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Research Article

Metal Oxide Sol-Gels (ZrO_2, AlO(OH), and SiO_2) to Improve the Mechanical Performance of Wood Substrates

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Wood is a renewable material widely used in many applications due to its unique properties and distinctive look. However, as wood is organically constituted, it is slowly destroyed by the long-term impact of oxygen, UV radiations, water, and biological attacks (Mahltig et al., 2008). Therefore, protective treatments are necessary to improve the mechanical, thermal, and chemical properties of wood. In order to improve the mechanical properties of sugar maple (*Acer saccharum* Marsh.), as this species is widely used in the wood products industry, samples of sugar maple were impregnated with sols of metal oxides (AlO(OH), SiO_2, and ZrO_2). The weight gain and two different techniques of microscopy were used to evaluate the efficiency of the impregnation in the wood samples. The mechanical properties were evaluated using hardness test, scratch test, and impact test. It was shown that the maple samples impregnated with ZrO_2 led to the greatest improvement of the mechanical properties.

1. Introduction

Wood is a renewable material widely used in many applications, such as outdoor (sidings, shingles, etc.) and indoor products (hardwood floors, kitchen cabinets, furniture, etc.), due to its excellent properties and distinctive look. However, as wood is organically constituted, it is slowly destroyed by the long-term impact of oxygen, UV radiations, water, and biological attacks [1]. Therefore, protective treatments have to be used to increase its life in service. In addition the growing environmental concerns push the industry to develop and use nontoxic wood preservatives [2, 3].

Recently, it has been observed that one promising method to improve and provide new properties for wood materials is to modify the wood surface by the deposition of hybrid inorganic-organic materials with the sol-gel process. Hybrid inorganic-organic materials offer the opportunity to combine the desirable properties (i.e., toughness, elasticity, etc.) of organic polymers with those of inorganic solids (i.e., hardness, chemical resistance, etc.) [4]. The sol-gel process is simple, low cost, and it allows room-temperature deposition of hybrid inorganic-organic thin films on a wide range of substrates, including wood [2, 3]. This technique is appropriate for commodity production such as wood product industry. Depending on the sol-gel synthesized, various wood properties can be improved, such as color retention, mechanical properties, dimensional stability, and more.

Over the last two decades, the sol-gel process has been the subject of many studies. However, most of the studies on sol-gel process were carried on different substrates such as glass, metal, or textile. Using this process on substrates like wood brings out many special features, such as thermal treatments. Usually, coating metal oxide sols on substrates requires a really high temperature that cannot be used for wood substrates as the organic components would degrade. The application of sols to wood can be done in many ways; unlike the other substrates, the sol can be impregnated into the wood, and not just applied to the wood surface. Depending on the type of application or impregnation techniques used, the surface protection is different: using a brush or nozzle protects only on the surface, while a vacuum or vacuum/pressure impregnation gives full protection [1].

Nanoparticles such as silica (SiO_2) and aluminum oxide (AlO(OH)) are widely used in the coatings industry as they improve the scratch and abrasion resistance and the hardness of the coatings [5]. Table 1 compares the hardness (Mohs

Table 1: Hardness (Mohs scale) and refractive index of frequently used particles in the coating industry at the micrometric scale.

Properties	Al_2O_3	SiO_2	ZrO_2	TiO_2	ZnO
Hardness (Mohs scale)	8.0-9.0	7.0	8.0	5.5-6.5	5.0
Refractive index	1.7-1.8	1.55	2.15	2.6	2.02

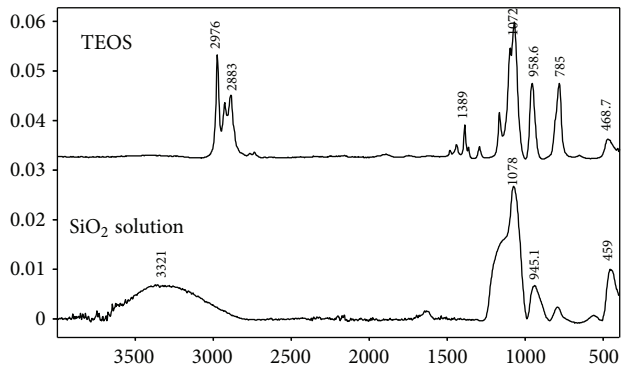


Figure 1: Infrared spectra of TEOS, the organic precursor, and the SiO_2 product found after the drying.

scale) and the refractive index of frequently used particles in the coating industry. Based on high values of the Mohs scale and refractive index that should not alter the perceived wood color, sols containing AlO(OH), SiO_2, and ZrO_2 were selected for this study.

The objective of this work was to improve the mechanical properties of sugar maple (*Acer saccharum* Marsh.) by sol-gel treatments with three different nanoparticles (AlO(OH), ZrO_2, and SiO_2). First, the penetration of the sol was evaluated by two different techniques of microscopy and by weight gain. Then, the hardness, impact resistance, and scratch resistance of the samples treated were evaluated.

