Nanotechnologies applied to the restoration and maintenance of wooden built heritage

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ABSTRACT: The paper presents a preliminary experimental campaign, which aims at investigating the possible application of carbon nanotubes to the mechanical improvement of timber structures. Different wood species are considered, as well as different solvents or resins as a dispersing media for carbon nanotubes. The experimentation is carried out on purpose exploiting exclusively the capillary properties of wood, in view of a possible on site application of the technique. Although still at a preliminary stage, these first results appear to be promising, and the research on the procedure is still in progress.

1 INTRODUCTION

In contrast with other fields of civil engineering and building recovery technology, the application of composite nanomaterials employed to reinforce wooden structures is a little known technique which requires, albeit partially, to be fully tested before being applied on a large scale. This holds true mainly for existing wood components (elements); with regards to new wooden elements, there is a much greater wealth of experience.

The use of nanomaterials and composite materials to strengthen wood was suggested seven years ago by several American researchers who studied the effects of carbon nanotubes-based composites on the mechanical characteristics of reinforced wooden elements [1].

In Italy, given the greater scope of recovery and conservation issues, research has focussed on methodologies for consolidating existing ancient structures. Experiments carried out on antique timber and existing structures are very complicated since the mechanical characteristics of the timber vary on account of the inevitable presence of membrane defects (knots, oblique wood fibre, lesions, etc.). However, experimental results have shown a clear trend in terms of efficiency concerning said recovery techniques.

The development of polymers reinforced with nanoparticles is one of the most promising approaches in the field of future engineering applications. The unique properties of some nanoparticles (carbon black and carbon nanotubes) and the possibility of combining them with traditional reinforcing elements (fibreglass, carbon fibre or Kevlar) have generated an intense research program in the nanocomposites sector [1–2]. Carbon black is made up of particles with a diameter of 30 nanometres (nm) and is commonly used as a charge to make polymers conductive in order to avoid the accumulation of electric charges. Carbon nanotubes have a diameter of several nanometres and their length measures several micron; they have very good potential for improving the electrical and mechanical properties of polymers, even with 0.1% weight content compared to epoxy resin [1–2]. Indeed, the resistance to traction of single wall carbon nanotubes or SWCNT can reach up to 600 GPa and the elastic modulus range between 1 and 5 TPa [1]. The difficulties lie in transferring these remarkable mechanical, thermal and electrical properties of nanotubes to the polymer matrix. Consequently the correct dispersion of the nanotubes in the polymer and timber interface, between the reinforcement and the polymer matrix, is crucial [1–4]. The dispersion
of carbon nanotubes in the matrix is complex given the widespread specific surface of the nanoparticles (1000 m²/g or more) which tend to favour the formation of agglomerates. Different techniques for dispersing said materials in solvents (acetone, ethanol...) in addition to ultrasounds, mechanical shaking or a combination of the two techniques, have already been tried out [1–7].

The interface adhesion can be improved by chemically functionalising the nanotubes surfaces; this generates strong covalent-type of bonding [2, 3, 6, 7]. The bonding between nanotubes and polymers allow the strain to be transferred from one stage to another.

Amino groups have been used for this purpose and double wall carbon nanotubes or DWCNT with or without a functional group surface can be purchased on the market (Nanocyl, Namur, Belgium) [8].

A picture of said experimental difficulties is provided by the results obtained with epoxy resins where by adding SWCNT in the best cases the mechanical resistance to bending stress is slightly increased, although in most cases, resistance is often reduced [5]. Recently, fabrics containing up to 39% in SWCNT weight impregnated with epoxy resin have been produced; once again the results obtained fell below expectations [9].

On the other hand, significant progress in mechanical resistance values has been made with polymethyl methacrylate (PMMA), polyvinylalcohols and with polystyrene-based composites [5]. Promising results have also been achieved with polyurethane resin composites with up to 10% in weight of nanotubes [10].

