

STUDY OF ARTIFICIALLY DEGRADED WOODS SIMULATING NATURAL AGEING OF ARCHAEOLOGICAL FINDINGS

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Simulation of waterlogged archaeological woods was carried out by immersion of fir and chestnut wood samples into sea water at different temperatures (room temperature and 40°C). The effects of metals in contact with woods were simulated by inserting in some specimens of the two types of wood copper or iron nails, the most important metals from the archaeological point of view. The effects of this ageing simulation on woods were studied by different characterization methods. At first we have performed gravimetric analyses, controlling the mass increase of immersed wood in function of the time of immersion and the temperature of the bath. Then, thermogravimetry, differential thermal analysis, differential scanning calorimetry in oxygen flux were used. The alteration of wood was observed by means of the peak temperatures of DTA, DTG and DSC variation and by the mass losses observed during heating, evaluated on the basis of the measured thermal data. The samples were woods powder obtained by milling. Complementary characterization of the woods was performed by evaluating the crystallinity of cellulose by means of X-ray powder diffraction. The change in colour of woods during ageing was checked by means of spectrophotometric measurements in the visible region.

X-ray fluorescence was used to investigate the penetration of metals into wood samples. An artificial ageing treatment with NaOH and O₃ was also performed.

Finally, a comparison between the effects of artificial alteration realised in our specimens and natural degradation observed in archaeological woods, was performed.

Keywords: degradation, thermal analysis, waterlogged wood

Introduction

As we know from the literature and from previous experimental data [1, 2] in the archaeological waterlogged woods the cellulose content tends to be destroyed. Wood degraded structure is principally composed by lignin. The natural ageing is therefore very difficult to be reproduced in a laboratory because of many factors which take part in the degradation process [3].

We have tried to study the waterlogged woods using some different techniques, coupling mainly X-ray diffraction and thermal and calorimetric measurements. Taking in consideration chemical and physical conditions of wood and water, we have immersed specimens of two kinds of wood, fir (*Abies alba*, soft wood) and chestnut (*Castanea sativa*, hard wood) into deionised [4] and artificial sea water. We checked the influence of the presence of the metals (copper or iron) too. Another effect we experimented is changing the temperature (room temperature and 40°C). As we think, it can accelerate the interaction effects water–wood, water–salts–wood and metal–wood.

Experimental

Chestnut and fir wood samples (5×5×3 cm) without nails have been immersed into artificial sea water at

room temperature and at 40°C to evaluate the effect of the temperature. Other samples contained copper and iron nails to assess the deterioration of woods due to the metals. As reference samples two untreated woods have been used. In order to study the effect of accelerated oxidation, wet woods have been immersed in a NaOH 0.5 M solution at 40°C for 3 weeks. Woods have been then submitted to the attack of O₃ for 3 h for a period of 10 days. This procedure was performed in the Milano Bicocca University's laboratory under the guide of Prof. Orlandi.

Fir and chestnut–wood samples were powdered using a rotating mill with agate balls, with a rotation speed of 700 rpm for 1 h to obtain fine and homogeneous wood powder. We performed thermal and thermogravimetric analyses using an STA Netzsch apparatus, in oxygen flux of 100 mL min⁻¹, operating as follows: 30–40 mg of powders were placed in 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 O₂ flux (100 mL min⁻¹) at the rate of 2°C min⁻¹; the different curves were compared. The apparatus used was a Mettler DSC 821.

Before carrying out the thermogravimetric and calorimetric analyses the samples were dried at 105°C for about 1 h.

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Wide angle X-ray diffractograms were obtained using a PW 1830 Philips Diffractometer (Ni-filtered CuK_α radiation); scans over a 2θ range of $3\text{--}30^\circ$ (step of 0.02° and acquisition time of 20 s). The crystallinity was calculated according to literature [4, 5]. X-ray fluorescence method was used to check the diffusion of metals inside the wood samples. The apparatus was an Assing Lithos 3000 portable X-ray spectrometer provided with Mo tube, a Zr filter and a semiconductor Si detector. Finally reflectance spectrophotometric measurements in the visible region were performed using a Minolta 2600d apparatus.

