

Nanocarriers as a Tool to Improve Modification Technologies of Porous Materials

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ABSTRACT

Modification of porous materials, natural or synthetic, is a very practical way to change or improve their properties. The impregnation and chemical modification of lignocellulosic products can improve their outdoor properties (*e.g.* dimensional stability) and protect them against moisture, UV-degradation, deterioration by micro-organisms or fire. The penetration of porous materials depends on their physical and chemical properties, as well as the nature of the pores. Therefore, the impregnation has limitations with respect to the size, viscosity, and chemistry of the impregnating component. This work presents a method for incorporating active components in porous materials by means of nano-sized particles that function as carriers of such components. Anchoring the additives to a carrier may allow a better control of them into the material, offering the possibility to make them active in a later stage, *in situ* and on demand. It is shown that the penetration depth and fixation of compounds in wood can be modified when using a carrier particle. In particular, it was observed that water-suspended nanoparticles such as laponite (25 nm diameter) allow the manipulation of penetration of chemicals in wood. Thus, this work presents nanocarriers as a promising tool to control the penetration and later chemical modification of porous material. Some benefits of controlling the penetration of components by nanocarriers are: temporary hinder of reactivity of the transported components, be able to use labile reagents by stabilizing them with the nanocarrier, triggered reactivity, delayed reactivity, release on demand of chemicals, and impregnation of multiple component systems avoiding chemical or physical interferences between them.

INTRODUCTION

The impregnation of porous materials, natural or synthetic, is a very practical way to change or improve their properties. For instance, the impregnation of lignocellulosic products can improve the outdoor properties (*e.g.* dimensional stability) and protect these products against UV-degradation, deterioration by micro-organisms or fire. However, the material modification is limited – among other factors – by the penetration depth of compounds in the material matrix. Reduced penetration can lead to enhanced leaching of the substances, reducing the impregnation efficiency. A drawback of the known incorporating methods is that frequently a poor penetration depth of the additive results in only a shell of additive on the outer surface of the porous material, where they are generally not uniformly distributed.

The penetration of porous materials depends on the size and nature of the pores and chemical properties of the materials in which the impregnation should take place. In principle, the impregnating substance should have a smaller size than the pore diameter (*e.g.* in the case of a dispersion) or a low enough viscosity to effectively fill the pores (*e.g.* in case of a solution). The second important parameter is the internal surface chemistry of the porous material. Surface energy, reactive or complexating moieties can interfere greatly with the impregnation process and limit the penetration depth. Therefore, the impregnation of porous materials has limitations with respect to the size, viscosity, and chemistry of both the additive and the material matrix. This work presents a method for incorporating compounds within a porous material, which is a promising tool to improve modification technologies of these materials, such as chemical modification of wood.

PRINCIPLE OF NANOCARRIERS

As outlined in the introduction, it is needed to develop a method which brings about an improved penetration, incorporation and distribution of additives and other active compounds within porous materials. Recently, it was found that it can be done by using a slurry of a nano-sized material that carries the compound. The method comprises impregnating the porous material with a slurry of nano-sized particles that carry specific compounds (Figure 1). The nano-sized carrier can interact with the transported substance in many different ways, for example, by surface adhesion, chemical bonding, or encapsulation.

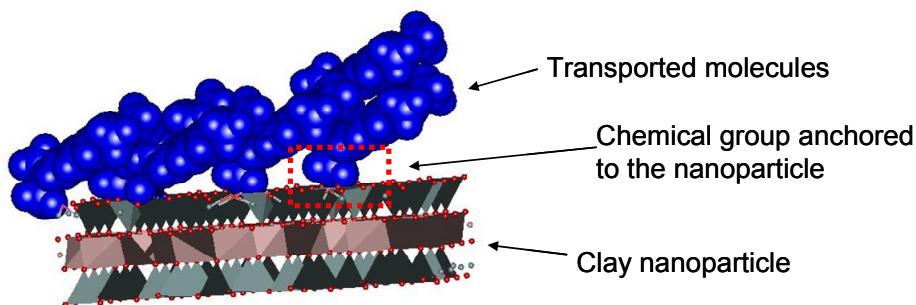


Figure 1: Schematic representation of the nanocarrier. Molecules attached to the nanoparticle form a stable system that penetrates through a porous material, transporting components that can be used for further (chemical) modification of the material.

