XII DBMC
International Conference on Durability of Building Materials and Components
PORTO - PORTUGAL, April 12th-15th, 2011

Durability of Nano-based Treated Wood Exposed to Accelerated Weathering

Selamawit Mamo Fufa [1]
Per Jostein Hovde [2]
Bjørn Petter Jelle [3]
Per Martin Rørvik[4]

ABSTRACT

Wood is a widely used material for the building and construction industries due to a number of its favorable qualities. However, wood is also sensitive to weathering factors which cause degradation. Nano-based modifications are new approaches aiming to overcome the drawbacks of wood and extend its service life, especially when it is used for outdoor applications. The unique properties of nanomaterials derived from their small size and high surface area have a great potential to improve important wood properties. In this study, spruce and pine wood species were treated with nano titanium dioxide and nanoclay based coatings and impregnation. The specimens were exposed to various accelerated weathering tests and the surface changes were investigated by colour measurements, and Fourier transform infrared characterization methods. From the test results, the durability of nano-based treated wood used in exterior claddings was assessed.

KEYWORDS:

Wood, Exterior claddings, Nanotechnology, FTIR, Accelerated weathering tests, Colour measurement.

---

[1] Norwegian University of Science and Technology (NTNU),Department of Civil and Transport Engineering, Trondheim, Norway, selamawit.fufa@ntnu.no

[2] Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, Trondheim, Norway, per.hovde@ntnu.no

[3] SINTEF Building and Infrastructure, Department of Material and Structures, Trondheim, Norway bjorn.petter.jelle@sintef.no and Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, Trondheim, Norway, bjorn.petter.jelle@ntnu.no

[4] Norwegian University of Science and Technology (NTNU), Department of Materials Science and Engineering, Trondheim, Norway, per.martin.rorvik@sintef.no

1. INTRODUCTION

Wood is composed of natural polymeric materials, including cellulose, hemicelluloses, lignin and extractives, which are subject to changes undergoing during its exterior application. Different environmental factors such as rain, solar radiation and temperature are ageing mechanisms that contribute to physical and chemical changes in wood; described as weathering. Weathering initially leads to fast colour change followed by large chemical modification and breakdown of the surface layer [Rosu et al. 2010]. In addition to the weathering conditions, the rate of degradation can also be dependent on the type of wood (soft or hardwood) [Anderson et al. 1991a; Anderson et al. 1991b].

There have been different studies which give an overview of the mechanisms of wood weathering [Anderson et al. 1991b; Colom et al. 2003; Pandey 2005; Rowell 2005].They clearly described that decrease in lignin content and chemical modification due to bond breakage in cellulose occur as a consequence mainly due to the combination effect of sunlight (UV radiation) and water. The colour and chemical changes were commonly identified by using colour measurements and FTIR analysis, respectively.

Wood treatments have a long history of use towards overcoming wood degradation from weathering when exposed to harsh exterior environments [Hill 2006]. However, these treatments may only be effective over the short term effect or contain hazardous chemicals. The growing interest towards improving the durability and sustainable utilization of wood in buildings urges the development of new wood treatment technologies. Nanotechnology becomes one of those treatment options widely used in current wooden buildings [Fufa and Hovde 2010]. The unique properties of nano-based materials derived from their small size and high surface area have a great potential to improve wood properties.

In order to investigate the performance of the treatments, wooden claddings should be subjected either to natural outdoor exposure or accelerated weathering tests prior to their utilization. Accelerated ageing has advantages over natural exposure as it is reproducible, controllable and may simulate the rate of degradation and long term effect of treatments within a short time period.

Fourier transform infrared (FTIR) spectroscopy is a very useful tool for obtaining information about the structure of wood constituents and chemical changes taking place in wood due to various treatments. Several studies have been carried out on identification of colour and chemical changes in wood caused by weathering [Jelle et al. 2008; Pandey 1999; Rosu et al. 2010; Temiz et al. 2007]. The effect of weathering at the surface of treated wood samples has been studied and it is observed that better performances of modified specimens are obtained as compared to untreated ones.

