

## Innovative modification of wood with nanoparticulate treatment

George Mantanis<sup>1</sup> and Dennis Jones<sup>2</sup>

<sup>1</sup> Technological Educational Institution (TEI) of Larissa, Dept. of Wood and Furniture Design and Technology, Lab of Wood Technology, GR 431 00, Karditsa, Greece [email: mantanis@teilar.gr]

<sup>2</sup> SP Technical Research Institute of Sweden, PO Box 5609, SE 114 86 Stockholm, Sweden [email: dennis.jones@sp.se]

**Keywords:** Chemical modification, Nano-based formulation, Nanotechnology, Surface modification.

### ABSTRACT

The dimensional stabilisation of wood is important for a number of reasons, but particularly in product stability and the reduction of stress on applied coatings. This is essential in obtaining high performance products such as window frames. Whilst significant inroads have been made with chemical and thermal modification processes, methods combining conventional impregnation and binding to wood, offer more financially sound routes to commercial application.

This work considers a range of novel nano-based formulations and how they alter some of the properties of wood. The formulations, produced by NanoPhos SA, comprise of three different nanoparticulate sizes, especially designed to penetrate into the wood. The finest nanoparticles are intended to penetrate through the capillaries and bond with the hydroxyl groups of cellulose, the larger particles penetrate to a moderate depth where they react with the wood polymers, while the formulation is completed with a nano-emulsion of paraffin to provide surface protection.

The paper will consider work to date covering such a range of nanoparticulate materials as swelling measurements / dimensional stability, spectroscopic and microscopic studies and surface hardness.

### INTRODUCTION

It has long been recognised that the use of wood in high-precision products is affected by the limited dimensional stability, particularly of European softwood species. The benefits of undertaking chemical or thermal modifications have been well documented in texts (Hill 2006) and at previous ECWM conferences. However the desire to achieve moderate improvements in performance through less technologically demanding processes has led to work on materials such as waxes. Traditionally, waxes have been used as additives in a range of wood treatments, either on their own following surface activation via plasma treatment (Avramidis *et al.* 2011) or with traditional biocides (Zahora 2000). However there still exists opportunities for wax-based systems incorporating additional agents to play a significant role in future treatments of both the wood surface and its bulk. One combination that has attracted interest in the scientific community in recent years is the combination of waxes with nanocompounds, which can be applied *via* emulsions.

The benefits of applying nanotechnology to wood treatments include the ability of the compounds to have a far greater degree of penetration into the wood. This allows compounds with the correct behaviour to alter the cell wall surface chemistry, which in the case of hydrophobic nanocompounds can afford higher protection against moisture.

The aim of this paper is to describe work into two forms of nanotreatment, SurfaPore™ W and SurfaPore™ F, assessing their properties via a range of methods.

## MATERIALS AND METHODS

Two nanotreatment solutions, namely SurfaPore™ W and SurfaPore™ F were supplied by the Greek company NanoPhos SA. Both treatments are water-based formulations comprising three different sizes of nanocompounds. The finest nanoparticulates (size) are intended to penetrate the capillaries of the wood and bond with the hydroxyl group present in the cellulose content. The next group of nanoparticulates (size) partially penetrate the wood structure and react with the wood polymers, whilst a nano-emulsion of paraffin wax creates a degree of surface protection and water repellency.

The compositions of SurfaPore™ W and F are respectively shown in Table 1.

*Table 1: Compositions and properties of SurfaPore™ W and F*

Property	SurfaPore™ W	SurfaPore™ F
Colour	Milky white	Milky white
pH	8.8	4.8
Boiling and flash point	>100 °C	>100 °C
Auto ignition point	>100 °C	>100 °C
Density	0.98 gcm <sup>-3</sup>	1.01 gcm <sup>-3</sup>
Viscosity	20 mPa s	4 mPa s
VOC content	38 g/l	0.15 g/l
Solid content	7.3%	23.0%

The solutions were used to treat sapwood samples (pre-cut to size 250 x 50 x 25 mm) of Corsican pine (*Pinus nigra*), sourced from Pindos mountain, Greneva, Greece. Samples were treated by immersion in the relevant SurfaPore™ solution for 20 seconds, with samples then dried to determine the weight uptake.

