THERMAL, XRD AND SPECTROPHOTOMETRIC STUDY ON ARTIFICIALLY DEGRADED WOODS

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Thermogravimetry, differential thermal analysis, differential scanning calorimetry in oxygen flux were used to characterize two wood types: fir and chestnut woods. They were characterized by the peak temperatures of DTA, DTG and DSC curves and by the different mass losses evaluated on the basis of the measured thermal data. The samples were woods in powder obtained during sawing. Complementary characterization of the woods was performed by estimating the crystallinity of cellulose by means of X-ray powder diffraction. In order to simulate the degradation of wet woods, fir and chestnut woods were put into deionised water and into artificial sea water for several weeks; some samples of woods contained Cu and Fe nails to ascertain the effect of these metals on the degradation process. The thermal and X-ray diffraction measurements were then performed on the wet woods, following the same previous procedure. X-ray fluorescence was used to investigate the penetration of metals into wood samples.

Keywords: degradation, DSC, DTA, TG, wood

Introduction

Degradation of cellulose is important in the conservation science of wood and wet wood. For this purpose the kinetics and the mechanisms of degradation of cellulose by different etching reagents have been the object of previous works developed in our laboratory [1–4]. Several papers related to a similar topic are reported in the literature [5–8]. We used an artificial ageing simulation of two types of wood, fir and chestnut, to study chemical mechanisms of archaeological waterlogged woods alteration. In this work we refer the results of this ageing evaluated by means of DTA and DSC analyses, thermogravimetry, X-ray diffraction, X-ray fluorescence and colour measurements. As regards thermal behaviour of wood, a first step of degradation occurs at about 250°C, with a small mass loss, whereas the most extensive degradation takes place causing a large mass loss at higher temperatures. The temperature depends on the particle size, the crystallinity of cellulose, the heating rate, the atmosphere of reaction and on the presence of metals [9, 10].

In the present work we have treated in a similar way fir (*Abies alba*) and chestnut (*Castanea sativa*) fresh woods, by using different heating rates and in an oxygen flux in order to ascertain and to compare their thermal behaviour before and after to be immersed in water. The effect of sea water and metal presence was also investigated.

Also we have performed X-ray diffraction analysis to obtain the crystallinity of cellulose before and after the treatment of woods.

Colour measurements were taken in order to check the effect of each treatment.

Experimental

The woods immersed into deionised water without nails have been used as referent samples. Other woods with copper and iron nails, metals of special relevance in archaeological field, have been immersed into sea water artificially prepared. The composition of artificial sea water is reported below:

$$NaCl=22 \text{ g L}^{-1}$$

$$KCl=0.65 \text{ g L}^{-1}$$

$$MgCl_2 \cdot 6H_2O=9.7 \text{ g L}^{-1}$$

$$NaHCO_3=0.2 \text{ g L}^{-1}$$

$$Na_2SO_4=3.7 \text{ g L}^{-1}$$

$$H_3BO_3=0.023 \text{ g L}^{-1}$$

$$CaCl_2=3 \text{ g L}^{-1}$$

Powders of fir and chestnut-woods were obtained during the sawing operation and accurately mixed in order to have homogeneous samples representative of both external and internal portions of wood. The specimens were also powdered by using a rotating

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mill with agate balls, but we did not use such powders in this work, because the severe alteration of cellulose crystallinity. To perform thermal and thermogravimetric analyses we used an STA Netzsch apparatus, in oxygen flux of 125 mL min⁻¹. 30–40 mg of powders were placed into alumina crucibles and heated at a constant rate of 10°C min⁻¹ until 650°C.

For DSC measurements 4–10 mg of powdered specimens, in Al crucibles, were heated in O_2 flux (100 mL min⁻¹) at different rates, 1, 2, 5 and 10°C min⁻¹; the rate of 2°C min⁻¹ was finally chosen in order to compare the different curves; the apparatus used was a Mettler DSC 821. Wide angle X-ray diffractograms were obtained using a PW 1830 Philips Diffractometer (Ni-filtered CuK$_\alpha$ radiation); scans over a 2θ range of 3–30° (step of 0.02° and acquisition time of 20 s). The crystallinity was calculated according to the literature [11, 12].

