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Investigation of the influence of Hemicelluloses on time dependent behaviour of wood.

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Abstract

As known the stress strain relationship in wood is dependent on time, humidity and temperature, including their variations and history.
This study focuses the attention on the influence of hemicelluloses on the time dependent behaviour and mechanosorption effects of wood. The experiments were performed on two sets of thin clear samples of Spruce (*Picea abies* Karst.). The first used natural non-treated wood as a reference while hemicelluloses in the second one were removed totally.
Specimens were tested by means of micro-tensile device equipped with a climatic chamber able to conditioning sample environment. Temperature was set at 20°C while cyclical RH changes from 30% up to 75% during application of load. Loads applied were respectively 20 and 40% of ultimate tensile strength. After mechanical test the specimens have been analysed by means of IR spectrometry in order to evaluate the effectiveness of hemicelluloses removal from the sample. Other adsorption tests were performed in order to obtain the sample's isothermal adsorption curve
The main results are:

- IR spectrometry shows complete removal of hemicelluloses;
- at the same value of RH% treated wood shows different values of moisture content than natural wood;
- time to reach the moisture content equilibrium is longer for samples without hemicelluloses;
- wood without hemicelluloses shows a lower viscoelasticity than natural wood with hemicelluloses, at constant climatic condition
- during the RH variations the increasing of deformation on wood without hemicelluloses is smaller than in "normal" Spruce.

Introduction

Mechanical wood behaviour can be investigated by applying an instantaneous or long time load. The first case is classified under *elastic* behaviour the second like *time dependent* behaviour.
Time-dependent behaviour depends on humidity, temperature, load and their variations. Wood shows viscoelastic behaviour with constant load and when the moisture content of sample and temperature are kept constant. Mechano-sorption behaviour is characterized by load and cyclic variation of moisture content.
Since Armstrong and Kingston's (1960) and Grossman's (1976) studies many other investigatins were performed in order to observe and explain viscoelastic and mechano-sorption behaviour and their relationship. Some of them indicate some kind of interaction between creep viscoelastic and creep mechano.sorptive (Hanhijarvi, Hunt, (1998)), while others retain that the two phenomena are not linked and their origin is different. (Navi, et al. (2002)). While for the viscoelastic creep there are some good explanation (Hoffmeyer et. al. (1989)), at moment for MS creep no exhaustive explanation has been formulated and verified by experiment, in particular at molecular level.
In this study the attention is focused on the influence of hemicelluloses during the time dependent and mechano-sorption behaviour of wood. Hemicelluloses are an important part of secondary cell wall considering their position, arrangement with the others polymers and their capability to link with water. With the elimination by selective hydrolysis from one set of sample, it was possible to observe the difference between natural and treated wood during the application of load and during the adsorption and desorption of water.

Materials and Methods

The experiments were performed on clear samples of spruce (*Picea abies* Karst.). Two set of sample were used: the first was wood at natural state as reference, the second consists in chemical treated wood. The chemical procedure was a selective hydrolysis with a solution of sulphuric acid (H_2SO_4) at 5% that removed the hemicelluloses (F.Heger (2004)).

Using a precision saw small stripes 0,7 mm thick (tangential direction), 30 mm long (grain direction) and 3 mm wide (radial direction), have been prepared. Both ends of the specimens were embedded in epoxy resin in order to allow their hooking in the clamps of the tensile test machine
With both set of samples different kind of measurement were performed:

Adsorption test

Adsorption tests were performed in order to obtain the sample's isothermal adsorption curve. Specimens were equilibrated at different value of relative humidity, 0%, 12%, 23%, 54%, 66%, 86%, 98% and then the internal moisture content (MC) was calculated.

$$MC = \frac{(w - w_0)}{w_0} * 100,$$

where w is the weight of wood specimen at a specific value of MC and w_0 is the weigh at 0% of MC.

IR spectrometry

With IR spectrometry is possible to know the qualitative chemical composition of wood, in this study this technique of investigation was used in order to verify the complete and effective removal of hemicelluloses. Test were carried out at Chemical Laboratory of University of Florence with an apparatus device by Perkin-Elmer, model SPECTRUM BX with a software SPECTRUM V.3.02.02. Sample preparation for the spectrometry followed the standard of TAPPI 264 om-88, TAPPI 207 om-88, TAPPI T 204.

Mechanical test

Short tensile tests were performed in order to calculate the module of rupture (MOR) of natural and treated wood. MOR was obtained using an universal testing.
For viscoelastic and mechano-sorption test a special micro-tensile device equipped with a climatic chamber able to conditioning sample environment was used. The device was accurately described by Navì (Navì et al. (2002)).
Load was respectively 20% and 40% of ultimate tensile strength and it was applied for 11 hours in a constant environmental condition characterized by RH% at 30% (creep VE), and then the RH changed cyclically from 30% up to 75-80% (creep MS).
In order to know the exact deformation dues to application of load, prior the MS experiments on the same sample were measured the deformation of free swelling and shrinkage.
During all tests temperature was constant at 20°C.

