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ORIGINAL PAPER

Nanocomposites based on esterified colophony and halloysite clay nanotubes as consolidants for waterlogged archaeological woods

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Abstract We have designed an innovative protocol for the consolidation of waterlogged archaeological woods by using acetone mixtures of halloysite clay nanotubes and a chemically modified colophony (Rosin). Firstly, we have investigated the thermal properties of HNTs/Rosin nanocomposites, which have been prepared by means of the casting method from acetone. The HNTs content have been systematically changed in order to study the influence of the inorganic filler on the thermal stability and glass transition process of Rosin. We have observed that the thermal properties of the hybrids are affected by the specific HNTs/Rosin interactions. Then, acetone dispersions of HNTs/Rosin composites at variable filler content have been employed as consolidants for waterlogged archaeological woods. The quantitative analysis of the thermogravimetric curves have provided the amount of consolidants entrapped into the wood structure. These results have been successfully correlated to the consolidation efficiencies estimated from the analysis of the wood shrinkage volume upon drying. The attained knowledge represents the basic step to develop a green protocol for the long term protection of wooden art-works.

Keywords Waterlogged archaeological woods · Esterified colophony · Halloysite nanotubes · Nanocomposites

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Introduction

In recent years Cultural Heritage studies have attracted a growing interest within several fields including the diagnostics (Mendoza Cuevas et al. 2015) as well as the protection (Giachi et al. 2011) of historical artefacts. In this regard, the conservation of waterlogged archaeological woods represents a challenging task in view of preventing the collapse of the wooden structure upon drying.

The degradation degree of the waterlogged woods is strongly dependent on the chemical and biological nature of the site. In general, low temperatures and anoxic conditions promote the wood conservation (Blanchette 2000), while the degradation of lignocellulosic polysaccharides and lignin is mostly due to the actions of bacteria (Bugg et al. 2011; Gelbrich et al. 2008) and fungi (Dedic et al. 2013). The degraded wood mainly consists of water and minerals, whereas the residual content of the organic components (lignin and holocellulose) is extremely low (Cavallaro et al. 2011a).

