Stiffness changes during low temperature thermal treatment of Scots pine, assessed by acoustic NDT

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ABSTRACT

The change, over time, in density, longitudinal modulus of elasticity, shear modulus and chemical structure of Scots pine (*Pinus sylvestris*) under thermal treatment (110, 120 and 140 $^{\circ}$C) was evaluated. The determinations of the specific changes were carried out by means of impulse excitation, ultrasonic time-of-flight and near infrared spectroscopy. The results show, that the stiffness and density decrease was linear with time, with no evidence of a slowing rate of degradation even at 140 $^{\circ}$C, after loss of more than half the original wood stiffness and more than a quarter of the original mass. At all temperatures the ratio between the longitudinal modulus and shear modulus was unchanged by the treatment for individual samples and the stiffness change was proportional to mass loss irrespective of the temperature and time. Examination of the NIR spectra revealed modifications in the amorphous carbohydrates structure and small changes in the lignin structure.

INTRODUCTION

Studies on wood thermal modification process have been conducted since the early 1950s with the aim to enhance the durability of wood for exterior applications. Usually thermal modification of wood is performed between 160 and 260 $^{\circ}$C, the lower temperatures inducing small changes in the wooden material properties, while higher temperatures induce strong degradation of the substrate (Hill 2006). Also the duration of treatment is very important. When wood is heated, the loss of water and volatile extractives takes place first, after which the less volatile extractives tend to migrate to the wood surface. For longer periods of treatment some chemical changes in the macromolecular structure may occur. These processes are accompanied by weight loss and also by colour change.

As a result of the thermal treatment, and depending on the treatment conditions, the following physical properties may change: improved dimensional stability and resistance to the microbiological attack, reduced hygroscopicity, impact toughness, modulus of rupture and abrasion resistance, darkening of material, *etc*. (Windeisen *et al*. 2007).

All these properties are also influenced by the chemical composition of the wooden material, the modifications varying across wood species. As noted before, at lower treatment temperatures relatively small changes take place, but these are proportional

with the period of the treatment. The present study deals with acoustic NDT measurements and NIR spectroscopy tests in order to evaluate the properties of heat-treated Scots pine wood at lower temperatures for a long period of time.

EXPERIMENTAL

Materials

Clear samples of Scots pine (*Pinus sylvestris* L.) of dimension of 20 mm (radial), 93 mm (tangential) and 300 mm (longitudinal) were heated in an oven at 110, 120 and 140 ±2.5 °C for periods of up to 205 days (Table 1). On a weekly basis the samples were removed from the oven, weighed hot and then allowed to cool in normal indoor conditions. They were then re-weighed, measured with digital callipers and by the acoustic methods. Finally the samples were weighed again and returned to the oven. Measurement of oven dry weight and cold weight permitted calculation of moisture content at the time of measurement (mean 0.4% st dev 0.1%). For each measurement point, separate samples were removed from the oven for spectroscopic analysis. The treatment time was recorded as the time the samples spent in the oven.

Table 1: List of treatments

Treatment	Description
1	4 pieces up to 170 days at 110±2.5 °C
2	4 pieces up to 130 days at 120±2.5 °C
3	4 pieces up to 205 days at 140±2.5 °C

* all samples were at approximately 8% moisture content when entering the oven initially

Longitudinal stiffness was assessed using time-of-flight measurements by using a Proceq Pundit Lab plus ultrasonic pulse velocity instrument. Transducers of frequency 54 kHz were used with manual pressure and a layer of rubber from a disposable nitrile glove to provide coupling (avoiding the use of gels). On these samples, individual measurements typically ranged ±0.5 µs (equating to ±2% in the measurement of $E_{dyn,ultrasonic}$), but by taking an average of 30 measurements this could be reduced to ±0.05 µs, the precision of the Pundit Lab plus instrument (±0.2% of $E_{dyn,ultrasonic}$).

The impact excitation method employed was based on the standard test procedures for ceramic materials. The shape of the samples was a compromise so as to obtain flexural ($E_{dyn,flexural}$), longitudinal ($E_{dyn,longitudinal}$) and torsional (G_{dyn}) resonance modes on the same sample. The aspect ratios were outside the limits of the shape factor corrections in EN 843-2 and so the more complex corrections in ASTM E1876 were used. In order to provide better precision in the frequency domain, the sound of several hits was recorded and analysed together.