Dimensional stability was determined by undertaking a water soak evaluation. Samples were first oven dried (103± 2 °C for 24 hours) prior to weighing and measurement in an automated calliper system, capable of measuring all three dimensions simultaneously. Samples were then soaked in distilled water for a period of 5 days, weighed and measured, then dried. The process was then repeated.

Samples were prepared for scanning electron microscopy (SEM) using a UV laser ablation technique (Wålinder *et al.* 2009). Thus, a krypton fluoride (KrF) laser beam (from a Lumonix PM886 laser) of wavelength 248 nm was passed through a series of lenses and masks to create a suitable focal point where the specimen surface was placed. The sample was then moved with the use of a computer controlled position sensitive trigger pulse generator, using a pulse width of 20 ns. Typically pulse frequencies of 5-10 Hz are used, with energy levels between 300-400 mJ. SEM images were prepared using a Hitachi Tabletop microscope TM-1000.

Infrared spectra in the mid-region were acquired using a Perkin-Elmer FT-IR- 2000 in attenuated total reflectance mode, equipped with a TGS detector. Sixteen scans were averaged at 2 cm<sup>-1</sup> resolution in the range of 600-4000 cm<sup>-1</sup>. Samples were analysed in duplicate using Spectrum version 3.02.01 and graphing software Origin 7.5.

Brinell hardness measurements were made according to the proposed European standard prEN 1534. A steel ball with a diameter of 10 mm was pressed into the sample materials at a force of 1 kN. The diameter of the remaining impression was visually determined using a lens with a magnification of 8. The hardness was determined according to the formula shown in Equation 1.

$$H_B = 0,102 \cdot \frac{2 \cdot P}{\pi \cdot D \left( D - \sqrt{D^2 - d^2} \right)} \quad (1)$$

where:

P = Force (N)

D = Diameter of the steel ball (mm)

d = Diameter of the remaining impression (mm).

## RESULTS AND DISCUSSION

Treatment with SurfaPore™ W and F were found to result in weight increases of 0.57% and 1.89% respectively. The difference in weight uptake approximated to the difference in levels of the solids content of the treatments. The use of longer treatment times and vacuum impregnation would further increase the levels of uptake.

### *Dimensional stability*

Early water soak analysis showed that there was a slight improvement in dimensional stability for samples treated in radial and tangential directions, with a more appreciable stabilisation in the longitudinal direction (Table 2). These values are comparable to those obtained for studies into the shrinkage and swelling of Corsican pine from green to dry state (Usta and Guray 2000).

*Table 2: Percentage increase in dimensions of treated and untreated Corsican pine*

<i>Treatment</i>	<i>% increase tangential direction</i>	<i>% increase radial direction</i>	<i>% increase longitudinal direction</i>
SurfaPore™ W	9.8	4.1	<0.1
SurfaPore™ F	9.8	4.2	0.2
None (control)	10.4	4.4	0.3