Consequently, the wood porosity is strongly enhanced generating a relevant worsening (Riggio et al. 2014). Filling the cavities with a proper consolidant plays a crucial role to confer robustness and stability (Giachi et al. 2010). An effective consolidation of the waterlogged archaeological wood was achieved by using biocompatible polymers, such as colophonies (Donato et al. 2010) poly(ethylene) glycols (Cavallaro et al. 2013a; Cipriani et al. 2013; Christensen et al. 2012), poly(propylene) glycols (Donato et al. 2010), beeswax (Cavallaro et al. 2015a) and cellulose ethers (Walsh et al. 2017). Literature reports that highly volatile solvents are efficient for the wood impregnation because they are able to more favourably transport the consolidant polymers and quickly evaporate after the treatment (McKerrel et al. 1972). Within this, acetone dispersions of colophonies revealed as the most successful procedure for the conservation of waterlogged woods (Shamsi and Geckeler 2008). Both the natural and esterified colophonies are effective in the in the wood stabilization (in terms of shape and dimensions) with respect to the humidity variations (Giachi et al. 2011). Recently, inorganic nanomaterials were investigated for the conservation of art-works formed by lignin and cellulose, such as archaeological woods (Cavallaro et al. 2015a; Christensen et al. 2012) and papers (Cavallaro et al. 2014, 2016). It is reported that the combination of polymers and nanoparticles can generate an improvement on the consolidation of artworks based on lignocellulosic materials as consequence of the polymer adhesion to both the particles surfaces and the remaining wooden structure (Christensen et al. 2012). Among the nanoparticles, halloysite clay nanotubes (HNTs) were successfully employed for the protection of waterlogged archaeological woods (Cavallaro et al. 2015a). Chemically, the HNTs inner surface consists of a gibbsite octahedral sheet (Al–OH), whereas the shell is composed of siloxane groups (Si–O–Si) (Joussein et al. 2005). Halloysite is a promising nanofiller because of its hollow tubular morphology and tunable surface chemistry (Pasbakhsh et al. 2013). The length of HNTs is ca. 1 μm, while the external and internal diameters are 40–60 and 10–15 nm, respectively (Lvov et al. 2016). The peculiar surface chemistry endows a targeted modification driven by electrostatic interactions (Cavallaro et al. 2015b; Bertolino et al. 2017). Accordingly to their geometrical characteristics, HNTs are promising as fillers for the wood cavities. Moreover, HNTs are biocompatible as shown by several in vitro and in vivo studies (Fakhrullina et al. 2015; Kryuchkova et al. 2016; Fakhrullin and Lvov 2016) and their cavity can be can be easily loaded with functional molecules with magnetic (Vasilev et al. 2017) antimicrobial, (Aguzzi et al. 2013; Wei et al. 2014), antioxidant (Biddeci et al. 2016), surface active (Owoseni et al. 2014) and anticorrosion (Joshi et al. 2013; Abdullayev et al. 2012) activities. Due to these properties, HNTs are perspective as consolidants for a long term protection of art-works (Lvov and Abdullayev 2013). The addition of HNTs into polymer matrix induced an improvement of the mechanical perfomances (Cavallaro et al. 2011b; Arcudi et al. 2014) as well as the physical barrier properties (Sorrentino et al. 2007; Gorrasi et al. 2014). Within the cultural heritage applications, waterlogged woods treated by beeswax/HNTs composite exhibited a lower porosity degree with respect to those consolidated by pristine beeswax (Cavallaro et al. 2015a). Our work was focused on the development of an innovative green protocol for conservation of waterlogged archaeological woods. To this purpose, acetone dispersions of HNTs and Rosin were employed as consolidant mixtures. Specifically, Rosin^{100} (pentaerythritol ester of Colophony) was selected as polymer for the wood consolidation. The influence of HNTs on the thermal properties of the esterified colophony was investigated by Differential Scanning Calorimetry and Thermogravimetry. The thermal behaviour of the treated woods and the consolidation efficiency were determined by the shrinkage volume upon drying as well as by Thermogravimetry, which is a well-established technique for both the characterization of composites (Blanco et al. 2012, 2016; Belver et al. 2013; Rotaru et al. 2008) and the analysis of artwork materials (Duce et al. 2012; Sebestyén et al. 2015). The acquired knowledge represents the starting point for designing a green protocol to preserve the waterlogged archaeological woods using acetone dispersions of HNTs/Rosin hybrids.

Materials and methods

Materials

Rosin^{100} is from Bresciani srl. Halloysite nanotubes (HNTs) are from Sigma Aldrich. The deposit of HNTs is Dragon Mine (Utah, US). Acetone (99.5%, 0.791 g cm^{-3}) is a Panreac reagent. The waterlogged archaeological woods are from the ship Chretienne C, (II century, BC), discovered over the coast of Provence and kindly provided by Prof. Patrice Pomey of C.N.R.S., Université de Provence (France). According to the procedure of the Italian standard (UNI 11205:2007), the archaeological woods were identified as *Pinus Pinaster* (Cavallaro et al. 2011a).

Preparation of the HNTs/Rosin composites

We prepared a 50 wt% rosin solution in acetone under stirring for 2 h at 25 °C. Then, appropriate amounts of HNTs were added to the rosin solution and kept under stirring overnight in order to obtain stable and homogenous mixtures. The well dispersed dispersions were poured into Petri dishes at 30 °C to evaporate the solvent until the weight was constant. The HNTs concentration (C_{HNTs}) expressed as weight percent (grams of HNTs/100 g of the composite) was systematically changed within a wide range.

Consolidation of waterlogged archaeological wood

The waterlogged archaeological wood was consolidated through the immersion method as described elsewhere (Cavallaro et al. 2015a). HNTs/Rosin dispersions in acetone were employed as consolidant mixtures. The archaeological woods were kept in the Rosin/HNTs mixtures under stirring for three days. The efficiency of the treatment was evaluated by determining the shrinkage volume (ΔV_S) of treated and untreated wood samples. For each wood sample, the ΔV_S values were calculated as difference between its initial volume (measured after exposure at ambient temperature for 24 h) and its final volume (measured after the exposure at 100 °C for 24 h).

