procedure usually adopted for the on-site concrete production. The dielectric parameters are investigated by means of waveguide measurements in the frequency band 0.75–1.12 GHz that is currently exploited in mobile phone radio access networks. The obtained results are used to compute the electromagnetic shielding effectiveness of large wall-shaped concrete structures. A shielding effectiveness up to 50 dB is obtained for a 15 cm thick wall when the carbon nanotube inclusion is raised up to 3 wt%.

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attention has been focused to the frequency range 0.75–1.12 GHz, where many countries nowadays allocate the mobile phone radio access network bands. This is the lowest band currently exploited, and it is characterized by the lowest attenuation in the EM propagation through composites.

The electromagnetic interference (EMI) can be reduced by increasing the shielding effectiveness (SE) of the material around the devices. Few works related to the measurements of SE at low frequency can be found. Three main methods are available for SE measurements [23-31]. One consists of a fixture designed as an enlarged section of a coaxial transmission line, and is in full compliance with the ASTM test method D4935-1 requirements. This method makes use of relative low-sized samples (circles of 33 mm diameter), and the frequency range explored is 30 MHz–1.5 GHz; the measured data are related to the plane wave SE. In literature, measurements of SE are also carried out by using small coaxial air-line (Agilent 3/7 mm inner/outer diameter) able to work from 10 MHz up to 20 GHz [32]: on the other hand the very small samples dimension does not allow to work with concrete based composites. Another experimental setup for SE measuring is arranged by following CENELEC EN 50147-1 standard, which refers to measurements in the frequency range 75 MHz-10 GHz. The setup consists of: EM signal generator, amplifier, receiver, sending and receiving antennas, and a shielding cabinet which the test materials are

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integrated to. In the latter test, the materials are placed at the door of the cabinet, which is electrically large. The field incoming through the test material is much higher than the field incoming from other parts of the cabinet that can be thus neglected. Another method for SE measurements consists of two nested reverberation chambers: the frequency range depends on the chambers volume, and usually extends from hundreds of MHz up to 10 GHz. Other authors have used the waveguide method for the SE measurements of CNT filled concrete composites in the X-band (8.2–12.4 GHz) frequency [33].

Typically, the microwave characterization of the nanocomposite materials is successfully carried out by means of the waveguide method. The application of this precise technique has been limited to the X-band (8.2-12.4 GHz) or to even higher frequency bands (up to 18 GHz) in the most of the scientific publications. That is due to the measurement feasibility and reliability with relation to the waveguide sample dimensions. In the higher frequency bands the analysis is easier, since the dimensions of the waveguide sample holders are typically around $2 \text{ cm} \times 1 \text{ cm} \times 1 \text{ cm}$, or even lower. On the contrary, at lower frequencies the holders dimensions are much greater (ex. $24.8 \text{ cm} \times 12.4 \text{ cm} \times 10.7 \text{ cm}$ for measurements in the range 0.75–1.12 GHz). Furthermore, achieving an adequately homogeneous dispersion of the nanoparticles in the hosting matrix may become a demanding task for larger samples. Such issues are tackled in this research: the analysis is extended to the lowest band by realizing and measuring large samples. These latter are obtained by reproducing as much as possible the manufacturing procedure typically adopted in the preparation of concrete composites, within sight of a scale-up production scenario. The frequencies here considered, around 800-900 MHz, allow a greater propagation of the EM waves within the materials with respect to higher frequencies. That is why the national mobile telephony operator companies prefer the 800 and the 900 MHz frequency bands for mobile telecommunications: in this range the propagation of mobile phone signals through walls, and in general into building structures, is advantaged respect to what occurs at 12 or 18 GHz. The present study that is focused around 800 and 900 MHz, thus represents a novelty in the literature. A vector network analyzer (VNA) and a waveguide system have been employed to measure the EM transmitted and reflected power, in order to compute the naked and CNT-reinforced concrete composites relative electric permittivity. The obtained results have been used to evaluate the electromagnetic SE of large wall-shaped concrete structures. The present research should be thus of interest for mobile phone operators, in particular about the radio coverage planning to better approximate the EM attenuation range of buildings [34,35]. Moreover, high EM absorbing walls could be introduced in buildings to mitigate the human exposure to EM fields [36-40], to reduce the interference of electric devices in protected environments, and for security purposes against high-altitude electromagnetic pulses (HEMP) [41–43].