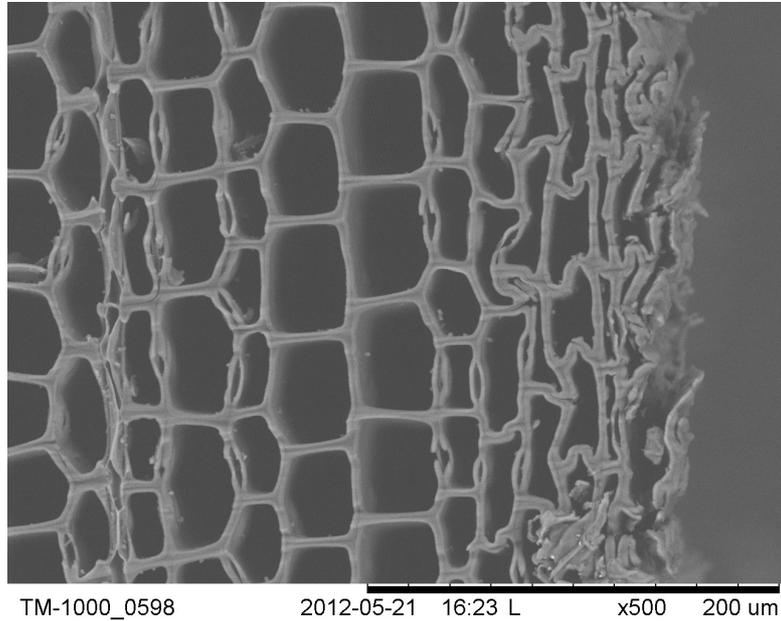
It is recognised that initial water soak evaluations can give exaggerated results, and evaluation is being continued to establish the overall effect of treatments.

### *UV-laser ablation and SEM imaging*

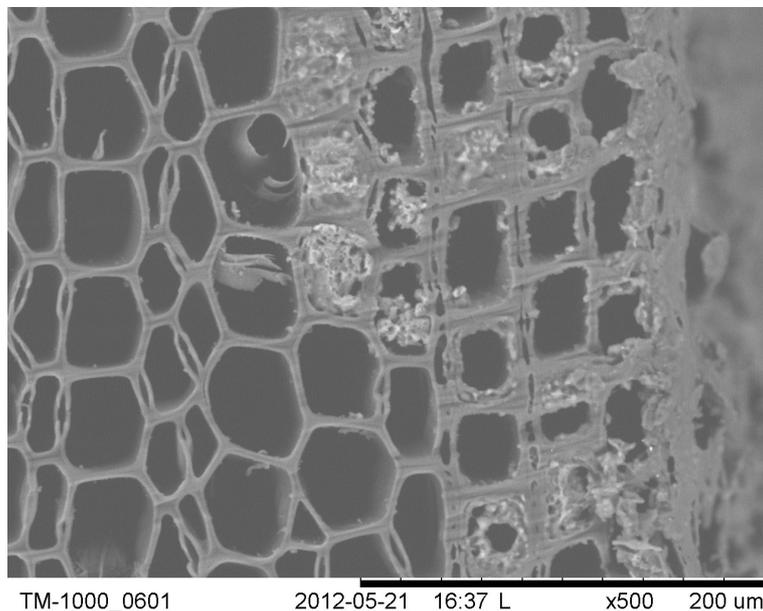
The advantage of using UV-laser ablation systems is that it is capable of breaking the covalent molecular bonds present in the wood sample. The result of this is a volatilisation of the surface material exposed to the laser pulse. The advantage of sample preparation by this method is the avoidance of cell-wall fracturing from the mechanical drawing of a microtome blade across the sample.

For the control blocks, processing appeared to result in considerable cell wall damage/deformation at the surface of the sample (Figure 1). This deformation is shown to the

right of the image (the outer edge of the sample). It would appear that both the SurfaPore™ W and F treatments realise a swelling in the outermost layers of the wood samples. The swelling of these outer layers is shown in Figure 2 for SurfaPore™ F. Figure 2 also apparently shows a degree of lumen filling close to the surface of the material,