2. Materials

2.1. Wood Samples. The wood species selected for this project was the sugar maple (*Acer saccharum* Marsh.), as it is widely used in the north American wood product industry. Sugar maple is a diffuse porous wood, with a specific density of 620 to 680 kg/m^3 [6]. Sugar maple is a hardwood, but as a commercial species, it faces competition from tropical wood due to the latter's high density and hardness. Samples used in this study were 5 cm × 5 cm × 1.27 cm, longitudinal, tangential, and radial wood directions, respectively, and were sanded at 150 grit with a wide belt sander (SCM, Sandya 20, Italy) and conditioned at 20°C and 50% relative humidity (RH) until constant mass before the treatment.

2.2. Sol Preparation. Aluminum isopropoxide (AIP), tetraethylorthosilicate (TEOS), 70% w/w solution of zirconium n-propoxide, n-propanol, and acetyl acetone (acac) were purchased from Sigma-Aldrich. Ethanol anhydrous

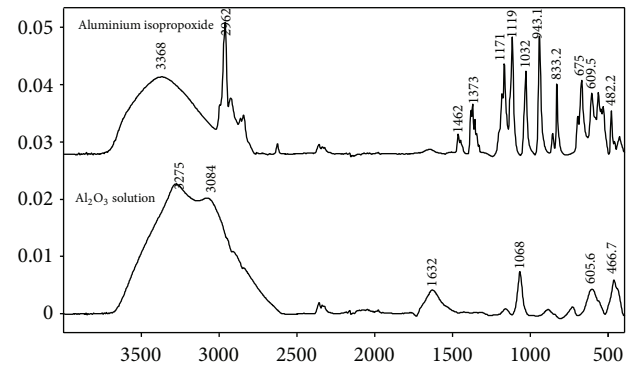


Figure 2: Infrared spectra of the aluminium precursor (aluminium isopropoxide) and the AlO(OH) solution.

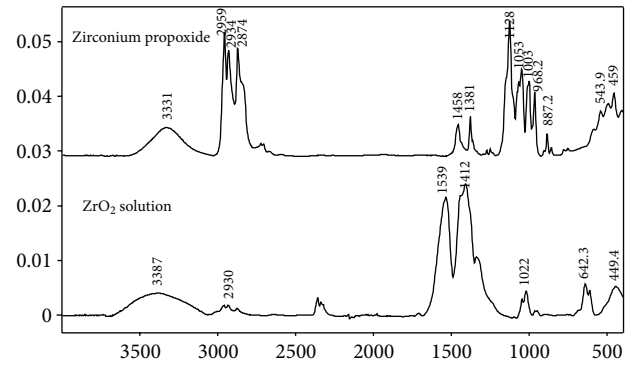


Figure 3: Infrared spectra of the zirconium precursor (zirconium propoxide) and the ZrO_2 solution.

was purchased from SAQ (Quebec, Canada) and p-toluene sulfonic acid was purchased from Laboratoire MAT (Quebec, Canada).

2.2.1. Synthesis of AlO(OH) Sol. AIP ($Al(O(CH(CH_3)_2)_3$) was mixed in deionized water (200 mole of water for 1 mole of alkoxide) under vigorous stirring for two hours at 85°C. Then, 0.2 mole of hydrochloric acid (1 M) for each mole of alkoxide was added to the solution as a catalyst and mixed for one hour at 85°C.

2.2.2. Synthesis of SiO_2 Sol. TEOS ($Si(OC_2H_5)_4$), anhydrous ethanol (CH_3CH_2OH), and distilled water were mixed together in a molar ratio of 1 : 4 : 16, respectively. A pH value of 3 was reached by adding hydrochloric acid (1 M) drop by drop. The sol gel was then heated for 1.5 hours at 60°C.

2.2.3. Synthesis of ZrO_2 Sol. A 70% w/w solution of zirconium n-propoxide ($Zr(OCH_2CH_2CH_3)_4$ in n-propanol was mixed with n-propanol ($CH_3CH_2CH_2OH$) and acac ($CH_3C(O)CH_2C(O)CH_3$). A solution of p-toluene sulfonic acid ($CH_3C_6H_4SO_3H$) in distilled water (4 M) was added to this mixture. The resulting solution was heated for two