Characterization

Thermogravimetry (TG) measurements were performed by means of a Q5000 IR apparatus (TA Instruments) under the nitrogen flow of 25 cm^3 min^{-1} for the sample and 10 cm^3 min^{-1} for the balance. The weight of each sample was ca. 5 mg. The experiments were carried out by heating the sample from room temperature to 900 °C with a rate of 10 °C min^{-1}. The temperature calibration was carried out by means of the Curie temperatures of standards (nickel, cobalt, and their alloys). The measurements were repeated three times, and the average values with the corresponding standard deviation are reported for all the thermogravimetric parameters.

Differential scanning calorimetry (DSC) experiments were conducted by using the differential scanning calorimeter TA Instrument DSC (2920 CE). The calorimeter was calibrated using the melting enthalpy of standard indium (28.71 J g^{-1}). Each sample (ca. 3 mg) was heated according to a temperature program of 20 °C min^{-1} in the temperature range comprised between −20 and 120 °C. The measurements were performed under a nitrogen flow rate of 60 cm^3 min^{-1}.

A microscope-mounted digital camera (Digitus-DA-70351) was used to capture the optical images of both the untreated and treated archaeological wood samples. The images were analyzed by ImageJ software in order to estimate the DVS values.

Results and discussion

Thermal properties of Rosin/HNTs composites

Figure 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves of both pristine Rosin and HNTs/Rosin nanocomposites.

All materials exhibited a weight loss in the temperature range between 25 and 150 °C (ML_{150}), which is related to their physically adsorbed water content. The mass loss occurring at ca. 350–450 °C is due to the thermal degradation of the organic molecules. Accordingly, the Rosin degradation temperature (T_d) was estimated from the maximum of DTG peak centered at ca. 400 °C. The composite materials evidenced an additional DTG peak centered at ca. 500 °C, which can be attributed to the expulsion of the water molecules confined in the HNTs interlayer (Duce et al. 2015; Cavallaro et al. 2011b).

The Rosin thermal stability was strongly altered by the HNTs addition (Fig. 2). In particular, the T_d versus C_{HNTs} function showed a decreasing trend (Fig. 2) indicating that the HNTs/Rosin interactions induce a thermal destabilization of the esterified colophony. Interestingly, the composite with a very large HNTs content (ca. 50 wt%) evidenced a T_d reduction of ca. 100 °C with respect to that of pure Rosin. Similarly, a decrease of the polymer resistance to the thermal

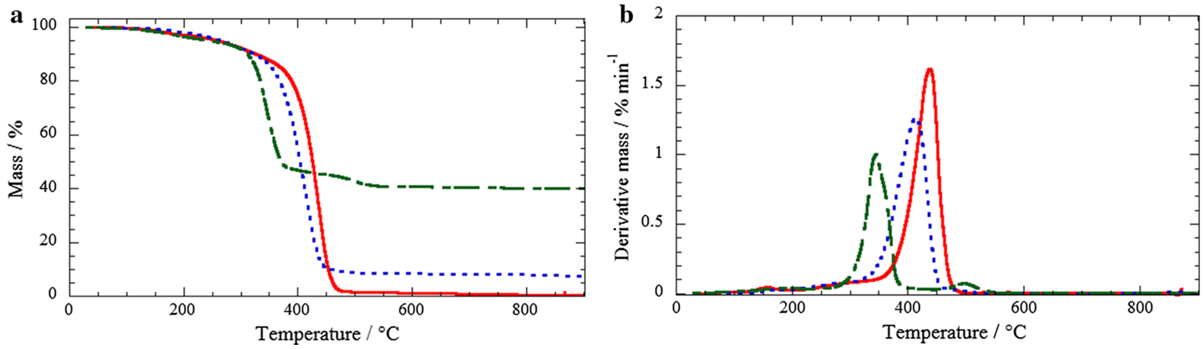

Fig. 1 TG (**a**) and DTG (**b**) curves for Rosin (*red solid line*), HNTs/Rosin at C_{HNTs} = 10.3 wt% (*blue dotted line*) and HNTs/Rosin at C_{HNTs} = 49.8 wt% (*green dashed line*)

