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Mechanical, chemical and acoustic properties of new hybrid ceramic-polymer varnishes for musical instruments

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ABSTRACT

Novel ceramic–polymer hybrid varnishes were designed to protect the wood surface of musical instruments. These hybrid coatings consist of chemically functionalized silica nanoparticles and synthetic solvent-based acrylic- and alkyd–polyurethanes. The nanoparticles were added to increase the abrasion resistance. An alkoxide was used to increase the number and reactivity of OH's groups on the wood surface improving the adhesion with the coating through a chemical link between them. The properties of the synthetic coatings were compared with those of a traditional varnish (based on alcohol and natural resins) to obtain a better performance. Two types of woods were used: maple and spruce. The samples were characterized by UV–Vis, mechanical and abrasion tests, water's absorption, acoustic properties, chemical resistance and SEM.

1. Introduction

Wood has been, from ancient times, a material of great importance to mankind, not only because of its abundance in nature or of its beautiful appearance, but also mainly due to its important properties and wide range of applications. Wood has been, and it is right now, one of the primary building materials used by the human being, and its cellular structure provides it with excellent properties such as low weight (density), high mechanical strength (in tension and compression), low thermal conductivity, good acoustic properties, and high endurance to outdoor conditions (when it is properly treated). It is also a highly versatile material because it can be bent or twisted in special and complicated shapes and is readily worked, fastened, and finished. Its final surface is pleasant to touch and its patterns are of great beauty [1–6].

There are external agents that can damage untreated wood surface by changing its texture and appearance: weather conditions (temperature, humidity, UV radiation, etc.), living organisms (fungus, bacteria, etc.), handling (stain, scratching, abrasion, human sweat, etc.), and so on. The human perspiration is particularly aggressive due to its acid character with a pH as low as 3.5; it

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contains, among other compounds, chlorides and sulfates that can stain and damage the wood's surface [7–9]. When unprotected wood is exposed to wetting and sunlight, it can exhibit rather serious cracking, probably as a consequence of a quick moisture loss, with its corresponding dimensional changes; this attack is especially notorious in polluted weathers where chemical compounds can damage, in some cases severely, the wood's surface. Then, it is a common practice to cover the wood surfaces with different kinds of coatings to protect them. Occasionally, coatings may contribute to the deterioration in the wood's properties: a deficient application on exposed wood parts may retain excess of water favoring rotting conditions [10–13].

An important use of wood as a construction material is in the fabrication of musical instruments: its cellular structure, density and constituents are partially responsible for its important acoustic properties [14]. Wood is generally an economical building material from renewable sources; however, fine woods appropriated for the construction of fine musical instruments are rare and expensive. Today, a significant number of musical instruments involve, in their manufacture, wood pieces: their flexibility allows transmitting, in an appropriate way, mechanical vibrations (musical notes): vibrational normal modes are strongly influenced by the wood morphology and density [15,16]. Then, the protection of wood surface of fine musical instruments is of primary importance in the performance and conservation, for future generations, of these invaluable instruments. Any damage (physical or chemical) on the wood surface can modify the acoustic response of the instrument in addition to its aesthetic aspect. Therefore, one important constituent in the fabrication of musical instruments is the protective coating [17,18].

The middle age was the golden age of the musical instrument construction; in this age, many of the varnishes were developed for violins, violas, cellos, guitars, etc. Nowadays, in the manufacture of musical instruments these traditional varnishes, based on alcohol and natural resins and were developed hundreds of years ago, are still in use [5,19,20].

At present, practically all coatings are based on synthetic polymers and show excellent properties in many senses. However, one of the weakest points of many polymeric materials is the lack of wearing resistance. Commercial products, mainly polymer and waxes, offer several attributes, essentially an improvement in the final appearance of the wood surface, but none protect against wearing. Then, if a polymer-based coating is going to be used to protect wood surfaces against wearing, scratching or any mechanical action, it has to be added with hard ceramic nanoparticles to provide the coating with this property [21]. The interaction between the ceramic particles and the resin is important because the aggregation of the nanoparticles can reduce the wearing protection making cloudy the varnish due to the light scattering effects. In this work, new hybrid ceramic–polymer nanocomposites were designed to protect wood surfaces of musical instruments against scratching, abrasion and chemical attack. These coatings possess high adhesion with the wood surface, high gloss and transparency. The mechanical, chemical and acoustic properties of these new varnishes were compared with the corresponding properties of one traditional varnish that was prepared with an old recipe.