In this study, conventional and nano titanium dioxide and nanoclay based impregnated wood specimens used for exterior claddings were tested. The changes undergone by the treated specimens were studied upon exposure of the specimens to an accelerated ageing test. The colour and structural changes that take place due to different treatments and environmental exposure conditions were characterized by colour measurements and FTIR spectroscopy.

2. EXPERIMENTAL

2.1 Overview of the Overall Study

The results presented in this paper are part of an ongoing and broad study where the effect of nano-based treatments on exterior wooden claddings exposed to artificial weathering is being assessed. Spruce and pine wood species were treated with a commercially obtained water based coating, stain and preservatives both alone and modified with nanoclay (hydrophilic bentonite) and titanium dioxide nanoparticles (rutile type). The effects of weathering on treated specimens were tested in laboratory using a vertical accelerated climate simulator and an Atlas SC600 MHG Solar Simulator. In the Atlas Solar Simulator, the specimens were exposed to solar radiation and water spray. The exposure condition can be determined based on the required test. Detail description of this apparatus is given in section 2.3 below. Here, only the results from impregnated spruce aged in the Atlas Solar Simulator are presented, the remaining results will be presented elsewhere.

2.2 Test Specimens

Norway spruce (Picea abies) with planed surface was used for easy measurement of the colour and gloss of the specimens. Before finishing, the test specimens are sawn to 10 cm width × 20 cm length × 1 cm thickness. All specimens were preconditioned at (20 ± 2) ^{o}C and (65 ± 5) % relative humidity (RH) based on ISO 554 standards. In addition to the reference untreated specimens, specimens were impregnated with preservative (labeled as Wnt) modified with 1% nano titanium dioxide , 1% nanoclay and a combination of nano titanium dioxide and nanoclay each with 1% . Treatments were mixed with 1% of the nanoparticles in order to see the performance of low concentrated nanoparticles on the overall wood properties. Each type of treated wood was represented by three series specimens. An overview of types of treatments is given in Table 1 below.

Table 1. Type of treatments used to modify spruce in this study

No	Treatment type	Abbreviation
1	Untreated	U
2	Wnt	W
3	Wnt modified with nanoclay	WNC
4	Wnt modified with nano titanium dioxide	WNT
5	Wnt modified with both nano clay and nano titanium dioxide	WNCT

2.3 Accelerated Ageing Tests in Atlas Solar Simulator

Accelerated ageing laboratory test was performed in Atlas SC600 MHG Solar Simulator with 2500 W metal halide global (MHG) lamp giving a solar radiation intensity at the specimen surface 55 cm below the climate chamber glass ceiling at 100% lamp power (applying no external lamp filters). The exposure was performed by cycles of 20 h solar radiation at 63 ^{o}C and 50 %RH followed by 4 h water spray at 10 ^{o}C and 100 % RH. The water nozzles located at each side of the apparatus sprayed a total of 1 l/h. In every 24 h cycle, the exposure duration consisted of 4 ageing cycles each with 5 h solar radiation and 1 h water spray. Colour and chemical changes of the specimens were monitored by taking out the specimens at regular intervals. The results from up to 336 h exposure are presented in this paper.

2.4 Colour Measurements

Colour changes of the specimens were easily determined by using CIEL*a*b* colour scale method. The L^*, a^* and b^* colour parameters of the specimens before and after ageing were recorded using Mercury 3000 colorimeter with D65/10^{o} light source. The two numbers in D65/10^{o} describe the angle of illumination and method of view or the angle at which the detector receives the reflected light. The measurements were taken at three points for each of the parallels and the average values are presented in this paper.