Results

Results of adsorption test

The results of adsorption tests are shown in figure 1 where the moisture content is plotted against the relative humidity at temperature of 20°C.

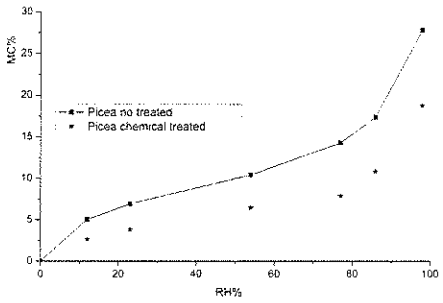

Figure 1 Isothermal adsorption curve of no-treated and treated wood

The dynamic of adsorption is similar for the two specimens, in fact both samples showed to be able to adsorb more water at the beginning of the process, from 0% to 20% of RH%, and at high value of RH%, up to 90% .
Anyway between treated and no treated wood there is a difference in the value of moisture content at same condition of relative humidity. Wood without hemicelluloses have always less water linked at the cell wall, and the hygroscopic equilibrium is lower.

Results of IR spectrometry test

IR spectrometry gives a spectrum of energy adsorption; the presence of chemical component is shown by the presence of a peak. Considering that we worked in transmittance the peaks have the concavity toward the low.

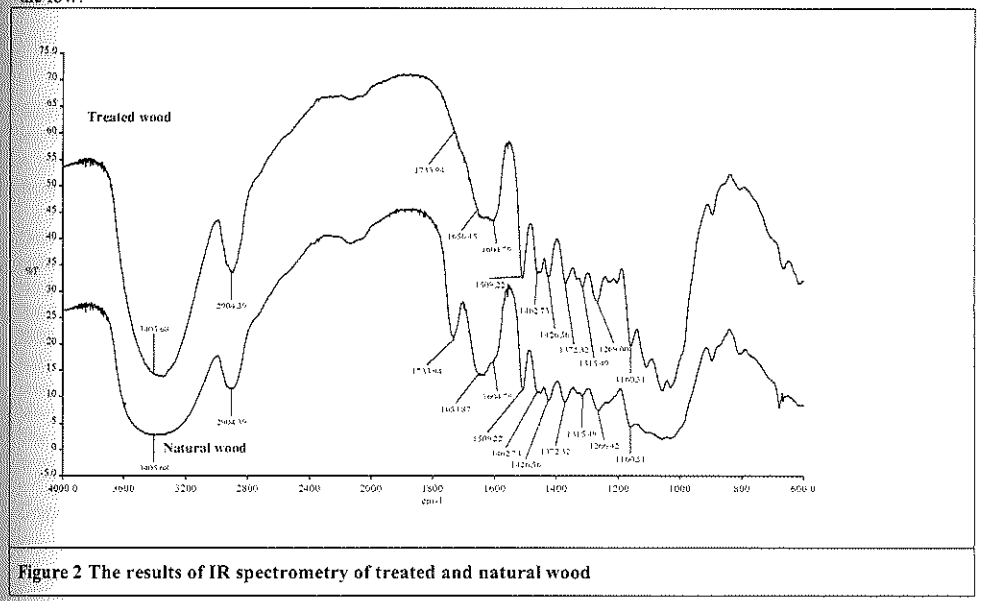

Figure 2 The results of IR spectrometry of treated and natural wood

Figure 2 shows the adsorption spectrum of natural and chemical treated wood of spruce. The biggest difference between two spectrum was at weight length of 1733.94 cm^{-1}. A peak at this value corresponds at the presence of hemicelluloses in the wood structure. The curve of treated wood didn't show any kind of peak at this characteristic value, it means that the hemicelluloses have been completely removed by the selective hydrolysis, while others important chemical modification didn't occurred in wood composition.

Results of mechanical test

The aim of experiment was to establish the influence of hemicelluloses on time dependent behaviour of wood.

Figure 3 shows the results of test on normal and treated wood.