Results and discussion

Gravimetric analysis

First result we obtained was the mass variation of the samples of two types of wood consequence of water absorption and dissolution of soluble components of wood. Fir, as a softwood, absorbed more water than chestnut. As an example, in Fig. 1 it is shown the behaviour of woods at a temperature of 40°C . The effect of metals brings to a further water absorption. In the case of chestnut this absorption is probably balanced from the extraction of polyphenols and the wood degradation.

As we reported before, to study the wood ageing we used especially X-ray diffractometry, TG and DSC measurements. These methods give much information on the deterioration of wood.

Thermogravimetry

As we can see in Fig. 2 the major mass loss 96.5% occurs for untreated wood. From TG curve we can distinguish four steps. First step ($100\text{--}220^\circ\text{C}$) corresponds to the loss of water and volatile substances. In the second step one find the combustion of amorphous hemicellulose ($250\text{--}275^\circ\text{C}$); in the third step ($275\text{--}350^\circ\text{C}$) the amorphous components proceed

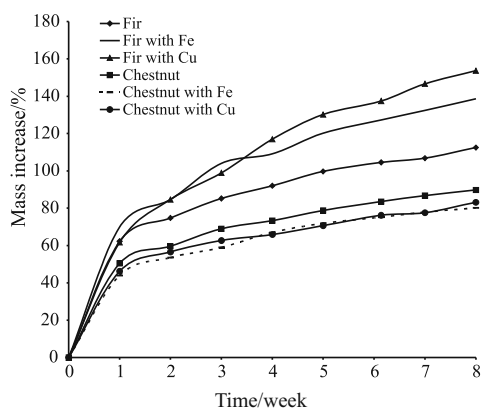


Fig. 1 Mass increase of woods immersed into sea water at 40°C

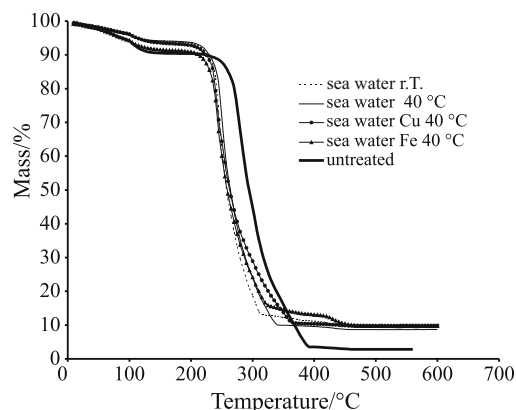


Fig. 2 Comparative TG curves between untreated fir and fir into sea water after 8 weeks

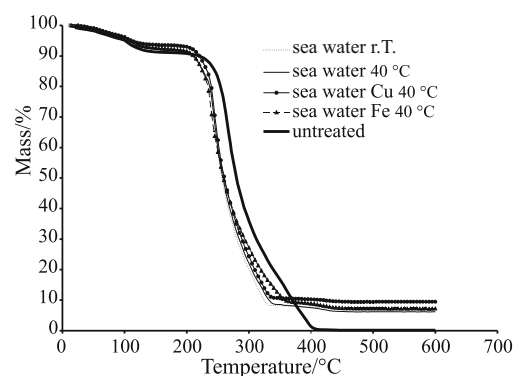


Fig. 3 Comparative TG curves between untreated chestnut and chestnut into sea water after 8 weeks

their combustion together with crystalline cellulose. In the final step ($350\text{--}450^\circ\text{C}$) the complete combustion of the residual compounds and lignin occurs. Observing the treated woods, we can note that the combustion begins at lower temperature compared with untreated wood. This is due to the degradation process. It is a good result even though the artificial ageing was only eight weeks. Last step for fir with iron and copper nails starts at 320 and 370°C , respectively. The mass loss in the first case is higher. This means that the copper destroys the lignin more than iron. Approximately mass loss for treated woods is 90%. Unfired is produced owing to salts, metal ions and tar [4].

A similar behaviour is shown by chestnut wood (Fig. 3).