This method enables the deep and uniform penetration of functional compounds into porous materials, making them much more efficient for their particular purposes. Another advantage is that nanocarriers can help to prevent undesired reactions (for example with free water) by temporarily inactivating specific reagents. In addition, it allows the control and manipulation of multiple components. For example, multiple components can be impregnated simultaneously by being attached to specific nanocarriers, who will release them on demand to react at different stages.

MATERIALS AND METHODS

Spruce samples of 20x20x20 mm³ were conditioned at 20 °C and 65 RH until constant weight, prior measurements. The sample were sealed on 5 edges and the remaining edge

was dipped in the treatment medium over a period of 20 hours, at 20°C, and pressure lower than 15 bars. The treatment medium was an aqueous suspension of 1% weight nano-sized clay particles – laponite having $1 \times 25 \times 25 \text{ nm}^3$. Here the laponite was tested as nanocarriers. Methylene blue was tested as the component to be carried, for convenience due to easy visualization. A reference solution of 10% methylene blue in water, pH = 6, was also employed for comparison. Preliminary results are obtained by visual observation of blue coloration (or absence of coloration) in the wood samples. Detailed information on the penetration of components is obtained by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

Figure 2 shows a wood block sample impregnated with a solution of methylene blue in water (left). In this case, only the surface of the sample displays some blue colouration, indicating the lack of methylene blue penetration in the present experimental conditions. By the contrary, when a nanoparticle is added to the impregnation medium (in this case an aqueous suspension of laponite and methylene blue), the penetration depth of methylene blue into the wood sample changes significantly (Fig. 2, right image). This test exemplifies that in the presence of the nanoparticle, the methylene blue solution penetrates deeper in the wood sample, inducing also a more uniform distribution of the transported component.

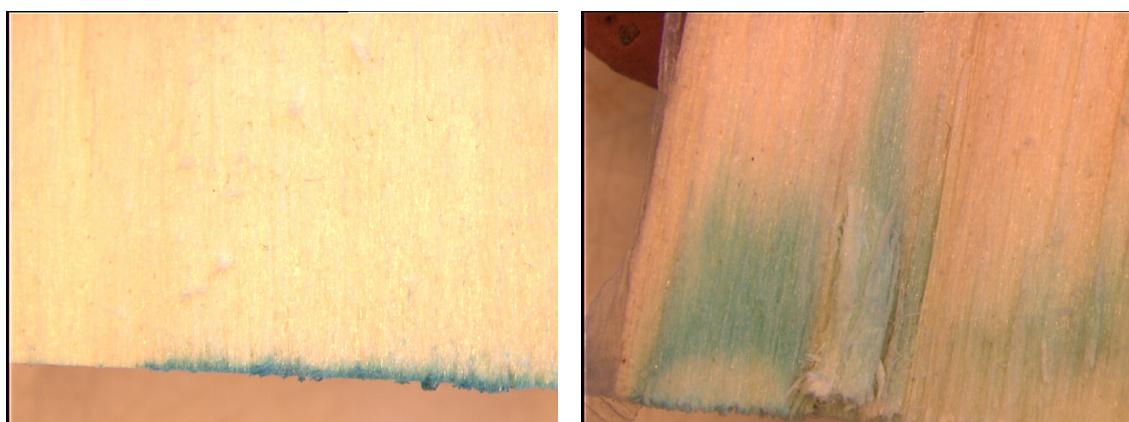


Figure 2: Photographs of the inner area of impregnated Spruce blocks. Left: reference sample impregnated with an aqueous solution of methylene blue. Right: Sample impregnated with methylene blue using laponite nanoparticles as carrier.