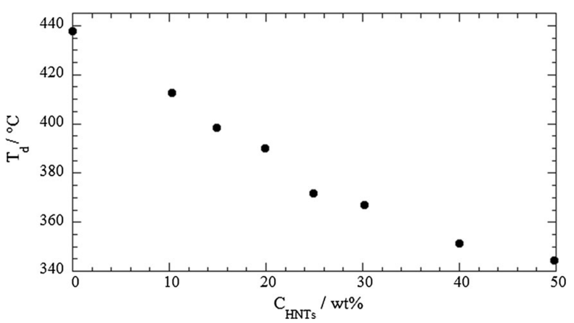

Fig. 2 Dependence of the Rosin degradation temperature on the HNTs concentration

degradation was detected in PEG20000/HNTs containing a large filler content (Cavallaro et al. 2013b). The T_d decrease could be due to the partial deterioration of the Rosin structure induced by the filling with HNT. Consequently, the diffusion of the volatile products of the polymer degradation is favored in the nanocomposite materials.

Furthermore, TG curves endowed to determine the experimental HNTs/Rosin composition of the hybrid materials by the residual masses at 800 °C (MR_{800}). The C_{HNTs} values were calculated by using the rule of mixtures (Cavallaro et al. 2011b) once the mass loss of the pure components were known and by taking into account their water contents (ML_{150}). Mathematical details concerning the determination of the HNTs/Rosin composition for the nanocomposites is presented in the Supplementary material. Table 1 highlights that a good agreement between the experimental and stoichiometric composition was observed. On this basis, we can conclude that the casting method from acetone was successful to obtain composites with HNTs homogeneously dispersed into the Rosin matrix.

The specific matrix/filler interactions influenced the Rosin glass transition, which was studied by DSC measurements in terms of glass transition temperature (T_g) and heat capacity change (ΔC_p). It should be noted that ΔC_p values were normalized to the Rosin weight fraction by considering the experimental composition of the investigated materials (Table 1). A step change in the heat flow curves was observed at ca. 60 °C (Fig. 3) whose inflection point can be attributed to the T_g of Rosin.

We observed that T_g is not significantly affected by the presence of HNTs (Fig. 4a). Contrary to this, ΔC_p linearly reduces with the filler content (Fig. 4b) according to the Rosin immobilization onto the HNTs surfaces. Similarly, the addition of silica into poly(dimethylsiloxane) (Fragiadakis and Pissis 2007) and polyimide (Bershtein et al. 2002) generated a systematic ΔC_p decrease because of the reduced mobility of the polymer adsorbed onto the nanoparticles surfaces. Namely, the polymer chain mobility is constrained due to interaction with the surface of the particles.

Consolidation of waterlogged archaeological wood

The HNTs/Rosin mixtures were investigated as consolidant for waterlogged archaeological wood by using the immersion procedure described for HNTs/Beeswax hybrids (Cavallaro et al. 2015a). According to the TG data, the nanotubes are uniformly dispersed into the Rosin making these dispersions promising for the treatment of porous materials, such as the archaeological woods. We studied the influence of HNTs/Rosin weight ratio (R) on the wood consolidation efficiency, which was estimated from TG experiments.

Table 1 Thermogravimetric parameters of the investigated materials and comparison between the stoichiometric and experimental HNTs concentrations in the nanocomposites

Material	C_{HNTs}/wt% (stoichiometric)	ML_{150}/wt%	MR_{800}/wt%	C_{HNTs}/wt% (experimental from TG data)
Rosin		1.30 ± 0.02	0.543 ± 0.009	
HNTs		1.66 ± 0.03	83.1 ± 1.2	
HNTs/Rosin	10.3	0.672 ± 0.008	8.02 ± 0.09	8.3
HNTs/Rosin	14.9	0.559 ± 0.009	11.4 ± 0.6	12.3
HNTs/Rosin	19.9	0.94 ± 0.01	15.3 ± 0.6	17.4
HNTs/Rosin	24.9	0.92 ± 0.01	23.2 ± 0.7	26.9
HNTs/Rosin	30.2	1.13 ± 0.02	25.9 ± 0.7	30.5
HNTs/Rosin	40.0	1.62 ± 0.03	35.2 ± 0.8	42.2
HNTs/Rosin	49.8	1.664 ± 0.03	40.1 ± 0.8	48.2