The L^*, a^* and b^* parameters are also used to determine the total colour change, ΔE, as a function of irradiation time, using the following equation:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 - (a_2^* - a_1^*)^2 - (b_2^* - b_1^*)^2} \qquad (1)$$

where L_1^*, a_1^* and b_1^* are the colour coordinates of the specimens before ageing and L_2^*, a_2^* and b_2^* are values after ageing. The L parameter stands for lightness where the value of the change in ($\Delta L^*=L_2^*-L_1^*$) vary from 0 (black) to 100 (white). For the chromatic coordinates, a positive value of

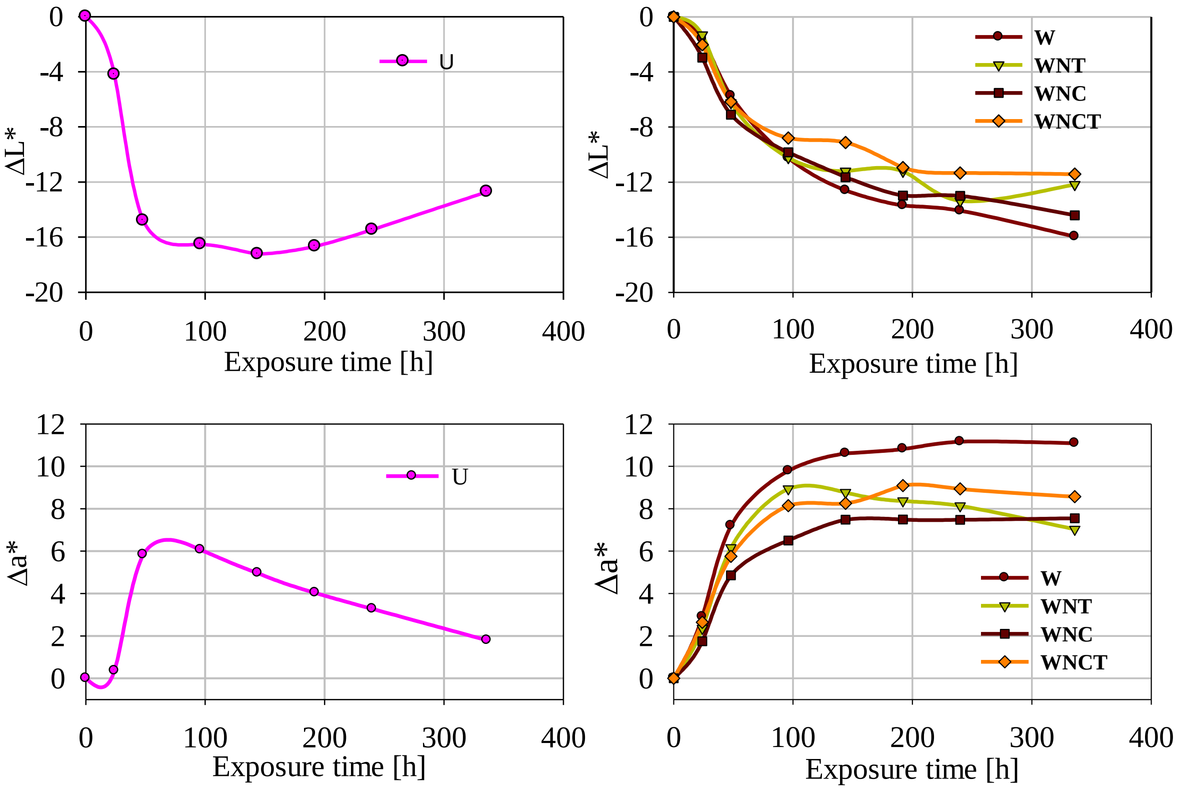
$\Delta a^* = a_2^* - a_1^*$ shows a red shift, and a negative value shows a green shift on the green-red scale, while positive value of $\Delta b^* = b_2^* - b_1^*$ illustrates yellow shift and a negative value shows a blue shift on the blue-yellow scale.