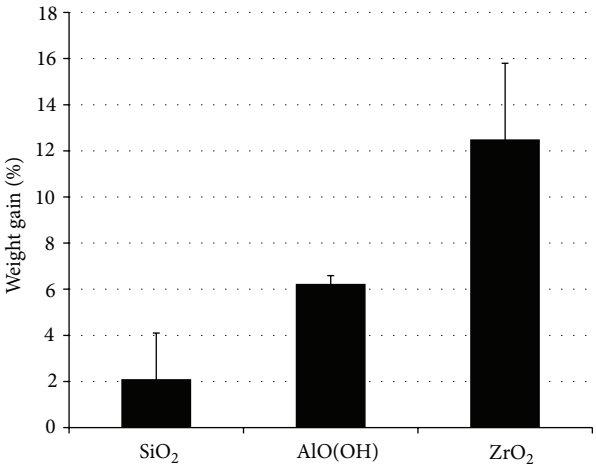


FIGURE 4: Weight gains of maple samples treated with the SiO_2, AlO(OH), and ZrO_2 sol-gels.

hours at 60°C. The final zirconium concentration in the sol-gel was 0.8 M and the molar ratio of acac and distilled water to zirconium was kept to 1 : 10 : 1.

2.3. Wood Samples Treatment. Thirty samples of sugar maple were used for each treatment. First, the wood samples were weighed and then soaked in the solution. A vacuum at 81.2 MPa was generated for one hour and then the samples were returned to ambient pressure for two hours. After the treatment, the wood samples were slightly wiped with a paper towel and they were dried at room temperature for 24 hours. The samples were then placed in an oven for 24 hours at 103°C for water and solvent evaporation and to promote the condensation reaction. After curing, the wood samples were weighed again to determine the gel retention (weight gain).

3. Methods

Infrared spectroscopy was used to follow the reaction of the different sols. The apparatus used in this project is a Tensor 37 Fourier transform infrared spectrophotometer equipped with a Platinum ATR (diamond crystal) from Bruker, using a resolution of 4 cm^{-1}.

Weight gain of the samples was obtained by measuring the initial and final weight (after sol-gel impregnation and curing) of the samples. Sample weighing was done at the same temperature and humidity conditions before and after the sol-gel treatment (20°C, 50% RH).

Two different microscopes were used to assess the penetration of the sol-gels in the wood.

Transmission electron microscopy (TEM) was used for the observation of gel penetration in the wood substrate. Each wood sample was cut to obtain 200 nm thick wood slices, using a Reichert-Jung ultramicrotome, model ultracut E (Vienna, Austria). The transmission electron microscope used was a JEM-1230 (JEOL) and the images were recorded at an acceleration voltage of 80 kV.

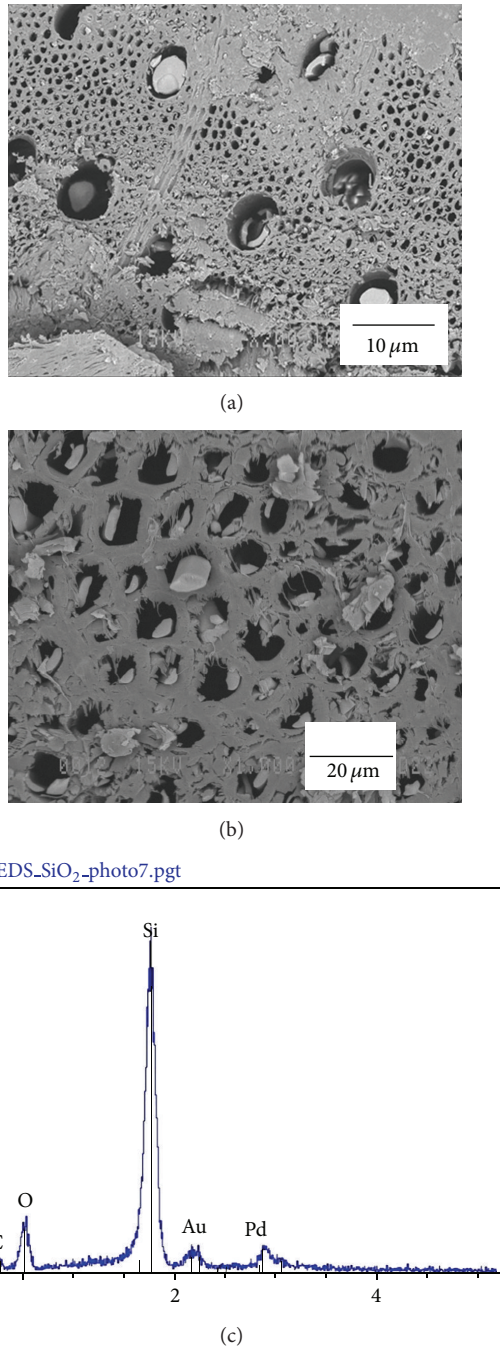


FIGURE 5: Scanning electron microscopy images of the maple samples treated with the SiO_2 sol ((a) and (b)) elemental analysis spectra recorded for the particles found in the wood cells (c).

Scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDS) was performed using a JSM-840A (JEOL) microscope equipped with a NORAN EDS detector. Prior to SEM investigation, the wood samples were microtomed and then gold palladium was coated in a vacuum sputter. In addition to the images obtained, this technique allows the precise identification of the different chemical elements at a specific location.

