A. Sandak *et al.*, *J. Near Infrared Spectrosc.* **24**, 549–553 (2016)
Received: 31 January 2016 ■ Revised: 24 June 2016 ■ Accepted: 5 July 2016 ■ Publication: 19 August 2016

JNIRS JOURNAL OF NEAR INFRARED SPECTROSCOPY

Virtual Issue: Papers Presented at NIR-2015, October 2015, Foz do Iguassu, Brazil
Special Issue: Wood and Wood Products

openaccess

Weathering kinetics of thin wood veneers assessed with near infrared spectroscopy

Anna Sandak,[a] Jakub Sandak,[a]* Ingunn Burud[b] and Lone Ross Gobakken[c]

[a]Trees and Timber Institute IVALSA/CNR, via Biasi 75, 38010 San Michele all'Adige (TN), Italy. E-mail: sandak@ivalsa.cnr.it

[b]Norwegian University of Life Sciences, Department of Mathematical Sciences and Technology, Campus Ås, Universitetstunet 3, 1430 Ås, Akershus, Norway

[c]Norwegian Institute of Bioeconomy Research, Box 115, 1431 Ås, Akershus, Norway

Wooden elements may be subjected to mechanical, environmental or biological alterations during their service life. The most susceptible parts of wood structural members are the exposed surfaces since they are subjected to ageing, weathering and/or decay. Knowledge of the influence of weathering factors and polymer degradation mechanisms is essential for understanding the weathering process of wood. The goal of this study was to investigate the degradation of thin wooden samples exposed to short-term weathering. Tests were performed through the European summer (July), which according to previous research is considered as the most severe period for weathering of wood micro-sections. Fourier transform near infrared spectroscopy was used for evaluation of chemical changes of wood samples. Three approaches for data evaluation are presented in this paper: (1) direct spectral interpretation, (2) a concept for calculation of a weathering index W_{ind} and (3) kinetics of lignin changes in relation to the exposure direction for selected wavelengths. Observation of the effects of weathering will allow better understanding of the degradation process. The southern exposure site was slightly more affected by weathering than other sites. Results of this research will be used for future determination of the weather-dose response model and could be essential for predicting the future performance of timber facade elements.

Keywords: wood weathering, degradation kinetics, spectroscopy, NIR

Introduction

Wood is the world's oldest building material, but also a modern one. A major increase in use of wood in the building sector has been observed, as it is considered as a highly sustainable and renewable material. Bio-based building materials used today (including wood) may be well characterised from the technical point of view, but there is often no reliable model to describe their performance during their life cycle. Estimation of the degradation state is a first and fundamental phase for proper maintenance and conservation of wooden members.

Weathering is a term used to define the slow degradation process of materials exposed to an outdoor climate. Solar radiation, cyclic wetting, atmospheric temperature, relative humidity changes, environmental pollutants, mechanical abrasion and certain micro-organisms are the reasons for change in both the material exterior and the mechanical properties. For wood and other bio-based materials, weathering processes lead to a slow breaking down of fibres, roughening of the surface and reduction in glossiness. As a consequence, the material appearance is changed. Several factors affect the weathering deterioration speed and intensity. The timber species, type of finishing, architectural design and specific local climatic conditions are the main influencing factors.

The use of near infrared (NIR) spectroscopy for assessment and monitoring of timber members has been proposed by several researchers and an overview was recently presented.[1] Zanetti *et al.*[2] used NIR spectroscopy for prediction of wood weathering and for monitoring the condition of in-service wood structures. According to those authors, the high capability

ISSN: 0967-0335
doi: 10.1255/jnirs.1230

Table 1. Meteorological data acquired during weathering test.