2. Experimental

2.1. Materials

Two different types of woods widely employed in the construction of musical instruments were used: spruce and maple. Wood pieces of different sizes were prepared for several tests: $14.5 \times 1.0 \times 0.25$ cm for acoustic and mechanical, $2.5 \times 2.5 \times 0.25$ cm for abrasion, and $1.0 \times 1.0 \times 0.25$ cm for chemical resistance and water's absorption. For the UV–Vis analysis, the coating was applied on optical flat glasses. In all cases, five pieces of each type of samples were prepared for reproducibility.

Three different types of coatings were prepared: (a) alkyd–polyurethane prepared using alkyd hydroxylated resin (Reichhold, Mex) catalyzed with poly-isocyanate (Bayer, Mex), (b) acrylic–polyurethane prepared using acrylic hydroxylated resin (Bayer, Mex) catalyzed with the same compound, and (c) a traditional coating prepared using turpentine gum and linseed oil, both products were obtained from a drugstore. Toluene (Baker, Mex) was used as a solvent for the synthetic coatings. Silica nanoparticles (Degussa, Ger) of 16 nm were added to synthetic coatings at concentrations: 0, 3, and 5 wt%. An anti-adherent (AA), dimethyl polysiloxane (Degussa, Ger), was also added at concentrations: 0, 1, and 1.5 wt%; this anti-adherent produces coatings with good resistance to oil- and water-base compounds, increasing the protection to the musical instrument and providing a glossy finish. For comparison purposes, a commercial varnish (Comex, Mex) specially designed for wood application was also included in the abrasion resistance test; for this coating the primer suggested by the manufacturer was applied.

2.2. Wood surface preparation

In all cases the wood surfaces were ground using a sandpaper Fandeli No. 600 until a smooth flat surface was obtained; the wood dust was removed using a clean soft brush. A chemical modification was performed on the wood surfaces in order to increase the number and reactivity of the OH's groups that are going to react with the NCO's groups of the poly-isocyanate to link chemically the varnish with the wood and form the polyurethane; in this way it is also possible to reduce the penetration of the coating into the wood's pores reducing, as much as possible, any modification in the wood's density and in the mechanical properties which render, finally, in the acoustic response. To achieve this goal, the wood pieces were painted with titanium isopropoxide (Aldrich Chem., USA). This alkoxide is a very active compound that reacts rapidly with the primary hydroxyl of the cellulose (the main constituent of these types of woods) producing three labile OH's groups per each primary hydroxyl, as shown in the following schematic reaction:

$$\begin{aligned}&(\text{Cellulose})-\text{OH}+\text{R}-\text{O}-\text{Ti}{\equiv}(\text{OR})_3\\&\quad\rightarrow(\text{Cellulose})-\text{O}-\text{Ti}{\equiv}(\text{OR})_3+\text{ROH}\end{aligned} \tag{1}$$

where R stands for the isopropyl group. Because titanium alkoxide is very reactive and hydroscopic compound, it reacts with the moisture in the air producing the hydrolysis of the other three isopropoxy groups resulting in the following reaction:

$$\begin{aligned}&(\text{Cellulose})-\text{O}-\text{Ti}{\equiv}(\text{OR})_3+3\text{H}_2\text{O}\\&\quad\rightarrow(\text{Cellulose})-\text{O}-\text{Ti}{\equiv}(\text{OH})_3+3(\text{ROH})\end{aligned} \tag{2}$$

As can be seen, the role of this coupling agent is to increase the number and reactivity of the hydroxyl groups of the cellulose ring. These groups, together with the OH's groups of the hydroxylated resin, can react with the poly-isocyanate to link chemically the coating with the wood.

The modified wood pieces were placed on a stove at 50 °C for 1 h to finish the chemical reaction and to remove the water and alcohol produced during the reaction; some of the alkoxide (which does not react with the cellulose) reacts with itself due to the presence of moisture producing a white powder (titania), which is removed with a clean and soft brush. The wood's surface appearance remains practically unchanged after this treatment.