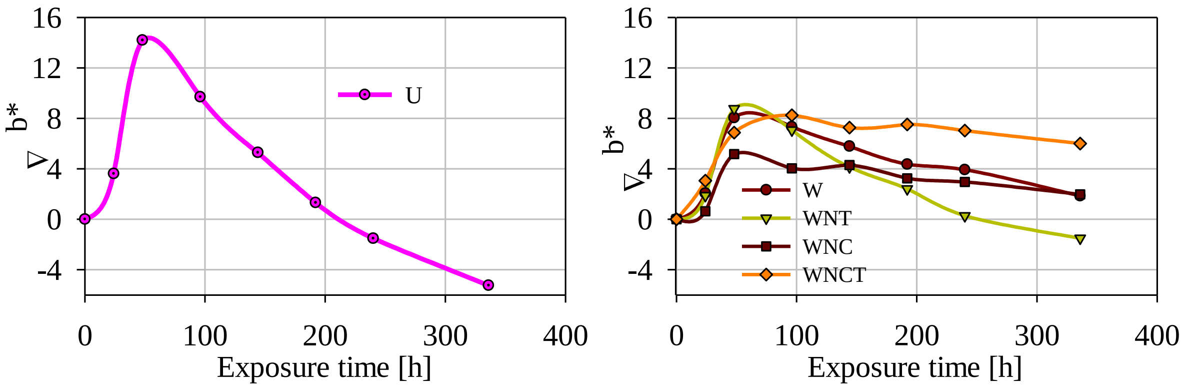
2.5 FTIR Spectroscopy

FTIR spectroscopy of the specimens was performed with a Thermo Nicolet 8700 FTIR spectrometer equipped with a horizontal attenuated total reflectance (ATR) accessory designed for single reflection. The ATR crystal is made of diamond due to the high refractive index and the excellent chemical and physical properties of diamond. Smaller wood specimens (chips) can be put into intimate contact with the sampling area through high pressure clamping. This yields high quality and reproducible spectra in the wavelength range from 4000 cm^{-1} to 400 cm^{-1} at spectral resolution of 4 cm^{-1} and 32 scans. Three FTIR spectra per each specimen were documented to increase the accuracy of the results by getting a satisfactory contact between the ATR diamond crystal and the specimen. The bands in the FTIR spectra of the specimens were assigned based on data available in literature [Pandey 1999; Pandey and Pitman 2003; Rowell 2005; Temiz et al. 2007].

3. RESULTS AND DISCUSSION

The colour changes of the specimens following the accelerated weathering process reflect the chemical changes that occurred in wood components due to photodegradation. Lignin is the wood component that is most susceptible for photodegradation due to its good light absorbing properties [Pandey 2005]. The colour of both treated and untreated wood changes rapidly during the first 100 h of exposure and is then reduced with an increase in exposure time. This is indicated in Figure 1, showing the lightness change (ΔL^*), green-red coordinate (Δa^*) and blue-yellow coordinate (Δb^*) upon exposure.





e) f)

Figure 1. Colour coordinates Δ*L** (a & b), Δ*a** (c & d) and Δ*b** (e & f) for untreated and impregnated specimens aged in Atlas Solar Simulator.

During artificial weathering, the colour of the surfaces changes rapidly from light to dark represented by decrease in the value of Δ*L** and increase in Δ*b** and Δ*a** values upon exposure. Initially, Δ*b** (yellowness) increases much more quickly than Δ*a** (redness) with exposure time. After attaining the maximum value, Δ*b** decreases again to lower values than for Δ*a**.The negative value of Δ*L** shows that surface becomes darkened with increase in exposure and this can be due to degradation of lignin.

For both treated and untreated wood the lightness changes were rapid in the first 48 h of exposure while all impregnated specimens reduce the change by about a half during the same period of exposure. For untreated specimens, the rapid reduction in the change of lightness continued up to 144 h and then the lightness increased significantly through the rest of the exposure. However, the colour of the untreated specimens changed appreciably and faded. For the treated wood the lightness decreased with increasing exposure. For two of the specimens exposed for 336 h the lightness even decreased to below the value for untreated specimen. For specimens treated with nanoparticles combined with preservative the colour change is delayed more than for the ones treated with preservative alone.