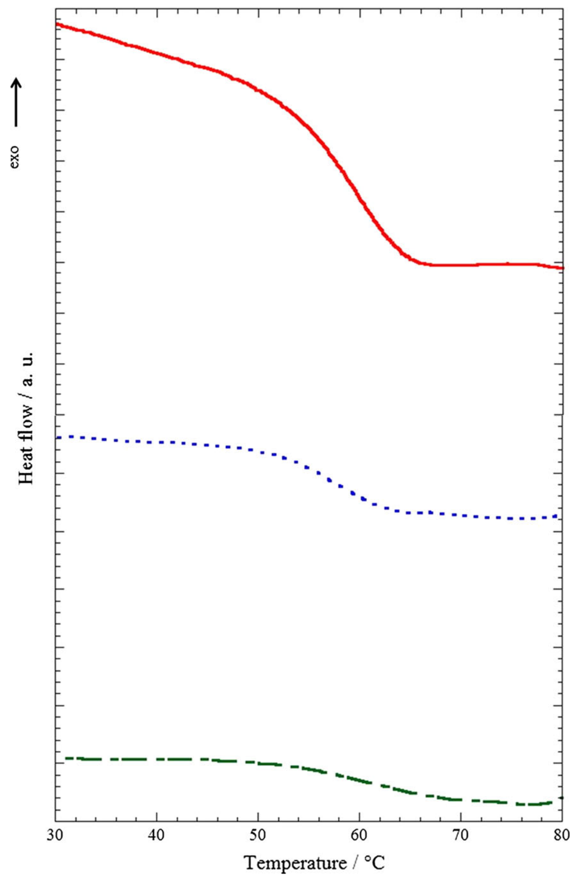

Fig. 3 DSC curves for pristine Rosin (*red solid line*), HNTs/Rosin at C_{HNTs} = 10.3 wt% (*blue dotted line*) and HNTs/Rosin at CHNTs = 49.8 wt% (*green dashed line*)

Some examples of TG curves for untreated and treated archaeological woods are reported in the Supplementary material.

As shown in Table 2, the presence of the consolidant caused a decrease of the water content in agreement with the entrapment of the Rosin/HNT system into the wood pores.

DTG curves of the treated wood samples (Fig. 5) evidenced a sharp peak centered at ca. 400 °C that can be ascribed to the Rosin degradation.

This finding proves the successful penetration of Rosin into the wood structure. On this basis, we determined the amount of Rosin entrapped into the wood by the analysis of the mass losses occurring between 200 and 460 °C ($ML_{200–460}$), in which the esterified colophony completely degrades. Table 2 collects the $ML_{200–460}$ for treated and untreated wood samples. In order to estimate the consolidation efficiency the $ML_{200–460}$ values were normalized to the water content (ML_{150}) of the investigated samples by using the equation

$$ML^*_{200-460} = (ML_{200-460} \cdot (100 - ML_{150}))/100 \tag{1}$$

Being that the wood partially degrades at 200–460 °C, the $ML_{200–460}$ of the pure wood was taken into account. Accordingly, the weight fraction of Rosin in the consolidated wood (χ_R) was calculated as

$$\chi_R = \left(\left(ML^*_{200-460}\right)_T - \left(ML^*_{200-460}\right)_U\right)/\left(ML^*_{200-460}\right)_R \tag{2}$$

where $\left(ML^*_{200-460}\right)_T$, $\left(ML^*_{200-460}\right)_T$ and $\left(ML^*_{200-460}\right)_R$ are the mass losses normalized to the water contents for treated wood, untreated wood and pristine Rosin, respectively.

