Treatment of natural wood veneers with nano-oxides to improve their fire behaviour.

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Abstract. Conventional flame retardants used to improve fire behaviour of wood based materials are commonly based on halogenated and/or nitrogenated chemicals. These chemicals are toxic and can harm the environment and human health. Some works describe the incorporation of nanomaterials to the polymeric systems to improve their fire behaviour. The aim of this work was to analyze the effect of several treatments based on the use of nanomaterials on the properties of natural wood veneers and mainly on their fire behaviour. Firstly, several modes for treating pine veneers (immersion, spraying and impregnation) were evaluated using a commercial flame retardant to select the most effective treatment. The treatment selected as the most effective was immersion in a bath of flame retarding agent for 30 minutes at standard conditions. Afterward, pine veneers were treated by immersion in aqueous dispersions which contained 3wt% of the following nanoparticles: SiO$_2$, TiO$_2$ and ZrO$_2$, respectively. The effect of each treatment on the properties of veneers was analyzed. The results obtained showed that the treatment based on the use of 3wt% SiO$_2$ aqueous dispersion was the most effective to improve the fire behaviour of pine veneers.

1. Introduction
Wood veneers are commonly used for manufacturing veneered and plywood boards which are greatly applied in the furniture and construction sectors. Wood veneers are joined themselves or onto the surface of wood based panels using an adhesive, usually urea melamine formaldehyde adhesive.

The use of veneered and plywood boards has some limitations from the fire behaviour point of view. On the one hand, it is common that these veneered boards do not achieve the fire reaction classification required for determined applications. For example, in Spanish public building projects is common the requirement of an M-1 classification for wood based panels according to the UNE 23721:90. Flame retardants which can be found in the market are effective for improving the fire reaction of veneers but those are not commonly used. Wood veneers are usually joined without any treatment.

On the other hand, commercial flame retardants which can be used to improve the fire behaviour of wood veneers are based on halogenated and/or nitrogenated compounds and these chemicals have a considerable toxicity and can harm the environment and human health. The treatment of wood based materials with these conventional flame retardants produces materials which pass standardization fire tests according to the normative in force; however the use of these chemicals as flame retardants involves several limitations: (i) a harmful exposure to these substances that are toxic for human health...
and the environment during their handling, (ii) the release of toxic gaseous substances when these flame retardants burn which are identified as the main cause of death during a fire [2] and (iii) the required high concentration of these chemicals produces a negative effect on physical and mechanical properties of wood based materials.

The use of nanomaterials to enhance properties or impart innovative properties of conventional materials has been extended during the last decades. The small size and great surface area of nanomaterials make them more effective at low concentrations than other conventional additives. Some works describe the incorporation of nanomaterials to the polymeric systems, mainly into thermoplastic materials, to improve their fire behaviour [3-6]. However, the use of flame retardant nanomaterials has not been exhaustively studied for wood based materials; works detected related with this research field are limited [7-9].

2. Experimental

2.1. Materials

To analyze the effect of each nanoparticle on the fire behaviour of wood veneers, pine veneers with 0.59 ±0.02 mm of thickness, 488 ± 28 kg/m³ of density and 3.2 ± 0.2 percentage of water were used.

Nanoparticles of silica (SiO₂), titanium dioxide (TiO₂) and zirconium dioxide (ZrO₂) were used for preparing aqueous dispersions which were used for treating pine veneers to improve their fire behaviour (Table 1). These nanoparticles and aqueous dispersions of them were prepared by L’Urederra Technological Center. These aqueous dispersions were prepared with a 1 wt% and 3wt% of each nanoparticle. Besides, a commercial flame retarding agent based on nitrogen compounds was used to optimize the best mode for carrying out the treatment of veneers.

![Table 1. Properties of nanoparticles](#)

| Nanoparticles | SiO₂ | TiO₂ | ZrO₂ |
|---------------|------|------|------|
| BET surface area (m²/g) | 216 | 120 | 87 |
| Diameter (nm) | 13 | 12 | 12 |

2.2. Experimental Procedure

A commercial flame retarding agent was used to optimize the methodology for treating pine veneers. Three methods were carried out for treated veneers at environmental conditions:

(i) Impregnation. A rod commonly used for applying conventional varnish was used for treating veneers by impregnation.