The total colour change illustrates the colour change upon exposure due to the modification of wood constituent polymers (mainly lignin). Table 2 shows the total colour change *(*Δ*E*) of both treated and untreated wood specimens during the short time of exposure to high intensity irradiation. Although Δ*E* decreases with increasing of exposure period for both untreated and treated wood, the highest discoloration rate was observed in untreated wood in the early exposure period. Untreated wood shows higher increase at the initial stage of exposure followed by reduction with increase in exposure time. Treated specimens show significant colour change reduction.

Table 2. Overall colour change *(*Δ*E*) of aged specimens at different exposure period.

Treatment	**Exposure time [h]**						
	24	**48**	**96**	**144**	**192**	**240**	**336**
U	6.40	20.9	20.5	18.5	17.3	15.8	13.2
W	3.90	12.2	16.0	17.5	18.0	18.4	19.5
WNT	3.29	12.4	15.3	14.8	14.2	15.7	14.1
WNC	3.50	10.0	12.5	14.5	15.3	15.3	16.4
WNCT	4.52	10.9	14.6	14.3	16.1	16.1	15.5

FTIR spectra of untreated and treated specimens exposed to the Atlas Solar Simulator before and after artificial weathering are presented in Fig. 2-6. In these figures only the results from the "finger print" regions, 1800-800 cm^{-1}, are presented, as most of the changes occur in this region due to the presence of various functional groups. Photo-induced degradation causes changes in the chemical composition of the functional groups mainly at transmittance peaks located around 1740 cm^{-1} (arise from C=O stretching in hemicelluloses), 1620 cm^{-1} (due to stretching of conjugated C=C attributed to lignin), 1508 cm^{-1} (due to C=C stretching of lignin) and 1261 cm^{-1} (C-O stretching vibration in lignin and hemicelluloses) [Jelle et al. 2008; Pandey 1999; Pandey 2005; Pandey and Pitman 2003; Temiz et al. 2007]. Most of these bands probably have contributions from cellulose, hemicelluloses or lignin.

Although the above mentioned peaks also appear in the result of this study, the peaks around 1510 cm^{-1} shows significant change and are thus presented here. The reduction in the absorption peak around 1510 cm^{-1} arises from C=C stretching frequency shows the formation of carbonyl groups and lignin degradation [Prakash and Mahadevan 2008]. The rate of degradation of untreated specimens is greater than that of treated specimens in this region. Specimens treated with WNT and WNC show delay in the reduction of this degradation. Note that the ageing process decreases the absorbance peak around 1510 cm^{-1} which may be partly masked or hidden by some of the treatments, i.e., especially the WNCT treatment as shown in Fig. 6. As a result it is difficult to describe the spectra of these treatments, i.e. compare the fresh (non-aged) absorbance peaks at around 1510cm-1 for all five samples (Figs. 2-6). Since the nanoparticles are small they can easily disperse into the wood structure and thereby strengthen the mechanical stability and hinder cracking, and thus reduce the degradation of wood components. Additionally, the titanium dioxide nanoparticles can absorb and reflect the incoming light, preventing light to degrade, for instance, lignin. Further studies are in progress to understand the effect of the nanoparticles on the wood properties.