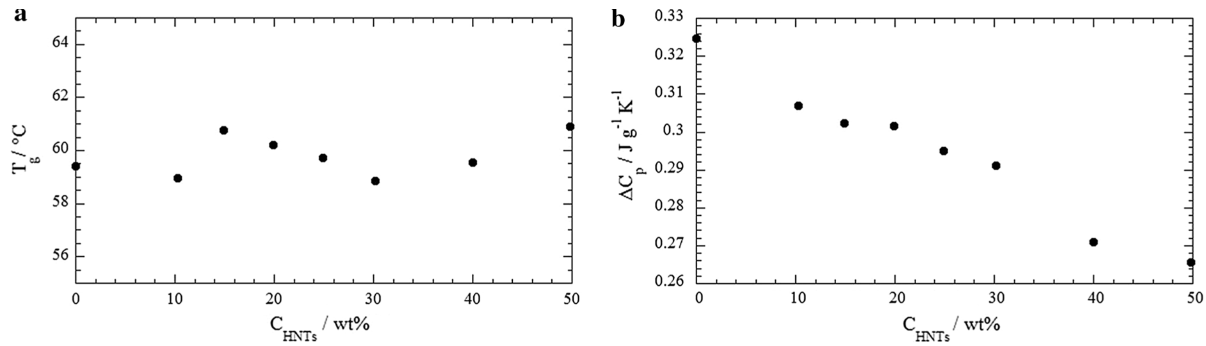

Fig. 4 Temperature (**a**) and heat capacity change (**b**) for the Rosin glass transition as functions of the HNTs concentration

Table 2 Thermogravimetric parameters for untreated and treated waterlogged archaeological woods

Sample	ML^a_{150}/wt%	$ML^a_{200-460}$/wt%
Untreated wood	8.35 ± 0.09	49.2 ± 0.9
Wood + Rosin	4.69 ± 0.06	73.0 ± 1.3
Wood + HNTs/Rosin (R = 0.11)	3.54 ± 0.06	77.1 ± 1.3
Wood + HNTs/Rosin (R = 0.25)	3.91 ± 0.05	75.5 ± 1.4
Wood + HNTs/Rosin (R = 0.43)	3.42 ± 0.07	79.9 ± 1.4
Wood + HNTs/Rosin (R = 0.66)	4.53 ± 0.06	60.8 ± 1.2
Wood + HNTs/Rosin (R = 1)	4.33 ± 0.07	52.0 ± 1.2

Figure 6 shows that the amount of Rosin entrapped into the wood structure is affected by the HNTs/Rosin weight ratio (R) of the consolidant mixture.

We observed that the presence of small amounts of HNTs favors the penetration of Rosin in the wood. In particular, the χ_R versus R function shows an increasing trend for consolidant mixtures with R $\leq$ 0.43. A further HNTs addition induced a strong decrease of the χ_R values because the wood pores are largely and preferentially filled by the nanotubes. The successful entrapment of the nanotubes into the wood structure was clearly evidenced by the DTG peak centered at ca. 500 °C (Fig. 5), which allowed us to calculate the HNTs weight fractions (χ_{HNTs}) by using an approach described elsewhere (Cavallaro et al. 2011b). The integration of the DTG peaks provided an accurate estimation of the mass losses (0.428 and 1.31 wt% for R = 0.66 and 1, respectively) caused by the expulsion of the two interlayer water molecules of halloysite. According to the corresponding mass loss of pristine HNTs (12.7 wt%) (Cavallaro et al. 2011b), we determined the χ_{HNTs} values in the consolidated woods