Day of exposure	Mean daily temp. (°C)	∑ radiation (MJ m^{-2})	∑ insolation (h)	Total daily rainfall (mm)	Mean RH (%)	Mean wind speed (m s^{-1})
1	17.8	29.96	14.3	11.4	84.1	0.8
2	20.0	59.63	26.1	0	59.0	1.9
4	21.7	104.56	45.7	1.6	72.5	0.5
7	17.0	162.16	70.4	42.6	92.7	0.5
9	18.3	201.54	89.7	0	68.1	0.9
11	19.8	250.54	108.4	2.0	67.6	1.2
14	22.0	324.02	139.2	0.2	68.0	0.9
17	24.2	407.06	172.8	0	59.8	1.0
21	19.9	469.26	201.7	0	79.5	0.1
24	21.0	526.58	228.5	0	69.6	0.8
28	19.0	580.76	255.1	13.4	88.9	0.5

for prediction of weathering time by means of partial least squares (PLS) models opens additional approaches to defining relevant surface treatments for timber conservation. Attempts to predict exposure times for weathered wood were also conducted.[3] Other tests including the effect of time, geographical location, exposure and coating type have also been carried out.[4,5] It was stated that after one year of weathering dramatic changes in the NIR spectra were observed. However with the progress of degradation, NIR spectra of samples exposed for one year were similar to those exposed for longer periods (several years). A slightly different approach for evaluation of weathered wood samples was presented by Tsuchikawa and Yamato,[6] who tested five categories of wood-based materials (solid wood, laminated wood, particle and fibre board, impregnated wood and overlaid wood) when exposed outdoors to sunlight and rain for up to six months. The purpose of that research was to investigate if wood weathering has an effect on the NIR classification of waste wood before recycling.

The goal of this work was to understand the degradation kinetics of thin wood veneers exposed to natural weathering by developing numerical models linking the extent of degradation with the dose of weathering. The duration of the natural weathering test was limited to four weeks and the evaluation of sample states during the weathering progress was assessed by means of NIR spectroscopy.

Materials and methods

Sample preparation

Experimental samples are part of the Round Robin test conducted within COST Action FP 1006 "Bringing new functions to wood through surface modification", where 28 sets of samples were exposed in 16 locations in Europe. Specimens were prepared from one piece of Norway spruce (*Picea abies* L. Karst) wood using a slicing planer (Super MECA-S, Marunaka Tekkonsho Inc., Shizuoka, Japan). The thickness of samples was *ca* 100 µm and the actual surface area exposed to weathering was 30 mm × 35 mm (width × length, respectively). Four sets of samples were exposed in San Michele, Italy (46°11′15″N, 11°08′00″E) for four geographical directions (north, east, south and west), and were collected after 1, 2, 4, 7, 9, 11, 14, 17, 21, 24 and 28 days of weathering. Additional sets of reference samples were stored in a climatic chamber for the whole project duration. Tests were performed in July (2014), which according to previous research[7] is considered as the most severe season in Europe for weathering of wood micro-sections. Also, the experimental setup used in this research (exposure angle of 45°) is considered as a very severe configuration due to the rapid leaching of degradation products from the surface due to the cleansing action of rain.[8] After collection, the samples were conditioned in the climatic chamber (20°C, 60% RH) to the equilibrium moisture content of *ca* 12%. Meteorological data were acquired during the test period and are presented in Table 1.

Fourier transform NIR measurements

Experimental samples were evaluated using a Fourier transform NIR spectrometer (VECTOR 22-N; Bruker Optics GmbH, Ettlingen, Germany). The spectral resolution of the instrument was 8 cm^{-1}, and the spectral range recorded was from 12,000 cm^{-1} to 4000 cm^{-1} (833 nm to 2500 nm). The spectral wavenumber interval was 3.85 cm^{-1} with zero-filling = 2. Each spectrum was computed as an average of 32 acquisitions. Three independent spectra were measured for each sample. Signal preprocessing included computation of derivatives, normalisation and smoothing. Derivatives were calculated according to the Savitzky–Golay algorithm, second-order polynomial and 21 smoothing points. Commercially available OPUS 7.0 (Bruker Optics GmbH) was used for data processing and mining.