Summarizing, carbon fibre nanotubes provide a number of advantages:

- they are morphologically and chemically compatible both with polymer resin, used as bonding material, and with wood, they are anatomically similar to strong piping bonded with a thermoplastic matrix and equipped with strong dissipative capacity with regards to fracturing energy;
- nanotubes allow the polymer bonding matrix to improve it own inbuilt deformation capacities considerably thanks to the transformation of a homogeneous bulk with vitreous behaviour into a micro-reticule with high level of porosity and deformability;
- the mechanical characteristics of the resin-fibre compound are considerable on account of the high specific resistance of the fibres which ensure great cohesive strength combined with high ductility. The combination of the two produces significant creep resistance without the composite, loosing any deformation capacity;
- the tubular structure of nanofibres has great permeability to vapour potential: this is an important characteristic when dealing with large surfaces treated with glue, and especially in the case of wood since any accumulations of humidity must be easy to disperse in order to avoid biotic degradation.

2 MATERIALS AND METHODS

The first step of the experimentation was dedicated to assess the efficiency of different impregnation techniques. The carbon nanotubes were dispersed by means of an ultrasonic probe for different time in ethanol and acetone. Such solvents are supposed to act as a transport medium to bring the carbon nanotubes directly into the channels of the wood microstructure.

Specimens with section equal to 2.5 cm × 2.5 cm were sunk in the suspensions for different times, as shown in Figure 1. We decided to exploit only the capillarity natural phenomenon instead of vacuum or other pressure assisted impregnation techniques. This choice was adopted in view of a future onsite application in existing timber structures.

The following wooden species have been selected for the analysis: fir, Douglas pine, oak and larch. Some samples were obtained from new timber, other from eighteenth century structures.

Nanocyl multiwall carbon nanotubes were used for the process. For economical reasons, the series 7000, not functionalized (Table 1), was used to set up the process, while series 3101 functionalized with carboxyl groups were used for the mechanical tests (Nanocyl®-3101 series are purified to greater than 95% carbon and then functionalized with COOH groups). In a second step, an epoxy resin (MAPEI epojet, [11]) was used for the dispersion in order to get a product for mechanical improvement that could be applied on the wood surface by painting, or act as a reinforced glue to connect different timber part.

Epojet is a two component solvent-free epoxy adhesive. The pre-measured portions (Part A = resin and Part B = hardener) must be mixed together before being used. Once mixed, Epojet becomes a liquid with low viscosity very suitable for injection. The mix ratio between part A and B is 4 to 1. This resin has been selected because of its low Brookfield viscosity (respectively 500 and 320 mPa.s for part A and B).

The efficiency of the impregnation procedure has been assessed with observation at the SEM microscope. The overall mechanical improvement of the timber specimen is going to be evaluated from comparison of mechanical tests performed on un-reinforced, impregnated and resin painted samples. The bending strength has been evaluated by the three-points bending test carried on with displacement control. The span of the samples was 370 mm and the load was applied with a velocity of 12 N/s.
3 RESULTS AND DISCUSSIONS

3.1 Mechanical characterization of un-reinforced wood

The un-reinforced behavior of four different timber species have been characterized, from a mechanical point of view, with standardized three-point bending tests. A picture of the test procedure is shown in Figure 3.

The oak old samples displayed the most fragile behavior, while Douglas pine appear to be sensitive...
to local buckling phenomena. The peak load ranged between 1340 N and 2770 N, provided that the cross section of the samples was 25 mm times 25 mm. The load displacement diagrams of each test is shown in Figure 4.

A direct comparison with reinforced samples will be provided in the future.

### 3.2 Carbon nanotubes dispersion in solvents

Four different suspensions have been prepared with different nanotubes (series 7000) concentrations. Further, each suspension has been used for impregnation as shown in Figure 1. In order to assess the efficiency of the impregnation the higher part of the specimen was cut and observed with the SEM. As a reference, also slices of not impregnated wood were observed (Figure 5).

The first suspension was prepared by dispersing about 0.1% carbon nanotube in ethanol, after 20 minutes of ultrasonication with an ultrasonic probe. A droplet of this suspension was sampled and set upon the SEM sample holder for observation. As illustrated in Figure 4 the dispersion was unsuccessful, since the nanotubes remained agglomerated. It is worth noting that the morphology of the cluster in Figure 6 is also due to the poor purity of the adopted carbon nanotubes as reported in Table 1. Due to this reason, the impregnation was not proceeded.

In the second dispersion we decided to increase the sonication time up to two hours, and the carbon nanotube content (1%). The resulting suspension (Figure 7) was more satisfying, but we could not proceed with the impregnation due to high viscosity of the suspension (which was close to that of a paste).