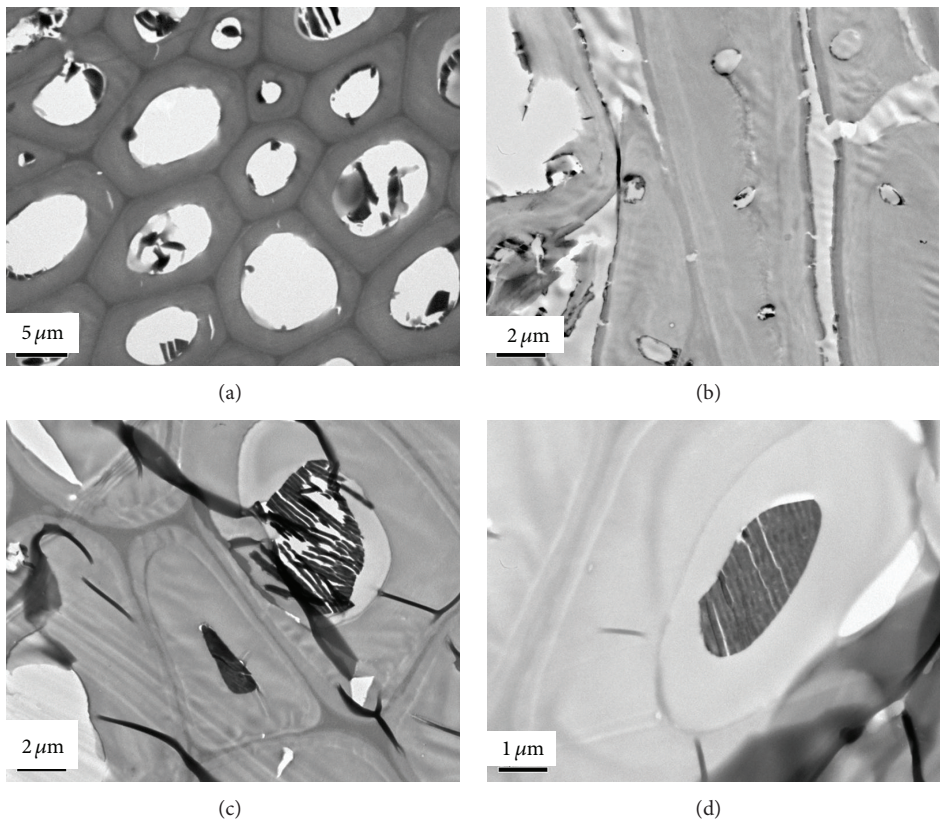


Figure 6: Transmission electron microscopy images of the wood cells of maple samples impregnated with the SiO_2 sol.

3.1. Mechanical Properties. Brinell hardness (HB) can be described by the following equation:

$$\mathrm{HB} = \frac{2 * F}{g * \pi * D * \left(D - \sqrt{D^2 - d^2}\right)}, \quad (1)$$

where F being the applied force, g the gravity acceleration, D the ball diameter, and d the print diameter. The method used here is based on the British Standard Brinell EN 1534-2000 method; a steel ball is pushed into the material at a constant speed until a penetration depth of 1 mm. An Alliance Rt/50 system from MTS Systems (MN, USA) was used. The test bench with a charge cell measures the applied force needed to achieve these results.

The scratch test was divided into two steps; first the scratches were made with a Taber Multi-Finger Scratch/Mar Tester using a weight of 15 N and a tungsten carbide 0.7 mm diameter tip. The test was performed back and forth on a pneumatic table at a speed of 10 cm/s. The depth and width of the scratches were measured with a 3D profilometer, the ContourGT-K1 from Bruker.

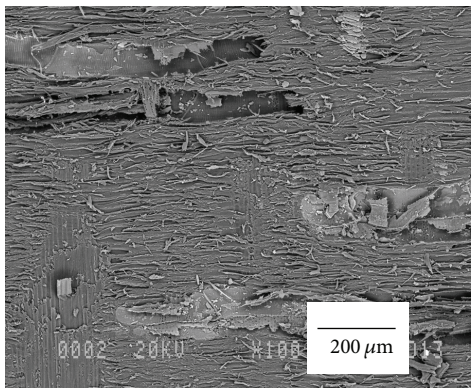
The impact resistance of the samples was measured using an impact tester; a ball weighing 0.91 kg was dropped on the sample from a 25 cm height. The impact print was manually measured using a caliper for the diameter (two measures were taken for each print) and a vertical tip mounted micrometer to measure the depth. This test is based on the standard test method ASTM D 2794-93.