(ii) Spraying. A HVLP spray gun with a nozzle of 1 mm and working at 4 bars was used for treating veneers by spraying.

(iii) Immersion. Veneers were treated in a bath for 30 minutes.

To determine the optimal methodology for treating pine veneers and, therefore, the most effective treatment, chemical composition of two sides of treated pine veneers was analyzed by Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR). An infrared spectrophotometer Tensor 27 (Bruker) provided with an ATR accessory with diamond crystal was used. 100 scans at 4 cm⁻¹ resolution were collected for each sample.

Optical Microscopy (Moritex, MSX-500Di) were used to analyze esthetical modification originated on the veneers surface by each treatment.

Thermogravimetric Analysis using a Q500 thermobalance (TA Instruments) with a constant heating rate of 10 °C/min until 1000 °C and under nitrogen atmosphere was used to determine the effect on veneers thermal properties of each treatment.

To evaluate the fire behaviour of veneers (non-treated and treated), fire test method according to the UNE 23721:90 standard were carried out.
3. Results and discussion

Surface chemical composition of pine veneers is constituted by typical chemical groups of cellulose and lignine: O-H groups (st O-H at 3335 cm$^{-1}$, δ O-H at 1645 and 1024 cm$^{-1}$ and C-O at 1263 cm$^{-1}$), C=O groups (st C=O at 1745 cm$^{-1}$) and CH$_2$ and CH$_3$ groups (st C-H at 2922 and 2855 cm$^{-1}$), Figure 1(b). Typical infrared absorption bands of commercial flame retardant are showed in Figure 1(b). This commercial flame retardant is mainly based on ammonium salts.

![Figure 1. ATR infrared spectra of (a) commercial flame retarding agent and (b) pine veneer.](image)

The treatment of pine veneers by immersion in a bath containing flame retarding agent for 30 seconds is more effective than other treatments (Figure 2(a)). The penetration of flame retardant is limited for impregnating and spraying treatments according to the chemical composition obtained by infrared analysis on each side of veneer (Figure 2(b) and 2(c)).
All treatments created chemical modification in both side of pine veneers as show obtained infrared spectra (Figure 2). Fire tests, according to the UNE 23721:90 standard, were carried out to obtain more information about the more effective treatment. The results obtained showed that immersion treatment was the more effective than others to improve fire behaviour of pine veneers. Non treated pine veneer was classified as M4 while pine veneer treated with commercial flame retardant obtained a M1 classification according to the UNE 23721 fire tests.

The best way for carrying out the treatment is by immersion of pine veneers in the flame retarding agent bath. Therefore, treatments of pine veneers with nano-oxides (SiO$_2$, TiO$_2$ and ZrO$_2$) dispersion were carried out by immersion.

The treatment of pine veneers with aqueous nanoparticle dispersion modifies the chemical composition on surface pine veneers as it can be observed in Figure 3. Besides of infrared absorption bands characteristic of cellulose and lignin, typical absorption bands of Si-O links are detected on 3wt% SiO$_2$ treated pine veneer infrared spectrum (Figure 3a). Infrared spectra of pine veneers treated with 3wt% TiO$_2$ and 3wt% ZrO$_2$ aqueous dispersion also show infrared absorption bands characteristics of these compounds. The modification introduced on the surface of pine veneer after treating them with nanoparticle aqueous dispersion is mainly due to the deposition of solid nanoparticles on the surfaces (Figure 4).
Figure 3. ATR infrared spectra of: (a) 3% SiO$_2$, (b) 3wt% TiO$_2$ and (c) 3wt% ZrO$_2$ aqueous dispersion treated pine veneers.

The treatment of veneers with aqueous nanoparticles dispersion produces a deposition of aggregates and/or agglomerates of nanoparticles which can be observed by microscopic analysis and as consequence a colour change of the veneer is produced by the treatment being more marked on the sample treated with 3wt% TiO$_2$ dispersion.

Figure 4. Images taken with optical microscope at 100x magnification of samples.