The sound was recorded with a 16 bit 48 kHz USB microphone with 50 Hz to 19 kHz range and analysed using the Sigview32 2.4.0 software (using Hann window and zero padding of the next power of two, unsmoothed), which uses the Kiss FFT library.

NIR spectra were recorded by means of a LabSpec 5000 FR Spectrometer in the spectral range 350 - 2500 nm by diffuse reflectance method. The contact probe was placed against the sample, and spectral data were collected. At each position the exposure time was five seconds, equating to fifty spectra being collected and then averaged. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific).

RESULTS AND DISCUSSION

Impulse excitation and ultrasonic time-of-flight are both well-established methods for assessing non-destructively the stiffness of a material. Their use on wood has become common in both scientific and industrial applications although the results obtained need to be treated with some caution. The 'dynamic stiffness' as measured by an acoustic technique differs from the equivalent 'static stiffness' that would be obtained from a pseudo-static test because of the complex ways in which dynamic waves propagate in wood, its rate dependent material behaviour and the assumptions of linear elastic, homogeneous, isotropic material behaviour in the resonance equations. However, these errors are systematic and for a particular sample and testing method it is a straightforward matter to track changes in stiffness by acoustic methods. The impact excitation method employed was based on the standard test procedures for ceramic materials. Due to the shape of these samples, there were many resonance peaks in addition to the basic longitudinal, flexural and torsional modes and their harmonics. In all cases the flexural mode was clear and unambiguous. The longitudinal mode was very difficult to discern in all cases, as there were a multitude of closely spaced peaks due to the complex modes of vibration for these sample shapes. By comparing frequency spectra for a sample at different treatment points it was possible to use the cases where the longitudinal peak was clearest (highest magnitude) to discern the peak for the longitudinal mode from the peaks for other modes for the other measurement points. In the case of torsional resonance it was found that exciting both sides of the sample (i.e. clockwise and anticlockwise impulses) resulted in better definition of the torsional resonance peak.
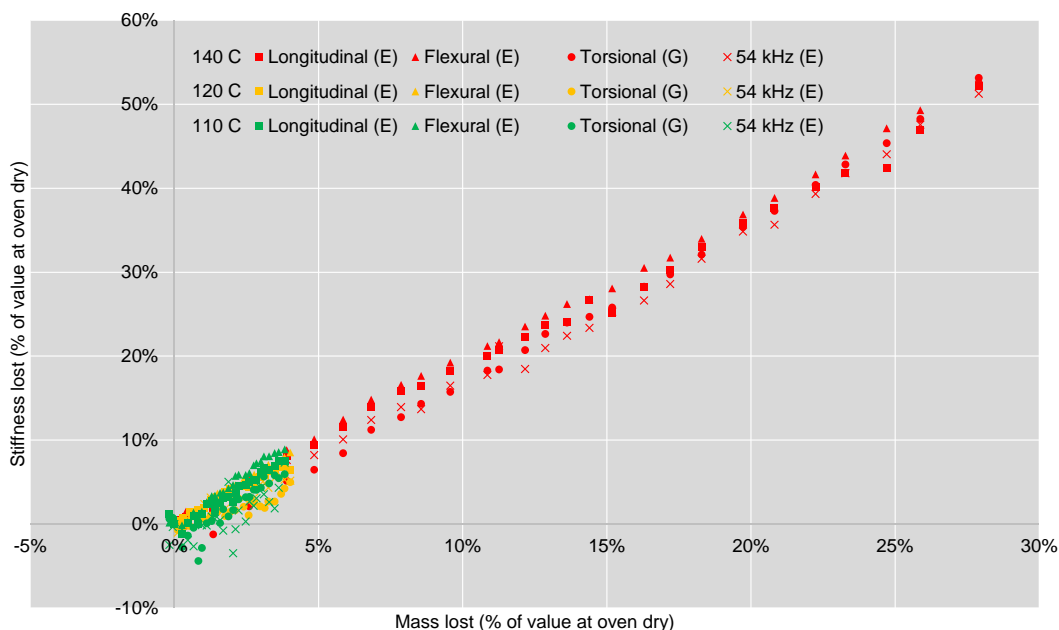

Figure 1: Loss of stiffness (in dry state) vs. loss of mass (averages of 4 samples)