Samples were analyzed by XRD in order to determine the presence of laponite nanoparticles in the wood blocks. Measurements were performed in different areas of the samples. Figure 3 shows spectral data obtained from an impregnated sample where no blue colouration – typical of methylene blue – was observed by the naked eye (Fig. 3, left) and where blue colouration was present (Fig. 3, right). In the first case, only oxygen and carbon signals are present, which arise from the wood matrix. In the second case, aluminium and silicon are also identified, which are the fingerprint of laponite. In all measurements, laponite was only detected in those places where blue colour could be observed. These results indicate that methylene blue does not penetrate independently, but it is transported by the laponite nanocarrier.

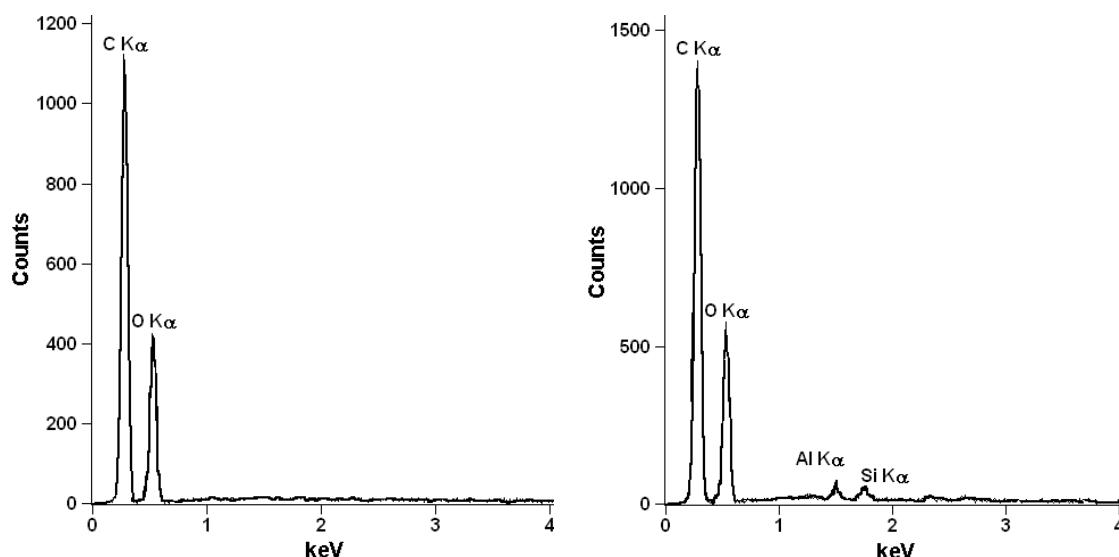


Figure 3: XRD spectral data of impregnated Spruce samples. Left: Spectrum obtained from a non-coloured area. Right: spectrum obtained from a blue-coloured area.

CONCLUSIONS

The incorporation of active components within a porous material can be controlled by means of nanocarriers. This work presented a method to impregnate porous materials with a slurry of nano-sized particles that function as carriers of a component. The technology enables the deep and uniform penetration of additives and functional ingredients into porous materials, allowing the control of those compounds for further material modification. The method offers further possibilities such as manipulation of reagents, protection of labile compounds, control of chemical reactions, and release of chemicals on demand, among others.

REFERENCES

- Eversdijk, J., Rentrop, C.H.A., Sailer, M.F., Fischer, H.R., Benz, D. (2007). Method for incorporating a functional additive within a porous material. WO2007032663 A1.
- Lorah, D.P. et al. (2002). Nanocomposite compositions and methods for making and using same. US 2002/058740 A1.
- Olsson, T., Mognis, M., Varna, J. and Lindberg, H. (2001). Study of the transverse liquid flow paths in pine and spruce using scanning electron microscopy. *Journal of Wood Science*, **47**, 282.
- Uhmeier, A. (1997). Pressure-impregnation technique for wood chips. *Journal of Pulp and Paper Science* **23**, J161.