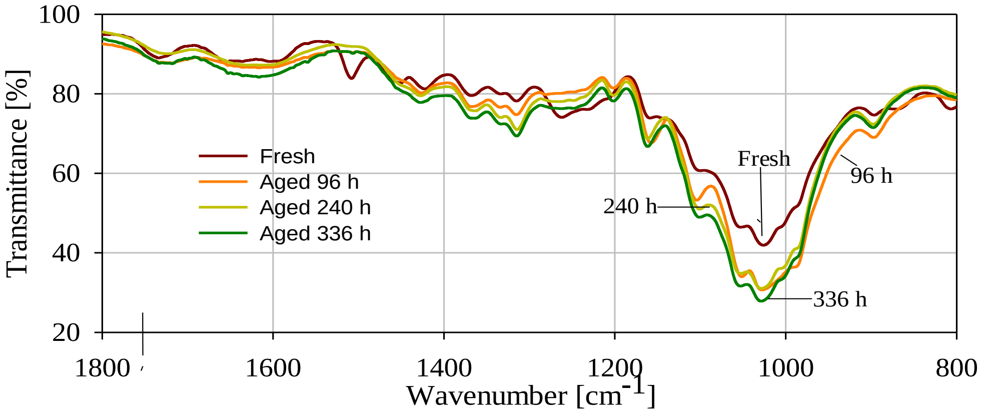


Figure 2. FTIR spectra of untreated spruce before and after exposure in Atlas Solar Simulator

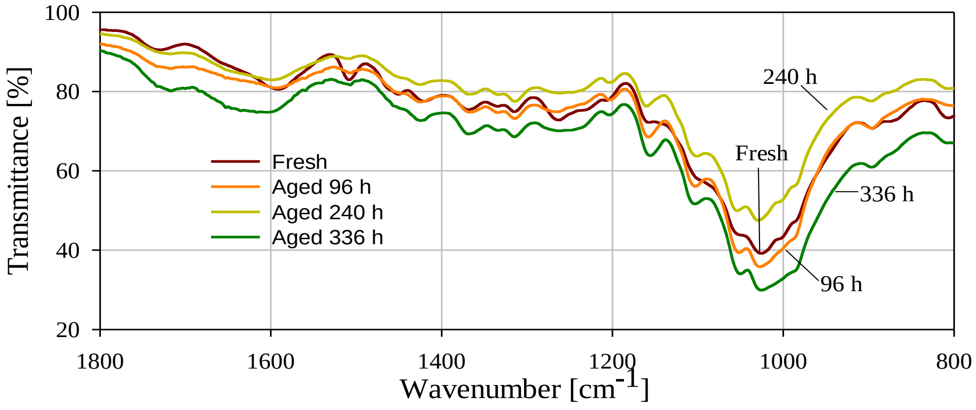


Figure 3. FTIR spectra of spruce impregnated with preservative (W) before and after exposure in Atlas Solar Simulator

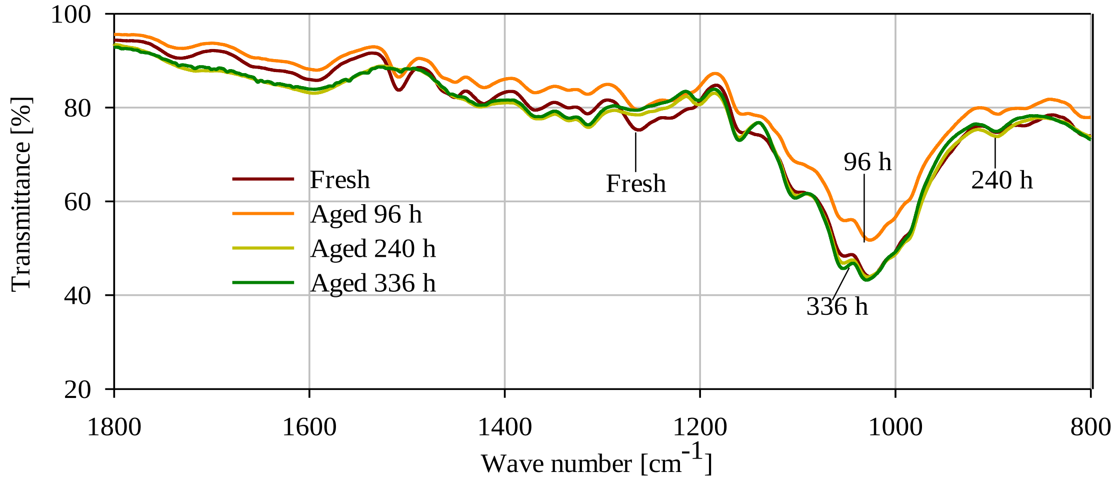


Figure 4. FTIR spectra of spruce impregnated with preservative and nano titanium dioxide (WNT) before and after exposure in Atlas Solar Simulator