DSC measurements

From DSC data shown in Figs 4 and 5 we can note that sea water attacks the cellulose in both its parts, amorphous and crystalline. The two exothermal peaks of cellulose and lignin combustion are more separated after the treatment into sea water compared with untreated woods. We can observe that increasing the water temperature a further degradation of the amorphous part, in-

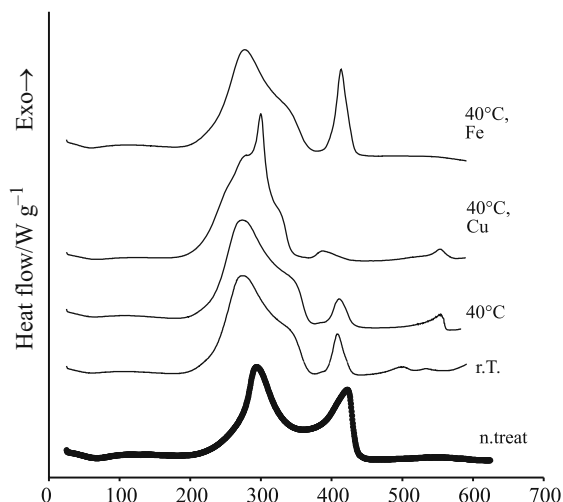


Fig. 4 Comparative DSC curves of fir into sea water after 8 weeks and untreated fir

cluding the lignin, occurs. Wood deterioration is accelerated by metals. The copper, more than iron, is able to degrade the lignin and both parts of cellulose. This is valid for both kinds of woods. In the case of woods with iron, the last peak could be ascribed to the combustion of compounds formed by interactions between wood and Fe. These reactions will be the object of further studies.

The effect of treatments with NaOH 0.5 M and O₃ was assessed by DSC thermal analysis.

The DSC curves obtained after treatments are compared with those of untreated woods. As an example in Fig. 6 the behavior of chestnut is reported. It is clear that the major effect observed is the attack of lignin component of wood.

Table 1 Percent crystallinity degree of cellulose before and after treatment

Woods	Crystallinity X _c /%
Fir not treated	32
Fir with Fe nails into sea water after 8 weeks T=40°C	28.5
Fir with Cu nails into sea water after 8 weeks T=40°C	21.5
Fir into sea water after 8 weeks T=40°C	31
Fir into sea water after 8 weeks R.T.	29
Chestnut not treated	30
Chestnut with Fe nails into sea water after 8 weeks T=40°C	24
Chestnut with Cu nails into sea water after 8 weeks T=40°C	23.5
Chestnut into sea water after 8 weeks T=40°C	26.5
Chestnut into sea water after 8 weeks r.T.	27

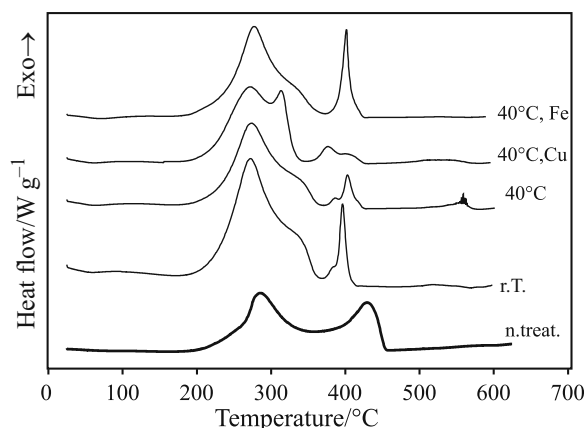


Fig. 5 Comparative DSC curves of chestnut into sea water after 8 weeks and untreated chestnut

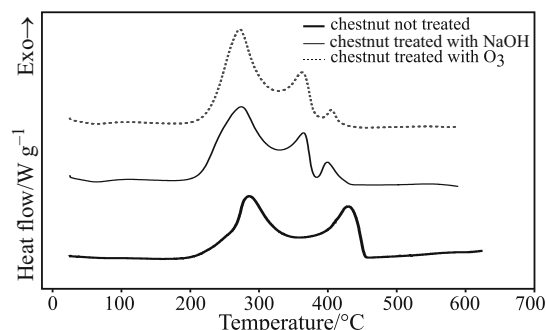


Fig. 6 Comparative DSC curves of chestnut treated with NaOH and ozone and untreated