X-ray fluorescence method was used to check the diffusion of metals inside the wood samples. The apparatus was an Assing portable X-ray spectrometer. The apparatus consists of a molybdenum tube, a zirconium filter and a silicon semiconductor detector.

Finally spectrophotometric measurements in reflectance in the visible region were performed by means of a Minolta 2600 d apparatus.

All measurements were repeated at least three times.

Results and discussion

X-ray diffraction

Table 1 collects the X-ray diffraction results in form of crystallinity values. They depend on the degree of alteration and the time of treatment.

Table 1 Average crystallinity values of treated and untreated woods

Wood	2θ	Crystallinity degree average X_C%
Not treated fir-wood	22.3	32
Fir-wood with Fe after 20 weeks into sea water	22.8	30
Fir-wood with Cu after 20 weeks into sea water	22.9	36
Fir-wood into deionised water after 24 weeks	22.9	31
Untreated chestnut-wood	22.3	36
Chestnut-wood with Fe after 20 weeks into sea water	22.6	31
Chestnut-wood with Cu after 20 weeks into sea water	22.7	30
Chestnut-wood into deionised water after 24 weeks	22.3	32

As it is clear from the above data, the effect of the immersion of wood samples into deionised water is very poor. Regarding to the woods with nails immersed into sea water we can observe that the degradation effect is more evident. The X-ray patterns are very different in the case of the two wood species.

For fir-wood the effect of iron leads to a decrease of crystallinity of cellulose and a general lowering of the overall X-ray diffraction curve. This decrease becomes more notable to the woods where we have copper nails. However, as evidenced by the crystallinity values, the effect of copper consists principally of the etching of amorphous region of cellulose. While the effect of iron consists principally of the etching and dissolution of crystalline cellulose.

A different behaviour occurs for chestnut-wood samples, where the effect of both metals, copper and iron, consists of the decrease of the entire X-ray diffractogram and the effect is comparable as shown by the significant lowering of crystallinity values.

Thermal analyses

The DSC curves obtained in an oxygen flow of 100 mL min⁻¹ at a constant heating rate of 2°C min⁻¹ for fir and chestnut-wood samples under different treatments are shown in Figs 1 and 2.

As we can see, the temperatures of the two main peaks change lightly, while the major change occurs in their width and mainly in their height. It reflects the fact that the content in cellulose varies considerably and the ratio between crystalline and amorphous cellulose varies too. It is also important to note the lignin peaks decrease. It is more evident in the case of wood with metals. Comparing both DSC and X-ray diffraction results one can observe that the effect of iron consists mainly the degradation of crystalline cellulose. The opposite happens in the presence of copper nails, where the amorphous components of
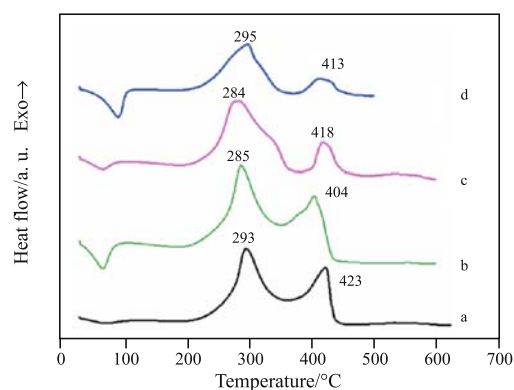

Fig. 1 DSC curves of fir wood: a – untreated; b – after 24 weeks in deionised water; c – with iron nails after 20 weeks in sea water; d – with copper nails after 20 weeks in sea water
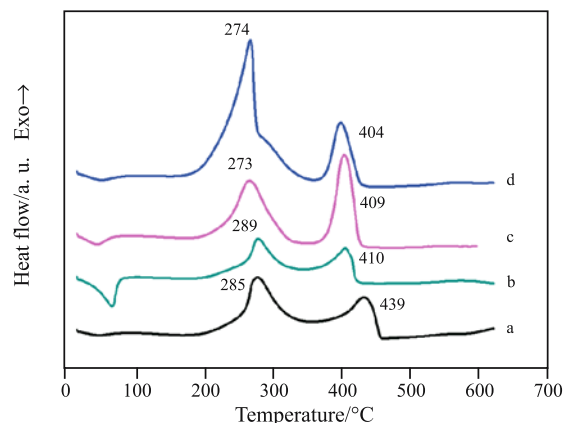
Fig. 2 DSC curves of chestnut wood: a – untreated; b – after 24 weeks in deionised water; c – with iron nails after 20 weeks in sea water; d – with copper nails after 20 weeks in sea water