Results and discussion

The visual appearance of the test samples changed after a relatively short time [Figure 1(a)]. It can be seen that the

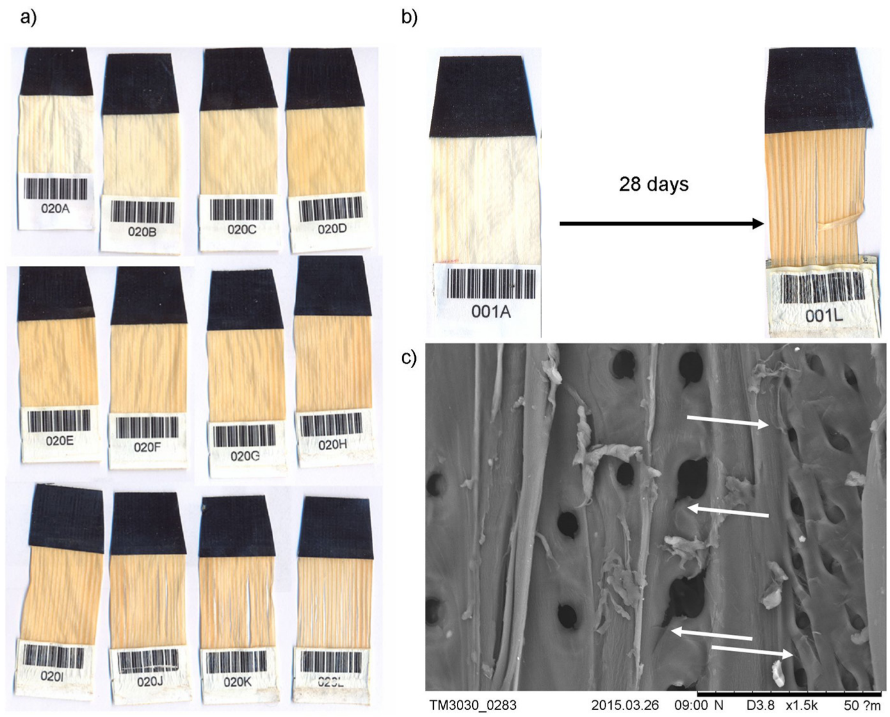

Figure 1. (a) Images of experimental samples exposed for different periods to the north, (b) the sample appearance before tests and after 28 days of weathering exposed to the south and (c) SEM image of sample after 28 days of weathering exposed to the south (arrows indicate points of the pitch cracks).

wood turned darker and more yellow, there was removal of fibres and the presence of cracks, and in some cases the first signs of fungal attack were visible (after two weeks exposure). According to Williams[9] the excessive shrinkage and swelling cycles of wooden members may result in unbalanced stress distribution followed by warping or checking. Figure 1(b) presents the sample before weathering and at the final degradation stage (day 28). In addition, scanning electron microscopy (SEM) analysis was performed [Figure 1(c)] showing that at the final weathering stage (28 days) the surface was very degraded, pits were eroded, cells were delaminated and advanced pollution and spore deposition was noticed. This makes it clear that the changes are occurring rapidly at both macroscale and microscale levels.

According to Müller *et al.*[10] yellowing of lignocellulosic materials and wood surfaces indicates the modification of lignin and holocellulose. The absorption of UV light induces lignin degradation and the photooxidation of $–CH_2–$ and –CH(OH)– groups. These reactions are combined with the yellowing of the wood surfaces. Müller *et al.*[10] observed that 72 hours of UV irradiation ($\lambda > 300$ nm) decreased the lignin content on the surface by up to 20% of the original values. Such a value will correspond to 7 days of natural weathering performed within this experiment (Table 1).