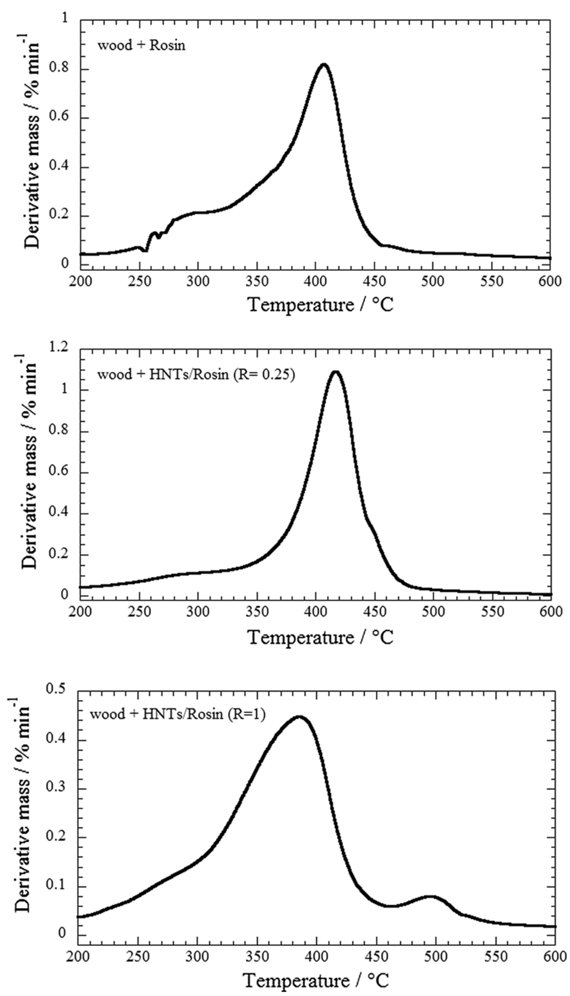

Fig. 5 DTG curves for woods consolidated by Rosin and HNTs/Rosin mixtures at variable filler content

(0.034 and 0.103 for R = 0.66 and 1, respectively). These results highlight that a preferential penetration of the nanotubes occurs for consolidant mixtures with a very large HNTs content. For R ≤ 0.66 the DTG curves of the treated wood samples did not show any reliable peak at ca. 500 °C (Fig. 5) and, therefore, the determination of the HNTs penetrated amount was not

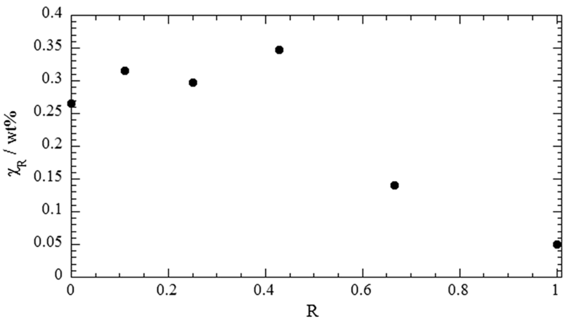

Fig. 6 Weight fraction of Rosin in the treated wood as a function of the Rosin/HNTs weight ratio of the consolidant mixture

Table 3 Pore volume of the wood filled by the consolidants for pure Rosin and HNTs/Rosin mixtures

Consolidant material	V_c/%
Rosin	24.7
HNTs/Rosin (R = 0.11)	29.4[a]
HNTs/Rosin (R = 0.25)	27.7[a]
HNTs/Rosin (R = 0.43)	32.4[a]
HNTs/Rosin (R = 0.66)	13.1
HNTs/Rosin (R = 1)	4.7

[a] The values are underestimated because the amounts of HNTs entrapped into the wood was not considered

conducted. Nevertheless, we can conclude that that the entrapment of HNTs is negligible compared with that of Rosin. As shown in Fig. 6, the Rosin/HNTs interactions promote the penetration of the esterified colophony for consolidant mixture with low HNTs content. Based on the TG data, we calculated the pore volume of the wood filled by the consolidant materials (V_c) by considering the density values for HNTs and Rosin (2.65 and 1.073 g cm^{-3}, respectively) and assuming that the specific filler/matrix interactions did not affect the volume of both components. Regarding the composite mixtures with a low HNTs content, the V_c are underestimated because the weight fraction of HNTs in the wood was not taken into account. As reported in Table 3, the addition of small amounts of HNTs induces a reliable increase of V_c compared to that of pure Rosin. It is noteworthy to note that a V_c enhancement of 30% was detected for HNTs/Rosin with R = 0.43. On the contrary, a significant V_c reduction was observed for HNTs/Rosin mixtures with a large filler content. We calculated a V_c decrease of 65% for HNTs/Rosin with R = 1.

The consolidation efficiency results were related to the shrinkage volume (ΔV_S) values for untreated and treated wood samples. Figure 7a shows the shrinkage volume for the waterlogged archaeological wood consolidated by HNTs/Rosin (R = 1) mixture. Optical photos of untreated and treated wood samples are presented in the Supplementary material.