4. Results and Discussion

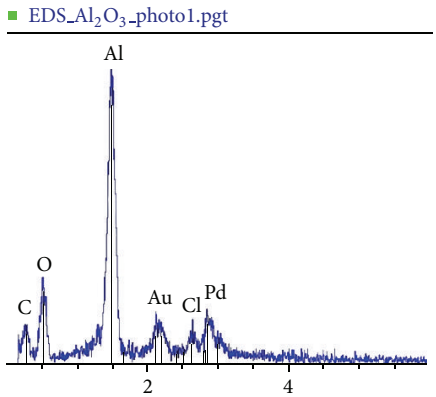
FT-IR spectra of the sol-gel precursors and the final product obtained for each sol-gel synthesis were taken.

4.1. SiO_2 Sol. The infrared spectra of TEOS, the organic precursor, and of the SiO_2 product obtained after drying the solution are presented in Figure 1. The infrared spectrum of SiO_2 is available in the literature. The strong band at 3321 cm^{-1} represents the OH stretching at the surface of the silica particles, the peak at 1078 cm^{-1} represents the Si-O-Si stretching vibration, the peak at 935 cm^{-1} represents the Si-OH stretching band, and finally the band at 459 cm^{-1} represents the Si-O out of plane deformation. The presence of these peaks confirms the synthesis of a SiO_2 gel.

Figure 2 presents the organic precursor, the aluminium isopropoxide, and the AlO(OH) product obtained after drying. The surface of the AlO(OH) is covered by OH groups (boehmite) and the band due to these species is presented above 3000 cm^{-1}. This band can be associated with the OH stretching of the absorbed water, with the bridged hydroxyl group with molecular water or with other OH groups, and

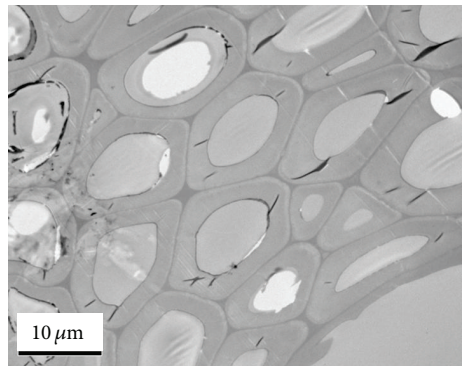


(a)

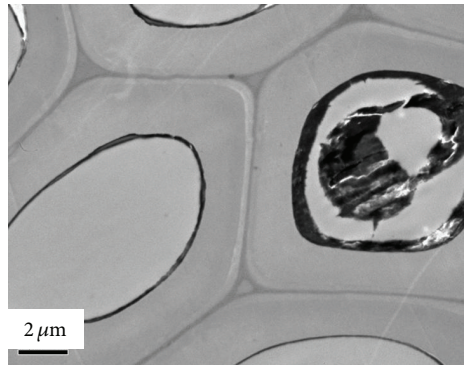


(b)

Figure 7: Scanning electron microscopy of the maple samples impregnated with the boehmite sol (a) and elemental analysis of the particles found in the maple samples impregnated with the boehmite sol.



(a)



(b)

Figure 8: Transmission electron microscopy images of the wood cells of maple samples impregnated with the boehmite sol.

with isolated OH groups. The disappearance of most of the aluminium isopropoxide peak also revealed that a reaction occurred.

4.2. ZrO_2 Sol. Figure 3 presents the spectra of the zirconium propoxide and of the ZrO_2 gel after drying. As ZrO_2 spectrum is not reported clearly in the literature, it is difficult to analyze the spectra obtained for the ZrO_2 gel. However, the disappearance of the group of peaks around 2900 cm^{-1} and 1000 cm^{-1} is a good sign of the sol-gel reaction.

4.3. Gel Retention

4.3.1. Weight Gain. Weight gains obtained for the samples treated with the three different sols are presented in Figure 4. Significant variations in weight gain can be observed from one sample to another. Samples treated with SiO_2 have a lower weight gain percentage than those treated with ZrO_2, which have the highest. Factors like molecular weight of the precursors could explain this difference. However, as the molecular weight of the principal precursor is smaller in the following order: AIP < TEOS < zirconium n-propoxide, there is reason to think that other factors affect the penetration of the sols, such as the hydrolysis time of alkoxides and the viscosity of the solution.

4.4. Microscopy

4.4.1. SiO_2 Gel. Figure 5 shows scanning electron microscopy images taken from the maple samples treated with the SiO_2 sol. On Figures 5(a) and 5(b), white aggregates can be observed in the wood cells. These aggregates represent SiO_2 gel particles as identified by the elemental analysis (Figure 6(c)). In fact, it was found that the particles present in the wood cells are mainly constituted of silicon and oxygen, thus the SiO_2 gel product. It is also possible to see that the particles did not bond to the wood cell surface and that they did not occupy the whole cavity of the wood cells. Transmission electron microscopy images (Figures 6(a) and 6(c)) also present this phenomenon. Figure 6(b) shows SiO_2 particles in the wood cells but also in the punctuations of the tracheids. The presence of SiO_2 particles in the punctuations could prevent the penetration of the sol further into the wood.