NIR spectra measured on samples at various stages of degradation clearly show the progress of changes related to functional groups of wood polymers. According to Pandley[11] the photodegradation of lignin was indicated by a rapid decrease in the lignin content accompanied by generation of carbonyl groups, whereas degradation of cellulose was indicated by loss of weight and reduction in degree of polymerisation. After 4 days of natural weathering, slight changes were observed in the band at 5587 cm^{-1} related to –CH groups of semi-crystalline cellulose. After 11 days of weathering, the progress of changes observed in the cellulose band mentioned above was relatively small; however, much clearer variation was observed in bands related to lignin and hemicellulose. With the progress of degradation, all bands highlighted in Figure 2 had a clearly different shape relative to the reference wood samples. This is in agreement with previous observations of Tsuchikawa *et al.*[12] who found that the degradation rates for amorphous regions in carbohydrates were faster than that for lignin. Moreover, –OH groups in the amorphous regions in cellulose, hemicellulose and lignin could be easily decomposed into low-molecular-weight matter caused by light irradiation. Very little spectral change was noticed in the band at 6450 cm^{-1} corresponding to the hydroxyl groups of crystalline cellulose. This is confirmation of the common understanding that crystalline regions of cellulose are the chemical structures of wood most resistant against weathering.[5] It is also consistent with the previous observation[13] that the lignin/carbohydrate ratio rapidly decreases with increasing irradiation time.

A novel approach using chemometric models was developed in parallel with the common spectral interpretation and evaluation. The PLS model was developed by regressing two points

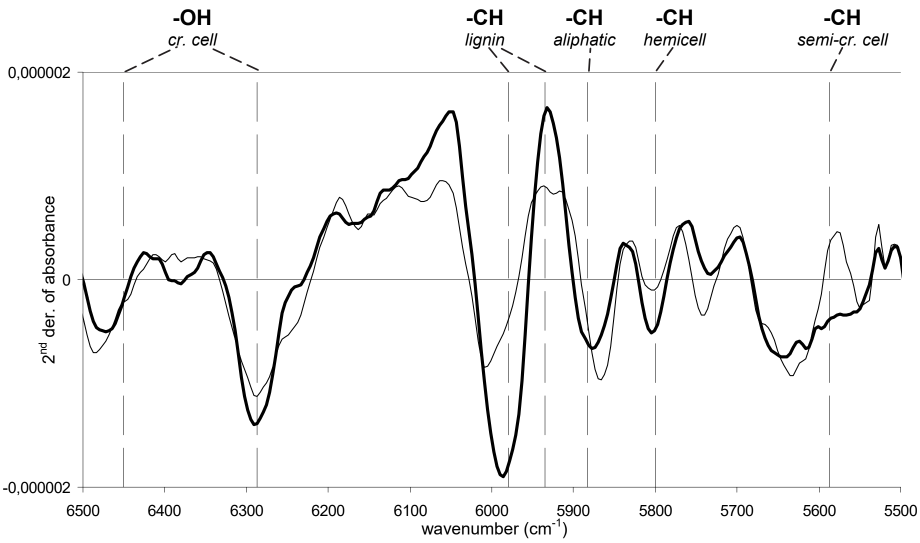

Figure 2. Second derivative of spectra of reference sample and wood weathered for 28 days.

defining the border values for the weathering state:

- the initial stage (weathering index W_{ind} = 0), modelled on the basis of the unweathered samples
- final stage modelled using spectra collected from the most degraded samples after 28 days of exposure (weathering index W_{ind} = 1000).

The PLS model developed was used in the second phase for prediction of the W_{ind} values for all the intermediate samples (weathered between 1 and 28 days). The Quant 2 Analysis tool pack, part of the Bruker OPUS software, was used for both PLS model development and the prediction of the intermediate indexes. It can be seen that western and northern exposure sites were slightly less affected by the weathering process (Figure 3).