By the impulse excitation (flexural, longitudinal and torsional resonance) and ultrasonic time of flight methods the small changes in longitudinal Modulus of Elasticity (Edyn) and radial-tangential Shear Modulus (Gdyn) were evidenced. All three methods of obtaining Edyn showed the same percentage change with time for each treatment, within the limits of the experimental error (approximately 2% of the absolute value) and, the correlation between them was seen to be unchanged by either the temperature

or the duration of heat treatment. The ratio of Gdyn to Edyn (which varies by sample) was also seen to be unchanged by either the temperature or the duration of heat treatment. These findings indicate that the thermal degradation process has a uniform effect on Edyn and Gdyn, regardless of the isotropic nature of the wood microstructure, and is consistent with the theory that the primary mechanism for stiffness loss is progressive degradation of hemicellulose at these temperatures. While cracking was observed in the samples, there was no evidence to suggest that the stiffness loss was caused by micro-cracks resulting from heating and cooling cycles. There was no clearly observed initial stiffening after reaching the oven dried state (although measurement points may not have been sufficiently frequent to capture this). There was no evidence of a slowing rate of degradation even at 140 $^{\circ}$C after loss of more than half the original wood stiffness and more than a quarter of the original mass.
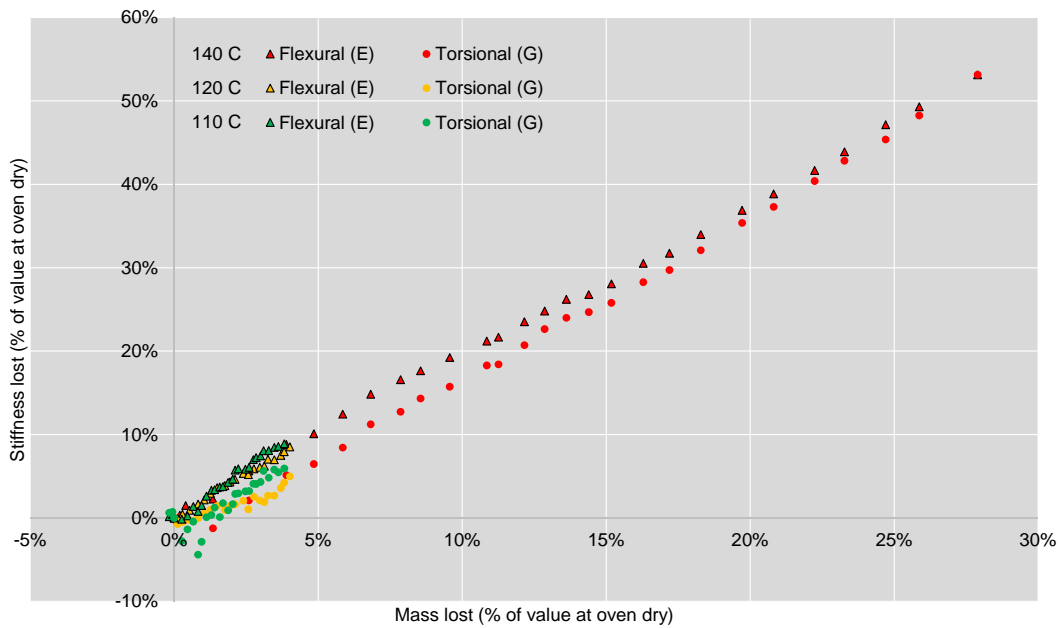

Figure 2: Clearer view of Figure 1 focusing on flexural and torsional resonance results)

$$[\text{Loss in stiffness}] = 1.8 \times [\text{Loss in mass}] \qquad (1)$$
$$(\% \text{ of oven dry value})$$

The drop in stiffness (both E_{dyn} and G_{dyn}) was seen to be linear in the range of temperatures and durations studied and was directly proportional to the mass lost irrespective of both temperature and time (Figure 1, 2 and Eqn 1). The results are summarised in Table 2.