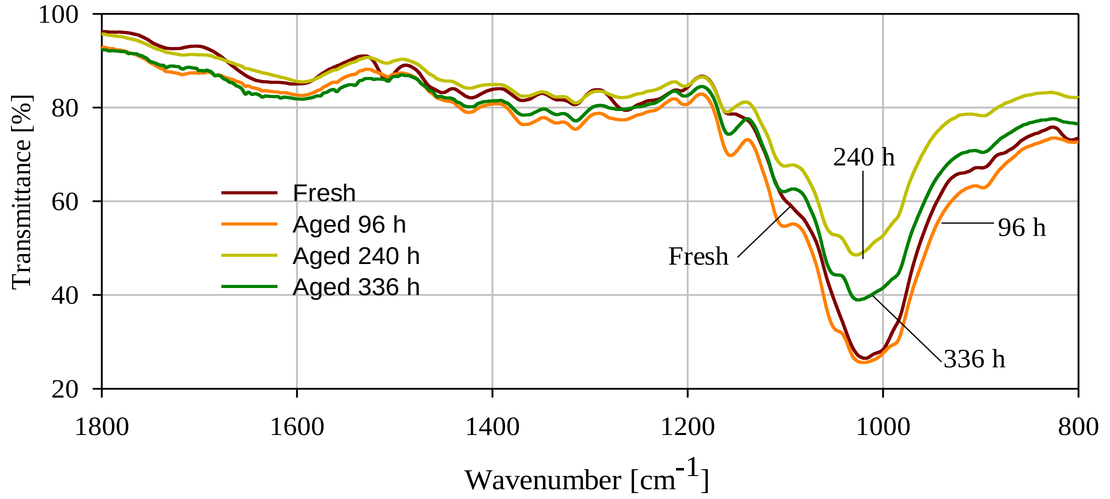


Figure 5. FTIR spectra of spruce impregnated with preservative and nanoclay (WNC) before and after exposure in Atlas Solar Simulator.

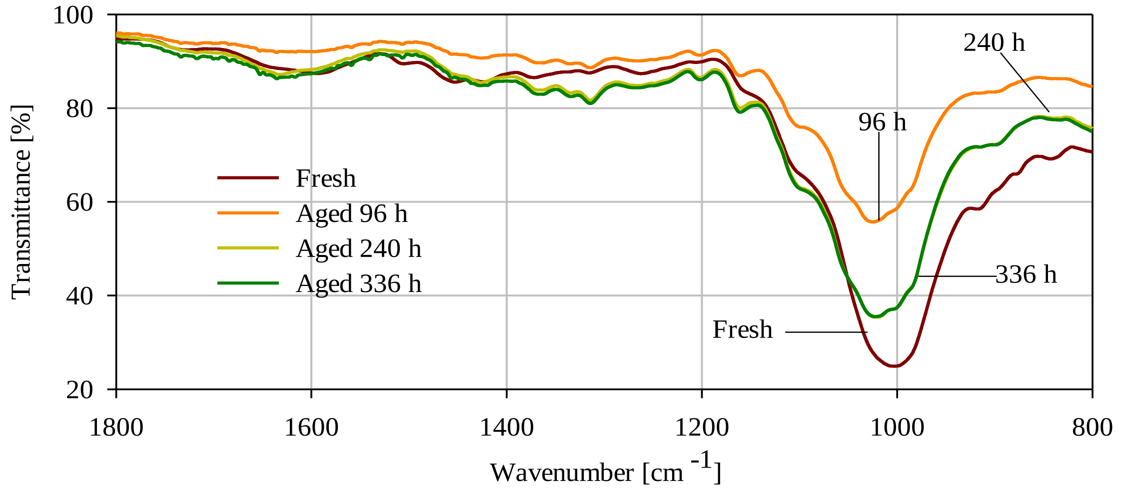


Figure 6. FTIR spectra of spruce impregnateda mixture of preservative, nano titanium dioxide and nanoclay (WNCT) before and after exposure in Atlas Solar Simulator.