2. Experimental

Three kind of cement-based mixtures have been realized and characterized. The first one has been prepared for reference purposes, i.e. it does not contain any CNT inclusion. It is a mix of commercial sieved sand of river (50 wt%), pozzolana (30 wt%) and cement (20 wt%). The first two components were supplied by Calcestruzzi Cipiccia S.P.A. (Narni (TR), Italy), the third one by Colacem S.P.A. (Gubbio (PG), Italy). The second and the third material typologies have been obtained by adding CNT powder at 2 wt% and 3 wt% to the reference mixture. The market price of CNTs is an important issue to be mentioned: the economic aspect is sometimes neglected in the basic research, but it must be considered in a

scale-up production. Industrial grade multi-walled carbon nanotubes (MWCNTs) supplied by Nanocyl with a cost of about 300 \$/kg were employed, i.e. the NanocylTM NC 7000 (average diameter around 9.5 nm, average length 1.5 μ m, carbon purity 90%, metal oxide 10%, surface area 250–300 m²/g) produced in multi-tons via the chemical vapor deposition (CVD) process. As reported in the technical datasheet, when the MWCNT inclusion weight percentage increases up to 3% the volume resistivity and surface resistivity of polycarbonate decrease from 10¹⁵ to 10³ Ω cm and from 10¹⁴ to 10² ohm sq respectively. Fig. 1 shows some scanning electron microscope (SEM) pictures of the involved materials. The typical bundles of the raw (as received) MWCNTs are well visible in the high magnification micrograph of Fig. 1a.

As aforementioned, the usual concrete composites manufacturing procedure was addressed, with the aim to reproduce an industrial production scenario. In particular, an electric power hand mixer mortar (power 1300 W) has been employed to blend the mixtures, while any typical nanocomposites advanced lab-treatment (mixtures ultra-sonication, nanoparticles functionalization, etc.) has been avoided to preserve the time/cost saving of the whole materials production process.

The phases of preparation of the MWCNT-reinforced concrete composite are shown in Fig. 2. First, pozzolana and sand of river are pre-mixed, after that, cement is added and blended. Water is finally poured into the mixture that is homogenized by means of the electric power hand mixer mortar for 1 h. In the last phase, the MWCNT powder is carefully added to the concrete mush that is mixed again for 2 h by adding water. It has been observed that an amount of water approximately three times higher than what required for the 'naked' concrete is needed when the MWCNTs (about 100-150 g to realize the 2 wt% and 3 wt% reinforced material respectively) are added to the concrete mixture. That is due to the high water absorption behavior by the high surface area nanoparticles homogenized in the mixture. In particular, Fig. 1c shows the preparation of a MWCNT reinforced mixture: it is quite evident that a relatively low wt% fills the most of the total volume. As far as the authors' experience is concerned, such filler percentages represent a tradeoff between the advantages in terms of EM absorption capability and the disadvantages due to the practical difficulties in achieving homogeneous dispersions with higher concentrations. During all the mixing steps the temperature was kept at around 20 °C.

The concrete mixture is finally poured in the waveguide sections (dimensions $248 \text{ mm} \times 124 \text{ mm} \times 107 \text{ mm}$). The samples are dried up for about 2 months at room temperature before measuring the dielectric properties. Two samples have been manufactured and tested for each composite typology, and the results evaluated on average. In order to assess the effectiveness of the MWCNT filling, the performances of the MWCNT-filled concrete samples have been compared to those of the unreinforced material. The unreinforced and the 2 wt% MWCNT-filled concrete morphologies are shown at low magnification in the SEM micrographs of Fig. 1b and c respectively, while the higher magnifications of the reinforced concrete samples are shown in Fig. 1d and e. The high density of the filament network in the reinforced material can be appreciated: these electric conductive paths, made of MWCNTs upon the concrete micro-granules, permeate the whole composite, thus increasing its electric resistive losses. Figs. 3 and 4 show some pictures of the sample manufacturing and of the experimental set-up adopted for the waveguide characterization.

The scattering parameters S_{ij} (i,j=1,2) [44] have been measured by means of a vector network analyzer (VNA: Agilent Tech PNA-L N5235) and a waveguide WR975 kit. A VNA consists of a signal source, a receiver and a display. The source launches a signal at a single frequency to the material under test, the receiver is tuned to that frequency to detect the reflected and transmitted signal from the material, and the measured response produces

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