As general result, the ΔV_S values of the treated samples are lower compared to that of the untreated

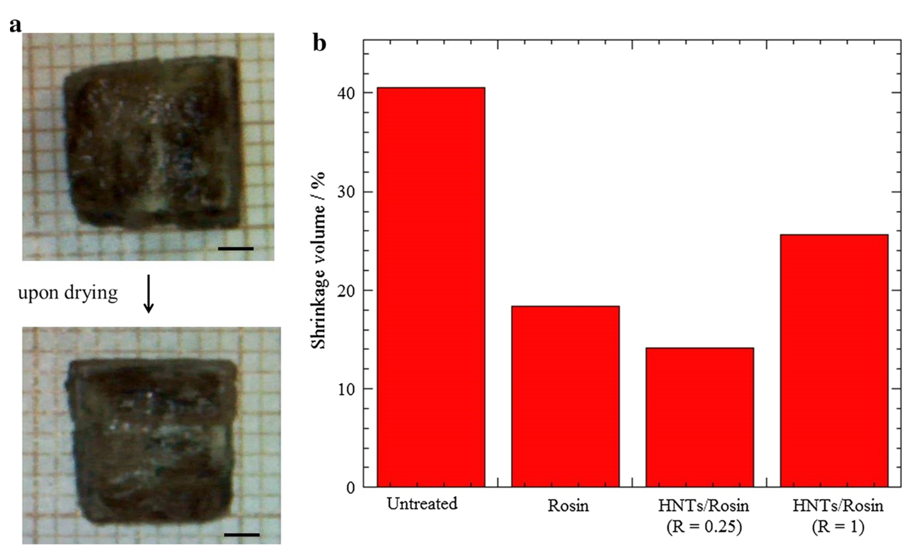

Fig. 7 **a** Optical images of wood samples consolidated by HNTs/Rosin (R = 1) in the initial stage (*up*) and after drying (*down*). The *scale bar* is 0.4 cm. **b** Shrinkage volume for untreated and treated archeological woods

one (Fig. 7b) confirming the successful consolidation of the waterlogged archaeological woods. As expected by the TG data (Fig. 6), the ΔV_S of the wood samples consolidated by HNTs/Rosin mixture depends on the specific composition of the consolidant mixture. The lowest ΔV_S value was estimated for the wood treated by HNTs/Rosin with $R = 0.25$, while the addition of a larger amount of HNTs ($R = 1$) induced a decrease of the consolidation efficacy with respect to that observed for pure Rosin (Fig. 7b). The ΔV_S results confirm that the presence of small amounts of HNTs favors the entrapment of Rosin into the wood pores improving the impregnation efficacy. Contrary to this, the composite mixture with a large HNTs content exhibited a lower consolidation ability respect to that of pristine Rosin because the penetration of the esterified colophony is strongly reduced. The anti-shrink efficiencies of the HNTs/Rosin mixtures range between 36 and 65%. These results are comparable to those obtained by using several protocols for the treatment of the archaeological woods (Grattan et al. 2006) highlighting the suitability of the HNTs/Rosin dispersions as consolidants.

Conclusions

Acetone dispersions of HNTs/Rosin nanocomposites were investigated as potential consolidants for waterlogged archaeological woods. We observed that the thermal properties of Rosin are strongly affected by the addition of HNTs. TG experiments evidenced that the resistance to thermal degradation of Rosin is significantly reduced in the presence of HNTs, which are homogeneously dispersed into the polymer matrix. Regarding the Rosin glass transition, the nanocomposites exhibited a decrease of the heat capacity change according to the polymer immobilization onto the HNTs surfaces. The efficacy of the wood treatment by HNTs/Rosin hybrids was estimated by the quantitative analysis of TG curves as well as by the shrinkage volumes upon drying. We found that the consolidation efficiency of the archaeological woods can be controlled by the concentration of the inorganic filler. The presence of small amounts of HNTs favored the penetration of Rosin into the wooden structure and, consequently, the shrinkage volume of the treated archaeological woods showed a relevant decrease compared to that consolidated by the pristine esterified colophony. Contrary to these results, a worsening of the consolidation efficiency was detected for nanocomposites with a very large HNTs content because of a strong reduction of the Rosin amount entrapped into the wood pores. The HNTs/Rosin mixtures can be considered perspective as consolidants for the conservation of waterlogged archaeological woods. The encapsulation of antimicrobial compounds into the HNTs lumen might be strategic for future advances and long-term protection purposes.

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