Table 2: Rates of property loss per day (24 hours of treatment time)

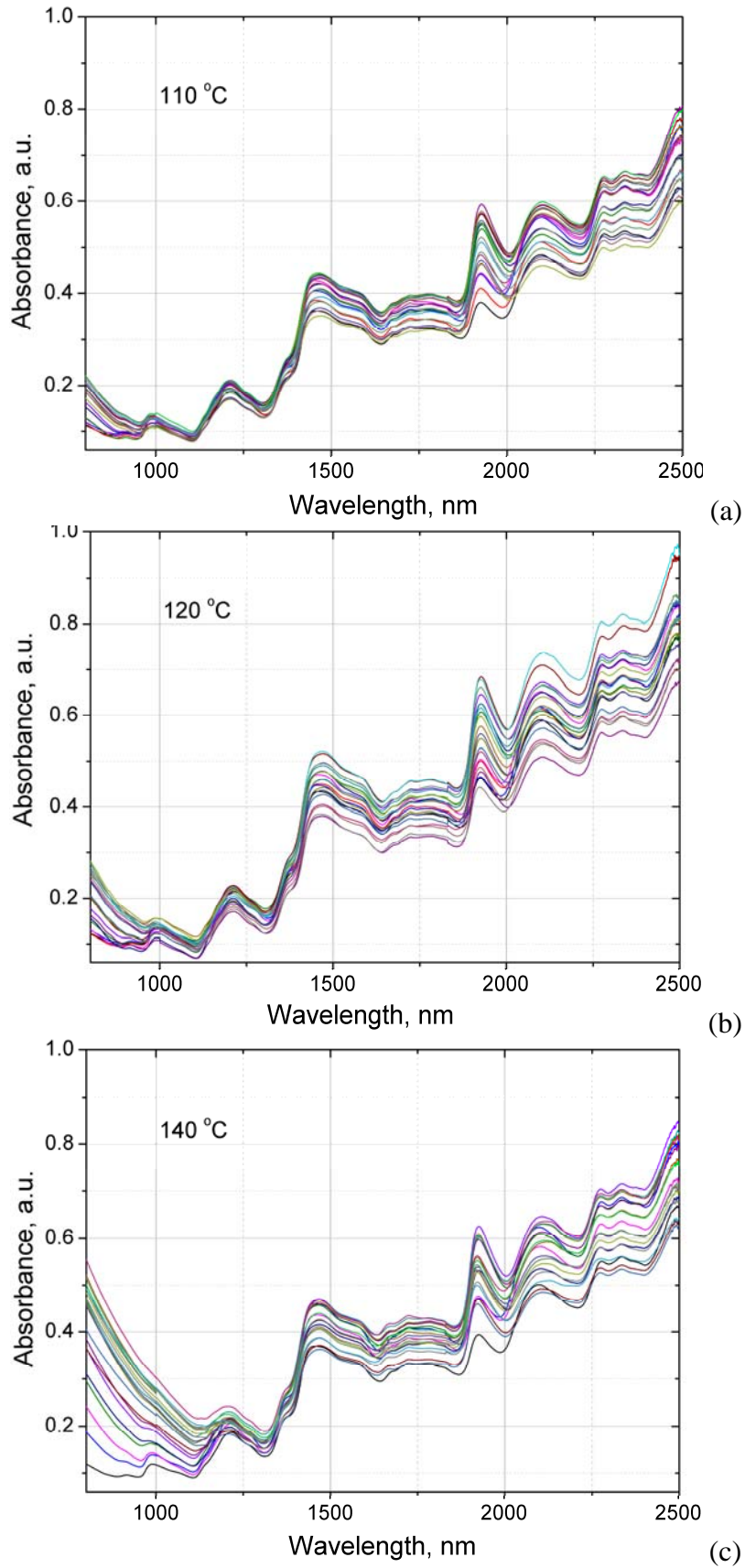| Treatment	Loss in property per day (after drying) % of initial oven dry value	
	Loss in mass	Loss in stiffness (E_{dyn} and G_{dyn})
110±2.5 °C	0.022%	0.04%
120±2.5 °C	0.031%	0.05%
140±2.5 °C	0.137%	0.24%

Figure 3: NIR spectra of the thermal treated Scots pine wood at 110 ᵒC (a), 120 ᵒC (b) and 140 ᵒC (c)