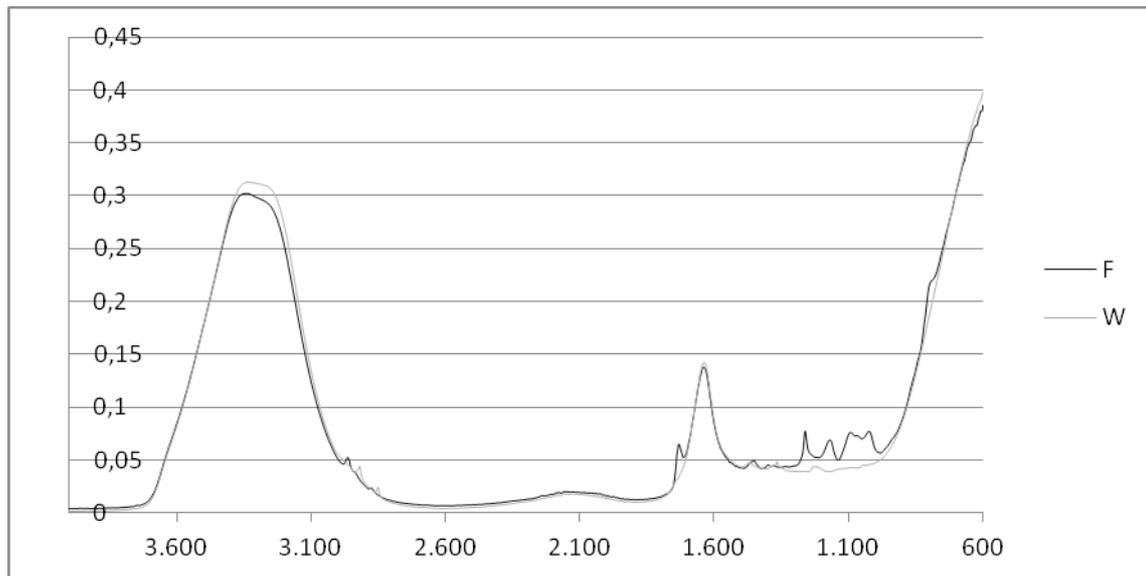
**Figure 1: SEM image of laser ablated control sample (outer edge to right of image)**



**Figure 2: SEM image of laser ablated sample treated with SurfaPore™ F (outer edge to right of image)**

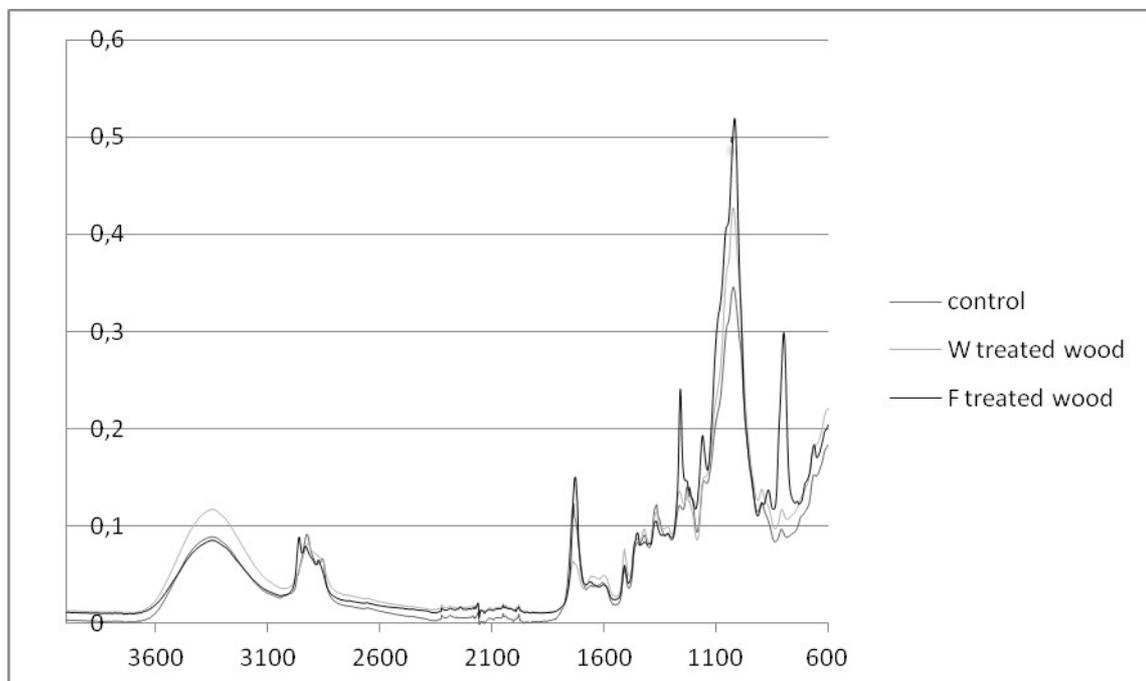
Analysis of the FT-IR spectra of the treatment solutions was undertaken in an attempt to identify peaks present in treated samples (Figure 3). Whilst any detailed spectral data cannot be gained from the hydroxyl region around  $3300\text{ cm}^{-1}$ , there appear to be minor peaks between  $2880$  and  $2990\text{ cm}^{-1}$ , which seemingly relate to the alkyl C-H stretching of the wax components present. There is also a significant peak at  $1646\text{ cm}^{-1}$  for both treatments, with an additional peak at  $1737\text{ cm}^{-1}$  for SurfaPore™ F. Closer examination