The treatment of pine veneer with aqueous nanoparticle dispersions produces a noticeable modification on their thermal properties which are sometimes related with the fire behaviour. The most effective treatment for modifying thermal properties of veneers is that based on the use of 3wt% SiO$_2$ aqueous dispersion. The results obtained by thermogravimetric analysis of 3wt% SiO$_2$ treated veneer show a weight loss on the second thermal decomposition lower than that for non-treated or treated with the other dispersions. Besides, the amount of solid residue obtained is higher than that obtained for non treated veneer or treated with aqueous nanoparticle dispersions based on 3wt% TiO$_2$ or 3wt% ZrO$_2$ (Table 2).
After testing the samples according to the UNE 23721:90 standard, the treatment based on the use of 3wt% SiO$_2$ aqueous dispersion was the more effective to improve the fire behaviour of pine veneers as shows the classification obtained for each sample (Table 3).

Table 2. Results obtained by thermogravimetric analysis of non-treated and treated pine veneers ($T_d$: thermal decomposition temperature, $WL$: weight loss).

| Sample          | $T_d$1 (°C) | $WL$1 (wt %) | $T_d$2 (°C) | $WL$2 (wt %) | $T_d$3 (°C) | $WL$3 (wt %) | Residue (wt %) |
|-----------------|-------------|--------------|-------------|--------------|-------------|--------------|----------------|
| Non treated     | 83.1        | 8.6          | 319.0       | 56.4         | 468.3       | 34.5         | 0.5            |
| 3% SiO$_2$      | 83.1        | 6.4          | 320.3       | 51.3         | 467.8       | 27.6         | 14.7           |
| 3% TiO$_2$      | 78.1        | 7.2          | 316.5       | 55.2         | 464.1/490.5 | 34.9         | 2.7            |
| 3% ZrO$_2$      | 86.9        | 7.8          | 319.0       | 56.0         | 460.3/494.3 | 33.2         | 3.0            |

4. Conclusions
The results obtained showed that immersion of pine veneers was the most effective treatment to achieve a good penetration of flame retarding agent.

The treatment of pine veneers with a 3wt% SiO$_2$ aqueous dispersion is the most effective to modify thermal properties of pine veneers and also to improve their fire behaviour.

As future works it would be interesting to analyze the effect of adding nanooxides in the formulation of wood based panels on their fire behaviour.

References
[1] Peraza Sánchez F. 2001 Protección preventiva de la Madera. Ed. Asociación de Investigación Técnica de la Madera y Corcho, 211-233.
[2] Takashi K., Fangming, D. et al. 2005 Nanoparticles networks reduce the flammability of polymer nanocomposites *Nature Materials* **4** 928-933.
[3] F. Laoutid, L. Bonnaud et al. 2009 New prospects in flame retardant polymer materials: From fundamentals to nanocomposites *Materials Science and Engineering* **63** 100-125.
[4] Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J. M., Dubois, Ph. 2009 New prospects in flame retardant polymer materials: From fundamentals to nanocomposites *Materials Science and Engineering* **3** 100-125.
[5] Goodarzi, V., Ali, S., Torabi, M., Motahari, S. 2008 Improvement of Thermal and Fire properties of Polypropylene *Journal of Applied Polymer Science* **110** 5 2971-2979.
[6] Wang, Z., Han, E., Ke, W. 2006 Effect of nanoparticles on the improvement in fire-resistant and anti-ageing properties of flame-retardant coating *Surface and Coatings Technology* **200** 20 5706-5716.
[7] Guo G., Park C.B., Lee Y.H., Kim Y.S., Sain M. Flame retarding effects of nanoclay on wood fiber composites 2007 *Polymer Engineering and Science* **47** 3 320-336.
[8] Giudice, C. A., Pereyra, A. M. 2009 Silica nanoparticles in high silica/álcali molar ratio solutions as fire-retardant impregnants for woods *Fire and Materials* **34** 4 177-187
[9] Miyafuji, H., Saka, S. 1997 Fire-resisting properties in several TiO$_2$ wood-inorganic composites and their topochemistry *Wood Science and Technology* **31** 6 449-455