Further, the structural modifications assessed by NIR spectroscopy were evaluated. The NIR diffuse reflectance spectra in the 800 - 2500 nm range are shown in Figures 3a-c. Independently to the treatment temperature applied, the NIR spectra, present similar trends with typical broad vibration bands associated to the chemical components of wood. Four spectral regions, 1000-1486, 1486-1667, 1667-2000 and 2000-2500 nm, associated with different groups from the wood structure were identified. The first region is assigned to the first and second overtones of OH groups, first overtone of C-H combination bands, and second and third overtones of C-H, Car-H stretching vibrations (Popescu and Popescu 2013, Schwanninger *et al*. 2011). In the thermal treated wood spectra only two broad bands at 1216 and 1456 nm are observed. The first one slightly decreases during time of heating and also with the increase of the temperature while the second one decreases and is shifted to higher wavelengths, suggesting variations in the methyl, methylene groups and acetyl groups from hemicelluloses and amorphous cellulose and also O-H groups. As the temperature increases, the stronger variations are observed, mainly for the band with the maximum at 1456 nm. The second region (1486-1667 nm) is assigned to first overtone of O-H stretching vibrations arising mainly from carbohydrates. The first overtone of aliphatic and aromatic C-H stretching vibrations, O-H combination bands and second overtone of C=O stretching vibrations are found in the 1667-2000 nm region (Popescu and Popescu 2013, Schwanninger *et al*. 2011), while the last region (2000-2500 nm) is a combination of bands arising from a high number of different coupling vibrations (Popescu and Popescu 2013, Schwanninger *et al*. 2011).

As can be seen from the Figure 3, in the last region there are important modifications, therefore the wide band with the maximum at 2096 nm is shifted to higher wavelengths, decreases in intensity, while its width increased with the increase of the treatment time and temperature. This band was assigned to the combination of O-H stretching and deformation vibrations in carbohydrates. Decrease of the intensity of this band is due to the loss of the hydroxyl groups from these compounds during the low temperature thermal treatment.

In comparison with infrared (IR) spectroscopy, in NIR spectroscopy it is difficult to assign the bands to specific functional groups because of the peaks overlapping. When there are overlapped bands, the reason of the spectral bands intensity increases or decrease can be due to a shift or a change in the location of the component bands. In order to improve the spectral resolution, second derivative (Savitzky-Golay method with 25 points) was used.
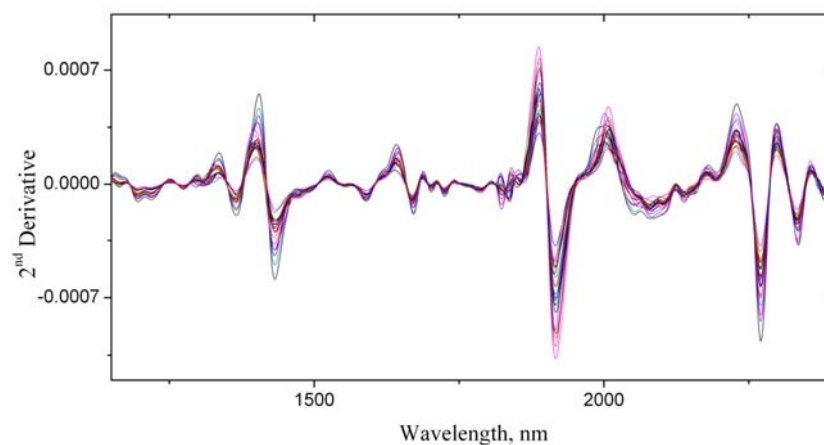

Figure 4: Second derivative of the NIR spectra of the thermal treated Scots pine wood at 110 ^{o}C

In Figure 4 the second derivative spectra of the 110 ^{o}C thermal treated samples are presented as an example. Here the variation of the bands in time can be more easily established and followed.

CONCLUSIONS

There was a high level of agreement between the acoustic methods, but the impact excitation technique outperformed the ultrasonic time-of-flight method in this case. All methods are capable of measuring the trend in stiffness and by tracking several measurement points a much better result was obtained than would have been from single before and after measurement points, which would have been clouded by random variation from sample to sample. Within the range studied, the loss in stiffness is proportional to the loss of mass irrespective of treatment duration and temperature. The ratio of shear modulus and longitudinal modulus of elasticity remained unchanged for a sample, even though there is no correlation between these properties across untreated samples. NIR spectra of the thermal treated wood samples for different periods of time at three different temperatures showed modifications in the amorphous carbohydrates structures, especially.

ACKNOWLEDGEMENTS

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