4.4.2. AlO(OH) Gel. Scanning electron microscopy images of a maple sample treated with AlO(OH) sol is showed in Figure 7(a). The white aggregates in the wood vessels represent the AlO(OH) gel as verified by the elemental analysis presented on Figure 7(b). Aluminum and oxygen, the two main components of the gel, were dominantly found,

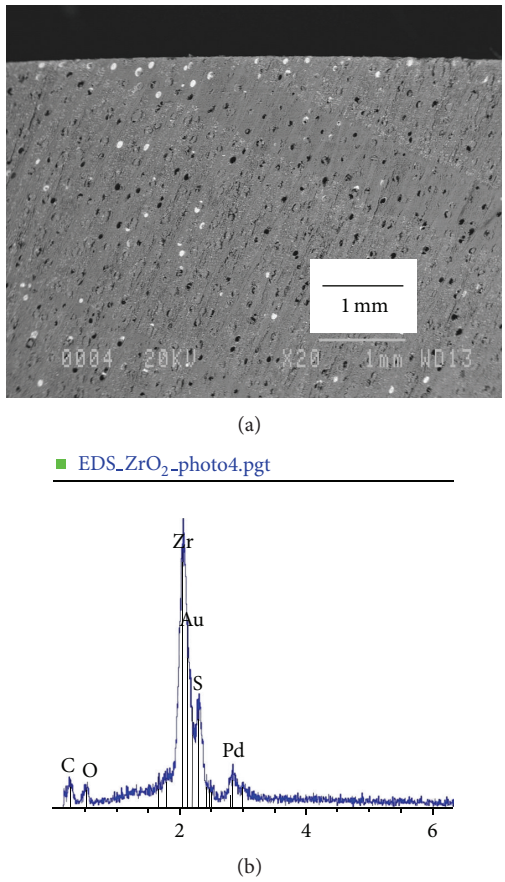


FIGURE 9: (a) Scanning electron microscopy image of the ZrO_2 sol-gel treated maple samples and (b) elemental analysis of the white spots observed.

then some carbon which probably comes from impurities or unreacted reactive, and finally chlorine which comes from the hydrochloric acid used during the synthesis to control the pH. Figure 7(a) also revealed that boehmite particles completely occupy some of the wood vessels and that they are bonded to the cell walls, which was not the case for the SiO_2 particles. However, transmission electron microscopy of the boehmite treated maple samples (Figure 8) shows that the gel is predominantly located on the cell walls only and do not occupy the whole cavity. This suggests that a condensation reaction has occurred between the cell walls and the gel. This reaction is favorable as it would create a composite effect and reinforce the wood samples.

4.4.3. ZrO_2 Gel. On the scanning electron microscopy images (Figure 9(a)), white aggregates can be observed not only at the surface but also deeper in the wood. These white aggregates were identified as the ZrO_2 gel by the elemental analysis (Figure 9(b)). Moreover, it can be observed that the ZrO_2 particles present in the wood cells seem to be firmly bonded to the wood and to occupy the whole wood cells cavity. Transmission electron microscopy images (Figure 10) present a totally different sol-gel compared to the one seen for SiO_2 and AlO(OH). In fact, Figures 10(b), 10(c), and 10(d) clearly show nanoparticles located not only on the cell walls but also on a 3D network.

4.5. Mechanical Properties. The hardness, scratch resistance, and impact resistance of the different treated maple samples were evaluated and compared with the results obtained for the untreated sugar maple samples. As the species are hardwood, achieving improvement of the mechanical properties is a challenge.

4.6. Hardness. The results obtained with the Brinell modified hardness test are presented in Figure 11. These results show that the Brinell modified hardness of maple samples was improved by the ZrO_2 treatment. In fact, sol-gel treatment with ZrO_2 nanoparticles increases the hardness by 20% more than untreated samples. The other two treatments (SiO_2 and AlO(OH)) did not increase the hardness significantly. When referring to the Mohs scale hardness, AlO(OH) is 9.0, SiO_2 is 7.0, and ZrO_2 is 8.0. Sol-gel treatments with AlO(OH) would be expected to have the greatest hardness improvement, followed by ZrO_2, and then SiO_2. However, other factors such as the nature of the interactions between the inorganic materials and the wood cells (condensation on the cell walls or no), as well as gel retention, are also expected to play an important role in the mechanical properties. The microscopy images showed a better chemical grafting for ZrO_2 followed by AlO(OH) and SiO_2. It is indeed possible to see particles bonded on the cell walls for ZrO_2 and AlO(OH), but not for SiO_2. This proves that chemical grafting (condensation) to the cell walls is important in achieving an improvement of the mechanical properties, regardless of the Mohs hardness of the material used. It is also possible that the SiO_2 treatment leads to the leaching of some wood components which could reduce the hardness.