Fig. 4 TG curves of chestnut wood: a – untreated; b – after 24 weeks in deionised water; c – with iron nails after 20 weeks in sea water; d – with copper nails after 20 weeks in sea water

wood are mainly degraded. In fact the second peak in this case is strongly decreased while its temperature remained practically the same.

With regard to chestnut-wood the combustion temperatures of cellulose vary lightly as well. The temperatures of the second exothermic peak are decreased in comparison with untreated wood. The width and height of two exothermic peaks change in the woods with metals, as result of the partial alteration of wood. The thermal effects due to cellulose and lignin are well split for samples with nails immersed in sea water. It is important to observe that the major change in the shape of the peaks is due to the Cu nails.

TG and DTA measurements

The samples in form of powder have been analysed and the curves are summarized in Figs 3 and 4.

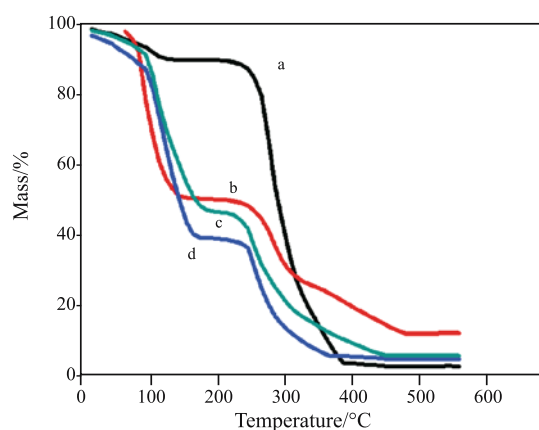The curve of untreated fir presents a characteristic behaviour due to different wood transformations. Until

Fig 3 TG curves of fir wood: a – untreated; b – after 24 weeks in deionised water; c – with iron nails after 20 weeks in sea water; d – with copper nails after 20 weeks in sea water
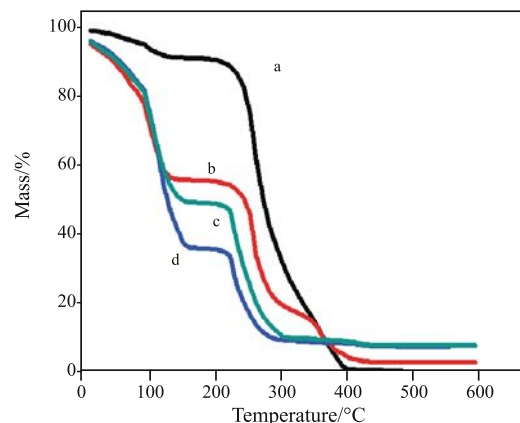
130°C the mass loss, due to humidity, is about 9%. Nearly at 250°C the oxidation of both crystalline and amorphous cellulose occurs. At 330°C the wood has lost about 64% of its mass. From 330 to about 400°C the oxidation of lignin occurs with a mass loss of 20%. The mass loss caused by the water release for all other treated woods vary from 50 to 60%. The TG curves of treated woods consist of two steps. The first one is attributed to depolymerisation and combustion of cellulose. The second one belongs principally to lignin. The combustion process continues beyond 400°C. In the case of fir in deionised water the temperature reaches 480°C.

The TG curve of untreated chestnut presents practically the same behaviour as fir wood does. Until 140°C the mass loss is about 8% due to loss of humidity. Nearly at 250°C the oxidation of cellulose begins. The wood looses about 64% of its mass at 320°C. From 320 to 400°C oxidation of lignin takes place with a mass loss of 28%. The water mass loss for all other treated woods varies from 45 to 65%. Regarding the treated chestnut woods the curve shapes are similar to those of the treated fir woods.