X-ray diffractometric measurements

XRD data reported in Table 1 show that the chestnut has a crystallinity degree lower than fir. The crystallinity degree of fir put into sea water at room temperature, 40°C and with iron nails decreases by 9, 3 and 11%, respectively, compared with not treated fir. The cellulose crystallinity degree of fir with copper nails into sea water at 40°C after eight weeks was reduced by 33%. The crystallinity of the chestnut put into sea water at room temperature and 40°C was reduced about 12%. The metals in the chestnut wood, submitted at the same treatment, bring a reduction of the same parameter of 20–22%. Iron attacks more the crystalline part of cellulose in the chestnut.

The colour measurements are in agreement with the wood degradation result. In other words, more increases the wood alteration more dark becomes its colour [6]. Also increasing the temperature the wood becomes darker. Regarding to the metals the alteration effect of copper is generally stronger than iron.

X-ray fluorescence measurements

From X-ray fluorescence one can also observe that the metal–wood interaction occurs mainly through the

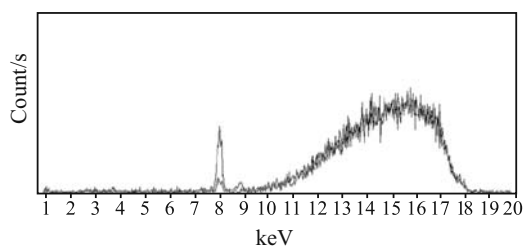


Fig. 7 X-ray fluorescence measurements for the treated fir in surface (higher Cu peak) and 4 mm inside (lower Cu peak)

solution. Metal ions present in water penetrate inside the wood with a limited depth. The spectra reported in Fig. 7 show the Cu diffusion into fir-wood. The first curve (red) is obtained on the surface of the sample and the second one (blue) was performed at 4 mm into wood.

Regard to the archaeological woods we have carried out a previous study [2] on some wood samples of a Roman ship from 1st century B.C. found in Pisa and from the Israel's ship to XVII-XIX century A.D. found in Tantura. In this study we have used both diffractometric and calorimetric data, and a comparison with artificially aged wood was performed. By means XRD analysis of the ancient ships' wood we observed that the cellulose content is insignificant and the material is almost all in the amorphous state.

Conclusions

Thermal analysis results a powerful tool in studying the degradation of wood. The examination of the shape of the curves can establish which component of wood is degraded, suggesting possible reaction mechanisms of alteration processes. We pointed out two schematic and different wood degradation mechanisms: the first one causes mainly the alteration of the crystalline part of the cellulose, the second one de-

grades principally the amorphous components of wood. We established too the important role that metals, like copper and iron, can play in the alteration process of waterlogged wood. The action of ozone in alkaline solution does not seem to cause a deep alteration, but the principal degrading factor remains the alkaline medium. This method causes wood alteration but does not seem to simulate natural aging. However wood so treated and deeply degraded will be used to check some protective materials, like acrylic polymers with a polymerisation 'in situ'.

Processes which simulate the natural weathering of wood remain very important in understanding the natural mechanisms of alteration, and they are preliminary to any restoration and conservation action.

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References

- 1 G. Giachi, F. Bettazzi, S. Chimichi and G. Stacciali, *J. Cultural Heritage*, 4 (2003) 75.
- 2 G. Luciano, P. Calvini, M. M. Carnasciali, E. Franceschi and U. Meo, *Congresso dell'AiAr*, Pisa, febbraio 2006.
- 3 B. Pizzo, G. Giachi and L. Fiorentino, *La diagnostica e la conservazione dei manufatti lignei*, Marsala Atti del Convegno, Nardini Editore, Firenze 2006.
- 4 E. Franceschi, I. Cascone and D. Nole, *J. Therm. Anal. Cal.*, 91 (2008) 119.
- 5 L. E. Alexander, 'X-ray diffraction methods in polymer science', Ed. Wiley Interscience, 1969.
- 6 A. J. Varma and V. B. Chavan, *Polym. Degrad. Stab.*, 49 (1995) 245.

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