of the high absorbance of signal at low wavelengths suggested the presence of a peak at around  $775\text{ cm}^{-1}$  in the SurfaPore™ F spectrum.



*Figure 3: FT-IR spectra of SurfaPore™ W and F, respectively*

The presence of the SurfaPore™ F peak at  $775\text{ cm}^{-1}$  becomes apparent when comparing the spectra of treated and untreated wood (Figure 4). There was also a significant increase in the peak at  $1260\text{ cm}^{-1}$  with SurfaPore™ F. The previous identification of a peak in SurfaPore™ F at  $1737\text{ cm}^{-1}$  would also account for some of the peak variation noted there, particularly in comparison to SurfaPore™ W.

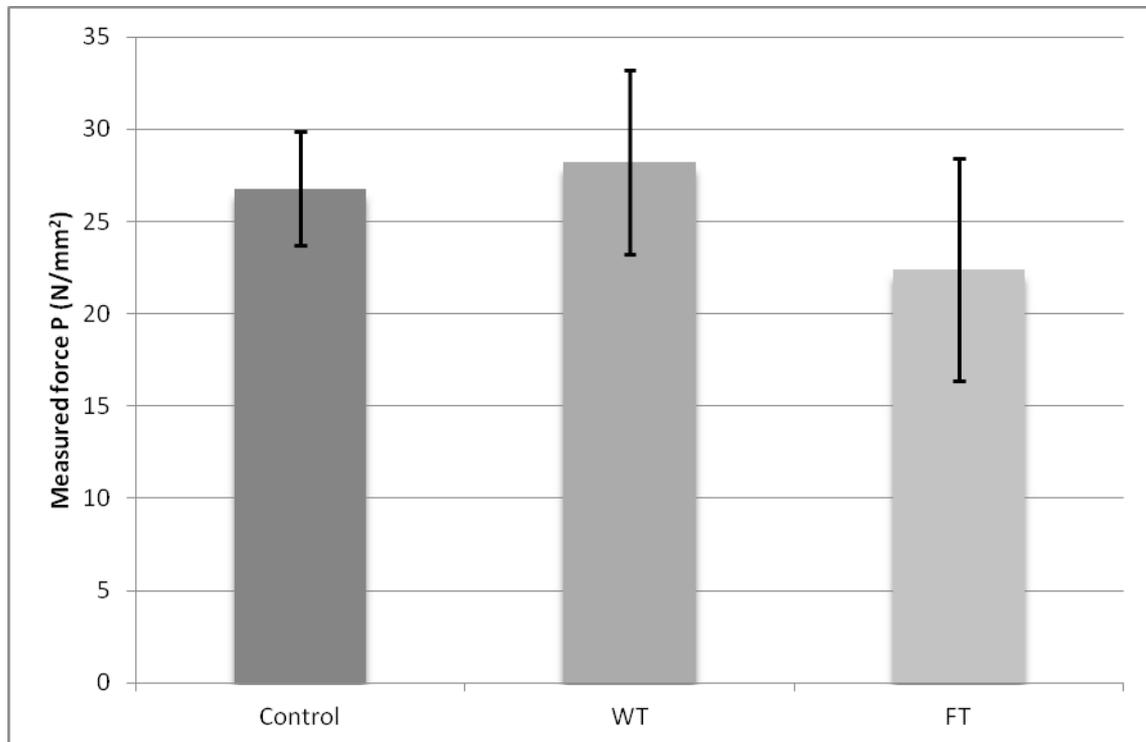


*Figure 4: FT-IR spectra of treated and untreated Corsican pine*

### **Brinell hardness**

Testing on the tangential face of the samples revealed that SurfaPore™ W realised harder surfaces following treatment, whereas SurfaPore™ F, which had a higher weight

gain, produced softer surfaces than the control samples (as indicated by measured forces applied in Figure 5). Determination of the Brinell hardness using Eqn. 1 showed that SurfaPore™ W and F had respective values of 2.9 kgf/mm<sup>2</sup> and 2.3 kgf/mm<sup>2</sup> compared to control values of 2.7 kgf/mm<sup>2</sup>.



*Figure 5: Measured force (P) for determination of brinell hardness of treated and untreated Corsican pine*

## CONCLUSIONS

The development and application of multi-functional treatments such as SurfaPore™ W and F can provide a degree of dimensional stability and water repellency to wood samples. It would appear that both treatments resulted in a degree of shape recovery of cell wall structure on processed surfaces. The higher solid content in SurfaPore™ F led to SEM observations of material uptake in the earlywood lumen. This higher uptake however seemed to reduce the surface hardness of the material, whereas the lower weight gain seen with SurfaPore™ W seemed to result in harder surfaces.