Similar observations were made by analysing the progress of changes of a selected band (4195 cm^{-1}) assigned to lignin.[14]

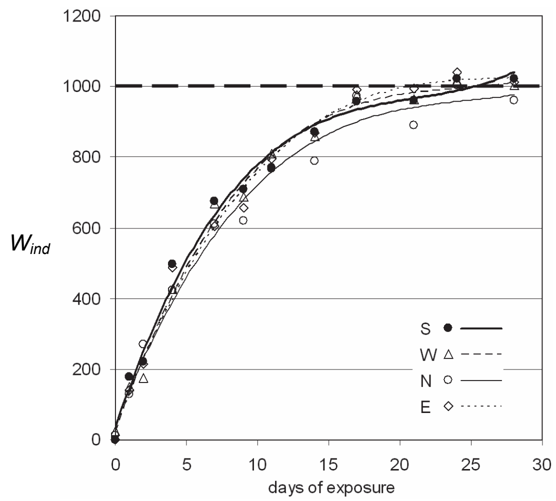

Figure 3. The weathering index rate W_{ind} predicted on the basis of PLS modelling of NIR spectra.

It is clearly visible that with an increase in the weathering duration, the absorbance changed in both raw spectra and the second-derivative spectra (Figure 4). Also, in this case the most intense changes were observed in samples exposed to the south.

The investigation of kinetics of wood weathering at the early stage showed slightly more advancement of the process in samples exposed to the south-facing direction. This is attributed to more intense solar radiation and greater total hours of insolation. This is in agreement with the results of other research on the same thin veneer sample set,[15] where the cumulative amount of solar radiation on a wooden surface exposed to four cardinal directions was simulated. It was evident that samples exposed to the south received twice as much solar radiation as those exposed to the northern direction and around 15% more than the western direction. Nevertheless, temperature also had an effect on the weathered sample surface, as did the time-of-wetness (period when the surface is wet by moisture due to rain, fog and condensation) and relative humidity of the surrounding air.[16] The detailed

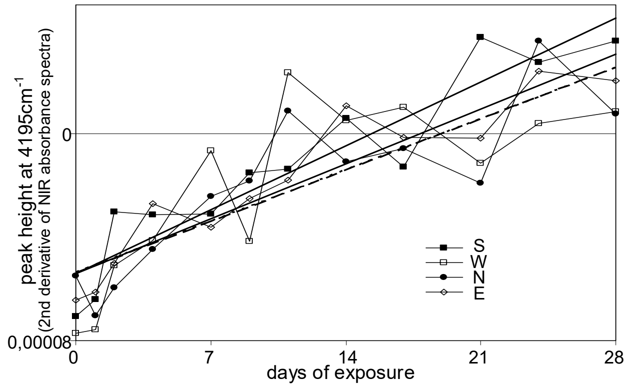

Figure 4. Kinetics of lignin changes (at 4195 cm^{-1}) in relation to the exposure direction as recorded in NIR.

numerical models linking the radiation dosage together with moisture variations and temperature as affecting the weathering kinetics are under development. Furthermore, the trends observed in this case study are compared with the degradation kinetic of similar samples exposed in other locations in Europe within the framework of the Round Robin test.

Conclusions

Knowledge of mechanisms of weathering and the role of the various factors is fundamental to assess the actual conditions of timber structures. This knowledge is also essential to predict future performance and to ensure long-term preservation and maintenance. Spectroscopy was successfully applied to the analysis of the short-term weathering process of wood. Analysis of changes in the NIR spectra allows a detailed understanding of the chemical kinetics of the weathering process, and consequently provides a base for development of numerical models that explain woody polymer deterioration. The research approach applied for NIR is now utilised in further analysis of the same samples measured with other methods (multi-sensor data fusion). An effect of the exposure location is also being considered, with the overall goal of this project being to develop a universal weather-dose degradation model for wood surfaces.

Acknowledgements

This work has been conducted within the Round Robin test initiative of the COST FP1006, STSM funded by COST FP1303, project BIO4ever funded within a call SIR by MIUR (RBSI14Y7Y4) and project WoodBeBetter "Increased use of wood in urban areas" (225345/E40) funded by the Research Council of Norway. The authors acknowledge the Italian Society of Near Infrared Spectroscopy SISNIR for providing a travel grant in order to attend the NIR 2015 conference where this work was presented as a poster. Special thanks to all participants of the Round Robin test.

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