Colour measurements

It is known that visible light may penetrate approximately 200 μm inside the surface of wood, causing a series of photochemical reactions, mainly involving lignin, leading to change in colour of the entire wood [13]. The chromophoric carbonyl and carboxyl groups formed by degradation of lignin are the principal responsible of colour changes.

In this work the degree of degradation of wood by means of the discoloration was checked and measured using the CIELAB method.

In the CIELAB system L^* represents the lightness, varying from 0 (black) to 100 (white) and a^* and

b* are the chromaticity coordinates, following the theory of opposite colours: +*a** indicates red colour, –*a** green; +*b** yellow and –*b** blue.

L*, *a** and *b** values contribute to describe the overall colour through the parameter *E* and the colour change can be obtained using the following equation:

$$\Delta E=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2}$$

where ΔL^*, Δa^* and Δb^* indicate the difference of final and initial values, relative to the wood specimens (5x5x3 cm) after the treatment and not treated. The colour measurements have been performed on three wood sections. Because of their colour difference, the radial and tangential sections from transversal sections were separated. The obtained ΔE differences are reported in Table 2, while spectrophotometric curves are exampled in Fig. 5.

The effect of the presence of copper and sea water for the discoloration of wood is clear.

The presence of iron has a very remarkable effect and more evident than that of caused by the copper and sea water.
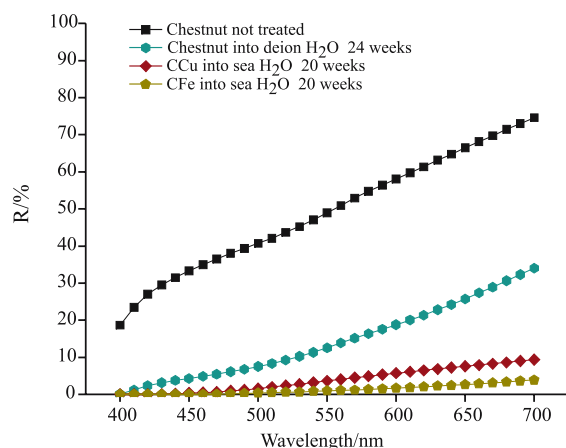
The untreated wood was a reference for our colour measurements. Regarding to both woods in deionised water, the ΔE almost have the same values. This fact shows that both woods have been discoloured at the same way by deionised water independently of the kind of wood. Keeping unvaried all the conditions of the experiments but adding iron and copper one can see that the iron alters the colour more than copper does. This alteration is more evident for chestnut. Looking at the results reported in two last columns of Table 2 and the average values of Fig. 5 it can be stated that the major colour alteration of fir was caused by copper. In the case of chestnut the major discoloration was due to iron.

X-ray fluorescence

The first results of the measurements performed on the surface of the chestnut wood sample containing Cu nails in deionised water for 20 weeks are shown in Fig. 6.

The curves are relative to different investigated zones: when the zones near to the copper nail were measured the peaks become higher. The lowest peaks of copper correspond to the concentration of copper ions in solution. In fact these peaks do not vary in all position far from nails.
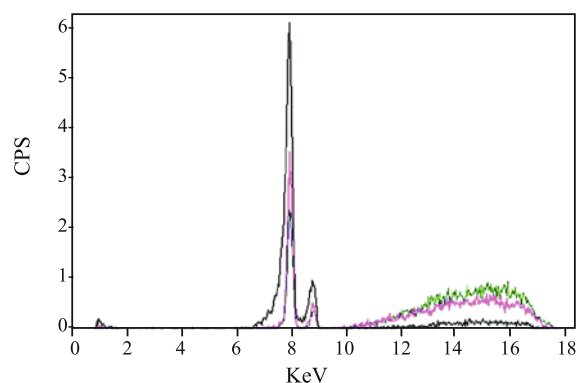

Fig. 5 Spectral reflectance curves for chestnut wood in deionised and sea water with iron and copper (average values for radial and tangential sections)