The third ethanol suspension was obtained with 0.5% carbon nanotube content and two hours sonication. This proportion allows a good dispersion preserving a moderate viscosity, and was chosen for further impregnation. Unfortunately, although the capillary process is active, there was no effective transport...
of nanotubes inside the sample, as observed with the SEM (Figure 8).

Because of this unsuccessful trials, we decided to change the solvent and adopt acetone in place of ethanol.

The acetone solution of 0.5% carbon nanotube weight content was sonicated for two hours and the resulting dispersion was good preserving low viscosity.

The wood sample was sunk into this suspension for twenty-four hours. Also in this case, almost no carbon nanotubes are observable at the top section of the sample from the SEM image (Figure 9).

In each case, the SEM analysis has been pushed up to the maximum allowable resolution (10000×) but we were not able to observe not even CNT clusters.

3.3 Carbon nanotubes dispersion in epoxy resin

The main difference between epoxy resins and the solvents described above pertains the higher viscosity. Therefore, first of all it has been necessary to find the optimal carbon nanotube content keeping constant the two hours sonication duration.

Proved that although the dispersion in the solvent was efficient, the overall impregnation technique was not working satisfactorily, we moved to investigate the dispersion using resin as a dispersing medium.

After some trials, we adopted a carbon nanotubes weight content equal to 0.3% with respect to the resin (A + B fraction).

We decided to disperse first the nanotubes in the resin component B, which has the lowest viscosity. Then the two components were mixed together during thirty minutes mechanical stirring at room temperature. The mix was poured into a mould and let curing for six hours at sixty degrees.

Unfortunately, this precaution was not sufficient to avoid clustering of carbon nanotubes, as evidenced by Figure 10, and in more detail Figure 11.

3.4 Mechanical behavior of reinforced wood

A preliminary assessment of the efficiency of the reinforcing procedure has been carried out in the following way. First some of the timber samples were coated with resin only, then other were coated with the CNT reinforced resin obtained after four hours sonication. The CNT content was increased up to 0.5% with respect to the resin.

All the coated samples were cured at room temperature for seven days, according to the manufacturer recommendations, and to simulate an in-situ intervention.
Figure 11. SEM detail image of CNT agglomeration in the epoxy resin.

Figure 12. Load displacement curves for the eighteenth century oak samples. Comparison between un-reinforced, resin coated, and CNT reinforced resin coated.

Figure 13. Load displacement curves for the Hemlok fir samples. Comparison between un-reinforced, resin coated, and CNT reinforced resin coated.

The preliminary results obtained from the few samples tested till now are in some case very promising, in other case not so unambiguous.

In the case of the eighteenth century oak samples, we observe an increase of about 19% in the peak load when only resin is used for the coating. If CNT reinforced resin is used for the coating, the gain in the peak load raises up to 42%.

On the other hand, as far as the Hemlok fir samples is concerned, an increase of about 45% is obtained in case of resin coating, regardless the presence of a CNT reinforcing in the resin. The influence of the CNT reinforcing appears even to be slightly disadvantageous, but this could be also due to the fact that we still have too few results to compare.

In general, the comparison must be continued considering more samples and more timber species.

4 CONCLUSIONS

In the paper a preliminary experimental campaign is described, which aims at investigating the possible application of carbon nanotubes to the mechanical improvement of timber structures. Different wood species were considered, as well as different solvents or resins as a dispersing media for carbon nanotubes. The experimentation was on purpose carried out exploiting exclusively the capillary properties of wood, in view of a possible on site application of the technique.

As far as the present results concern, the solvent dispersions appears, if properly designed, effective from the point of view of getting an optimal dispersion. None of them, unfortunately, appear to be efficient from the point of view of impregnation exploiting the solely capillary phenomenon.

On the other hand, the epoxy resin dispersions are still problematic since the aspect of carbon nanotubes clustering has not been solved yet.

The first results concerning the assessment of the timber retrofiting with CNT resin coating are somewhat positive, since they provide an increase in the flexural strength which is greater or at least equal to the one obtained with the resin alone.

These first results appear to be challenging, and the research on the procedure is still in progress [12].

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