4.7. Scratch Resistance. Scratch resistance was evaluated by measuring the depth and width of the scratches prepared by the multi-finger scratch/mar tester. Figures 12 and 13 present the depth and the width of the scratches, respectively. For both parameters, the ZrO_2 treated maple samples led to the best results. In fact, with the ZrO_2 sol-gel process, the depth of the scratches was decreased by 50%, and the width by 20%. AlO(OH) treated maple samples also present a good scratch resistance compared with the untreated maple samples. Since AlO(OH) is harder than ZrO_2, the better performance of the ZrO_2 samples could be explained by the higher sol-gel retention. A more significant retention would lead to a denser material and this could help in improving the surface mechanical properties. The SiO_2 treatment did not show significant improvements. The lack of bonding between the sol-gel material and the wood (no condensation with the hydroxyl groups on the cell walls), as well as the low material retention, could explain these poor results.

4.8. Impact Resistance. The impact resistance of the different samples, treated and untreated, is presented in Figure 14. The

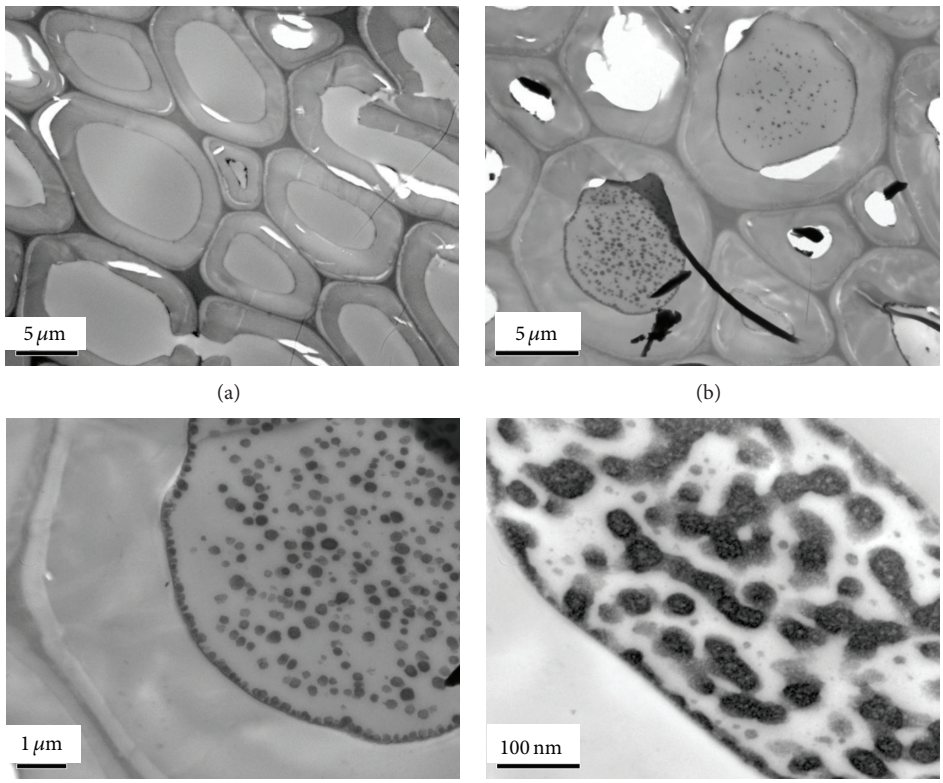


Figure 10: Transmission electron microscopy images of the wood cells of the maple samples impregnated with the ZrO_2 sol ((a) and (b)), ZrO_2 nanoparticles distribution in the wood cells.

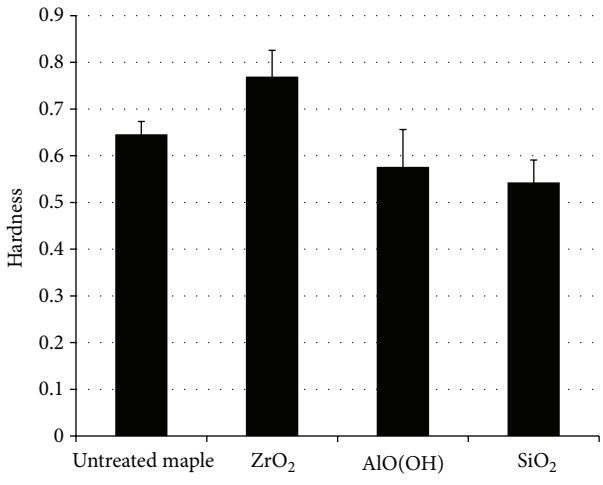


Figure 11: Brinell modified hardness of the untreated and sol-gel treated maple samples.