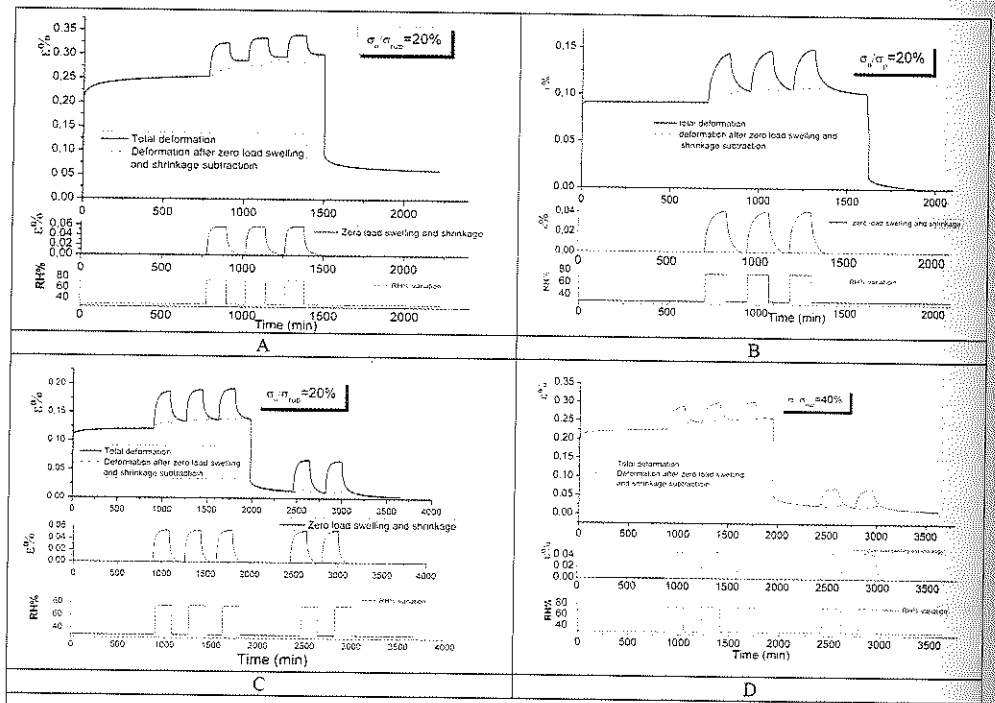

Figure 3 A) Test on natural spruce; B and C) Test on treated wood; D) Test on treated wood where load applied was 40% of ultimate tensile strength.

Some preliminary observations can done about the results of free swelling and shrinkage. While with no treated wood two hours was long enough to establish the hygroscopic equilibrium, with treated wood it was not sufficient . The test represented in figure 3B shows like the curve relative at free swelling and shrinkage was not flat. That's mean without hemicelluloses wood needs more time to adsorb water, also if the amount of adsorbed water is smaller, like it was shown in adsorption test (figure 1). When each cycle has been three hours long, like in experiment in figure 3c and 3D, samples have reached the moisture equilibrium. The amount of free deformation is similar in natural and treated wood because it was measured in longitudinal direction where the contribute to the deformation by the hemicelluloses is small.

During the firsts 11 hours of each experiments RH% was hold constant in order to observe viscoelastic behaviour. After the first instantaneous and elastic component of deformation wood stared to show the viscose increasing of strain. As it possible to see in figure 3 the amount of viscose deformation is different between treated and natural wood. In no treated spruce deformation increased more and for a longer period of time, while in spruce without hemicelluloses the line of deformation became flat very early and also the amount of strain was smaller, table 1.

Sample	Viscoelastic deformation*
Normal wood	0.04%
Treated wood 3B	0.005%
Treated wood 3C	0.01%

Table 1 Viscoelastic strain measured on treated and no treated spruce

* Viscoelastic deformation = total strain after 500 min of load – elastic strain

When specimen was loaded with 40% of MOR the viscoelastic component was higher, but in this case the test was performed near to the limit of linearity.

A possible explanation for the different viscoelastic behaviour is that with the removal of hemicelluloses there is less hydrogen bonds which are the favourite sites of sliding under load inside the cell wall.

Once that the viscoelastic component was finished, the RH% was cyclical changed form 30% up to 75% in order to observe the coupling effect of moisture content variation and load.

No treated spruce has shown a typical mechano-sorption behaviour, with an increment of deformation during the first cycle during wetting and drying process; with a smaller increasing of deformation during the next humidity cycle and with a big residual deformation after the unloading.

Also treated spruce showed an increasing of creep deformation dues to the moisture content change that is greater than the effect of time, the biggest increasing of deformation was measured during the first cycle.

Mechano sorption effect is detectable with a load of 20% and 40% of ultimate stress.

The presence of mechano sorption in the sample without hemicelluloses shows like the hemicelluloses are more related with viscoelastic behaviour than with mechano sorption effet.

Conclusions

The results from all tests performed on natural and treated wood of spruce are:

. selective hydrolysis with sulphuric acid has completely removed the hemicelluloses from the wood cell structure. IR spectrometry test confirmed the complete removal of hemicelluloses and it doesn't show any other relevant chemical modification.

. the water adsorption in treated and natural wood are different. Wood without hemicelluloses at same value of environmental relative humidity has a lower value of moisture content than natural wood and it needs more time to reach the hygroscopic equilibrium.

. when wood is loaded in constant condition of RH% and temperature wood without hemicelluloses shows a lower viscoelastic response than wood with hemicelluloses.

. mechano sorption effect is detectable both in treated and no treated wood. In wood without hemicelluloses the effect of moisture change and load are smaller but present.

. in the same test with wood without hemicelluloses there is an almost complete absence of viscoelasticity while the mechano sorption behaviour is present. That can be a confirmation that there are no relationship between creep VE and creep MS and their origin is different.