Further work is required to determine the levels of effectiveness of treatments, their degree of permanency (i.e. their fixation / bonding to the wood structure), as well as suitable applications.

## ACKNOWLEDGEMENTS

Work in this paper between DJ and GM was conducted as part of a collaborative agreement made within COST Action FP1006 “Bringing new functions to wood

through surface modification”. The provision of SurfaPore™ W and F by NanoPhos SA is hereby acknowledged, along with additional experimental analysis by colleagues at SP Trå, namely Kristoffer Segerholm, Marielle Henriksson, Stacy Trey and Magdalena Sterley. Author GM acknowledges also the support of NanoPhos SA (Lavrio, Greece) through cooperation project no. 3778 (Research Committee, TEI of Larissa).

## REFERENCES

- Avramidis, G., Scholz, G., Nothnick, E., Militz, H., Viol, W. and Wolkenhauer, A. (2011). Improved bondability of wax-treated wood following plasma treatment. *Wood Science and Technology*, **45**, 359–368
- Hill, C.A.S. (2006). *Wood Modification: Chemical, Thermal and other Processes*. John Wiley & Sons, Chichester, UK
- Usta, I. and Guray, A. (2000). Comparison of the Swelling and Shrinkage Characteristics of Corsican Pine (*Pinus nigra* var. *maritima*). *Turkish Journal of Agriculture and Forestry*, **24**: 461–464
- Wålinder, M., Omidvar, A., Seltman, J. and Segerholm, K. (2009). Micromorphology studies of modified wood using a surface preparation technique based on UV-laser ablation. In *Proceedings of the Fifth European Conference on Wood Modification, Stockholm, Sweden*, pp 103-110. ISBN 978-91-86319-36-6
- Zahora, A.R. (2000). Long-term performance of a “wax” type additive for use with water-borne pressure preservative treatments. *The International Research Group on Wood Protection*. Document No. IRG/WP/00–40159