Fig. 6 XRF patterns of chestnut-wood with copper after 20 weeks in sea water

Table 2 Colour changes of woods after treatment

Wood	Untreated	Deionised water for 24 weeks	With copper and deionised water for 18 days	With iron and deionised water for 18 days	With copper and sea water for 20 weeks	With iron and sea water for 20 weeks
Fir average value for radial and tangential sections	*E*=89.1 ΔE=0	ΔE=32.1	ΔE=19.9	ΔE=25.6	ΔE=39.3	ΔE=27.0
Fir average value for transversal sections	*E*=77 ΔE=0	ΔE=32.7	ΔE=27.3	ΔE=34.3	ΔE=64.6	ΔE=33.0
Chestnut average value for radial and tangential sections	*E*=78.7 ΔE=0	ΔE=35.5	ΔE=20.1	ΔE=38.2	ΔE=52.6	ΔE=57.7
Chestnut average value for transversal sections	*E*=71.4 ΔE=0	ΔE=30.9	ΔE=34.6	ΔE=61.0	ΔE=69.0	ΔE=69.0

Conclusions

Ageing wood simulation is useful in the study of archaeological waterlogged woods alteration. The impregnation of wood samples into deionised and seawater can be used as a first step to understand the chemical mechanisms which degrade the archaeological objects. Moreover, the most important is the contribution to the alteration process due to the metals in connection with woods. DTA, DSC, TG and X-ray diffractometry are helpful tools in the characterisation of woods and alteration reactions. In fact it was possible to outline two different reactions: the first one, involving the crystalline portion of cellulose, and the second one, involving mainly amorphous components of woods. Spectrophotometry carried out directly on the degraded woods is a quick way to check the alteration degree. The alteration effect depends on the type of wood. The deionised water does not cause the variation of cellulose crystallinity. Metals and seawater degrade both crystalline cellulose and amorphous part of wood and increase the combustion temperature ranges of cellulose and lignin. Regarding to chestnut the combustion temperature of lignin becomes lower. The most colour alteration was observed for chestnut with iron nails in seawater. The metal diffusion into wood occurs by means of the metals and ions in solution.

Further measurements will develop and examine carefully the following problems with regard to the ageing with ozone and the effect caused by changing temperature of impregnation water.

Acknowledgements

References

1 S. Vicini, E. Princi, G. Luciano, E. Franceschi, E. Pedemonte, D. Oldak, H. Kaczmarek and A. Sionkowska, Thermochim. Acta, 418 (2004) 123.

2 E. Princi, S. Vicini, E. Pedemonte, A. Mulas, E. Franceschi, G. Luciano and V. Trafiletti, Thermochim. Acta, 425 (2005) 173.

3 P. Calvini, A. Gorassini, G. Luciano and E. Franceschi, Vibr. Spectr., 40 (2006) 177.

4 S. Vecchio, G. Luciano and E. Franceschi, Ann. Chim., 96 (2006) 715.

5 S. Soares, G. Camino and S. Levchik, Polym. Degrad. Stab., 49 (1995) 275.

6 A. L. Dupont and J. Tétreault, Stud. Conserv., 45 (2000) 201.

7 M. Bartkowiak and R. Zakrzewski, J. Therm. Anal. Cal., 77 (2004) 295.

8 L. Campanella, M. Tomassetti and R. Tomellini, J. Thermal Anal., 37 (1991) 1923.

9 S.-I. Tsujiama and A. Miyamori, Thermochim. Acta, 351 (2000) 177.

10 B. Kaye, D. J. Cole-Hamilton and K Morphet, Stud. Conserv., 45 (2000) 233.

11 L. E. Alexander, X-ray Diffraction Methods in Polymer Science, Ed. Wiley Interscience, 1969, pp. 180–188.

12 A. J. Varma and V.B. Chavan, Polym. Degrad. Stab., 49 (1995) 245.

13 DN-S. Hon, Photochemistry of Wood, DN-S Hon and N. Shiraishi, Eds, Wood and Cellulose Chemistry, Marcel Decker, 1991, pp. 525–555.