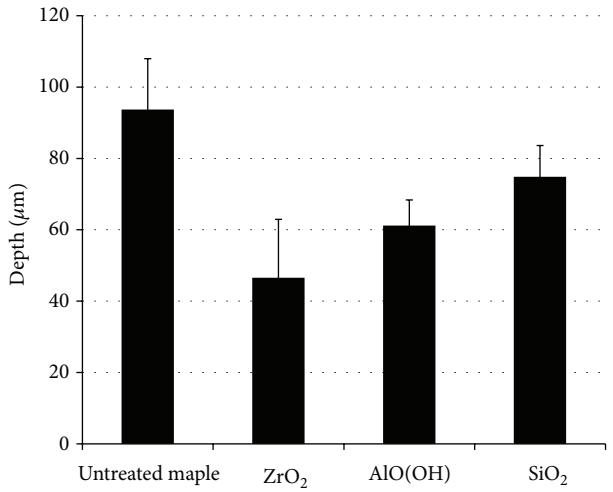


Figure 12: Depth of the scratches prepared on the untreated, ZrO_2, AlO(OH), and SiO_2 sol-gel treated maple samples.

ZrO_2 and AlO(OH) treated samples led to the best results with an impact defect decrease of 30%. The SiO_2 treatment did not seem to improve nor worsen the impact resistance. As previously stated, the gel retention and the good chemical grafting for ZrO_2 and AlO(OH) could explain the good results obtained in this section.

5. Conclusions

Sugar maple samples were treated with sols containing three different nanoparticles (AlO(OH), ZrO_2, and SiO_2), in order to achieve better mechanical properties. The different nanoparticles were selected for their good mechanical

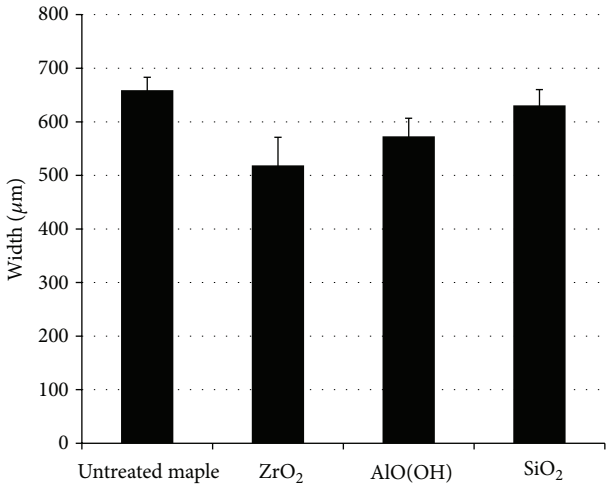


Figure 13: Width of the scratches prepared on the untreated, ZrO_2, AlO(OH), and SiO_2 sol-gel treated maple samples.

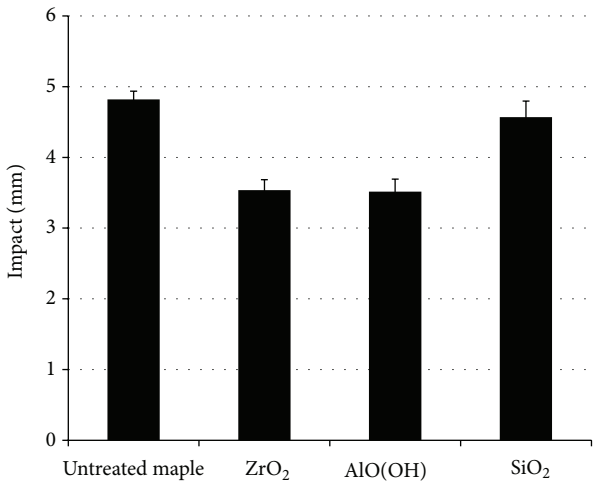


Figure 14: Impact resistance of the untreated and the sol-gel treated samples.

properties. The penetration of the sols was evaluated by two different kinds of microscopy and by weight gain.

The mechanical properties, that is, the hardness, scratch resistance, and impact resistance, were measured for the untreated and the sol-gel treated maple samples. The ZrO_2 treatment was found to be the most efficient treatment and led to the best mechanical performance, followed by the AlO(OH) treatment and the SiO_2 treatment. In fact, with the ZrO_2 sol-gel process, the hardness was increased by 20%, the depth of the scratches was decreased by 50%, and the width of the scratches by 20%, while the impact defect was decreased by 30%. These good results can be explained in part by the sol-gel retention, which was more efficient for the ZrO_2 than for the other two. Moreover, as reported in the literature, chemical bonding is expected to lead to good properties. In the case of ZrO_2 and AlO(OH), the sol-gel was attached to the cell walls, but that was not the case with SiO_2; the sol-gel material seemed to have only been deposited there. The improvement of the wood mechanical properties through this technique will help increase wood's service life and make it even more competitive in the market.

Acknowledgments

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