4. CONCLUSION

Accelerated ageing tests are useful to assess the degradation of wooden claddings coated with new types of paint before their real application. In this work, the effects of weathering on both untreated and treated specimens were studied. The results of colour measurements illustrate significant colour changes of untreated specimens especially at initial stages of exposure. Although the colour of treated specimens is also changed with increase in the exposure period, the treatments help to delay the colour changes significantly. FTIR analysis also confirmed that the effect of weathering on lignin degradation is less pronounced in treated wood specimens than that of untreated specimens. Specially, specimens treated with a preservative containing nano titanium dioxide and nanoclay show better protection of the specimens against weathering effects.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Moelven Wood and Jotun AS for providing materials and many helpful discussions; Erik Larnøy, Andreas Treu and Britta Witt of the Norwegian Forest and Landscape Institute for their support in impregnation and to Ole Aunrønning for assistance with various laboratory tasks. The financial support by the Research Council of Norway is also gratefully acknowledged.

REFERENCES

Anderson, E.L., Pawlak, Z., Owen, N.L. & Feist, W.C. 1991a, Infrared studies of wood weathering. Part II: Hardwoods, *Applied Spectroscopy*, 45, 648-652.

Anderson, E.L., Pawlak, Z., Owen, N.L. & Feist, W.C. 1991b, Infrared studies of wood weathering.Part I: Softwoods, *Applied Spectroscopy*, 45, 641-647.

Colom, X., Carrillo, F., Nogués, F. & Garriga, P. 2003, Structural analysis of photodegraded wood by means of FTIR spectroscopy, *Polymer Degradation and Stability*, 80, 543-549.

Fufa, S.M. & Hovde, P.J. 2010, Nano-based modifications of wood and their environmental impact: Review, World Conference On Timber Engineering, Riva del Garda, Trentino, Italy, 24-26 June 2010, pp 1093-1094.

Hill, C. 2006, *Wood Modification: Chemical, Thermal and Other Processes*, John Wiley & Sons Ltd, Atrium/Southern Gate/Chichester.

Jelle, B.P., Ruther, P., Hovde, P.J. & Nilsen, T.-N. 2008, Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) Radiation Investigations of Natural and Accelerated Climate Aged Wood Substances, Istanbul,Turkey.

Pandey, K.K. 1999, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, *Journal of Applied Polymer Science*, 71, 1969-1975.

Pandey, K.K. & Pitman, A.J. 2003, FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi, *International Biodeterioration & Biodegradation*, 52, 151-160.

Pandey, K.K. 2005, Study of the effect of photo-irradiation on the surface chemistry of wood, *Polymer Degradation and Stability*, 90, 9-20.

Prakash, G.K. & Mahadevan, K.M. 2008, Enhancing the properties of wood through chemical modification with palmitoyl chloride, *Applied Surface Science*, 254, 1751-1756.

Rosu, D., Teaca, C.-A., Bodirlau, R. & Rosu, L. 2010, FTIR and color change of the modified wood as a result of artificial light irradiation, *Journal of Photochemistry and Photobiology B: Biology*, 99, 144-149.

Rowell, R.M. 2005, *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Florida.

Temiz, A., Terziev, N., Eikenes, M. & Hafren, J. 2007, Effect of accelerated weathering on surface chemistry of modified wood, *Applied Surface Science*, 253, 5355-5362.