Paraloid B72 Versus Paraloid B72 with Nano-ZnO Additive as Consolidants for Wooden Artefacts

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This article presents the study of the opportunities and limits of employing nano-ZnO as additive to Paraloid B72 solutions used for consolidation of degraded, frail wood. The experiments were carried out on degraded spruce samples (Picea abies) in different conservation levels that were extracted from a frail wooden element of a massive gateway from the historic centre of Brasov (Romania) during its restoration. In this respect the samples were dimensioned at (20x20x30) mm and divided into three batches according to their initial conservation state: level I, very degraded samples with obvious loss of resistance and cohesion; level II, samples highly degraded but with structural cohesion and level III, samples with little degradation. Two consolidant formulations based on Paraloid B72 were used: a solution of 10% in ethanol and acetone mixture 1/1 (coded C_4) and a similar solution modified with nano-ZnO additive in proportion of 2.5 % (coded C_4-ZnO-2.5). All the samples were treated by total immersion for 1 hour in the prepared consolidants. The application treatment efficiency was evaluated by determining the consolidant uptake Csp [Kg/m^3] and retention WPG [%], while the actual effects of the consolidation procedure were evaluated by determining the compression strength parallel to the grain $\tau_{c//}$ [MPa] and the water absorption in a total immersion test, WA [%].

Keywords: wood consolidation, Paraloid B72, nano-ZnO, compressive strength, FTIR spectroscopy

Cultural heritage is by far a valuable set of material and spiritual assets. Most of these are inlaid in the cultural consciousness of people by common language and habits and the living environment but others may be gained by becoming aware of these assets in the surrounding environment. Simple hunting tools, household objects and furniture, shabby homes and luxurious palaces, they all bear the fingerprint of every culture.

Conservation of cultural heritage is hence essential and compulsory in order to ensure and transmit the cultural background of a people. An important operation in the conservation process is the consolidation treatment since most often old wooden objects present evidence of biological or chemical degradation which seriously affect their structural integrity and consequently reduce the mechanical resistance of the wooden material. The aim of such a treatment is to render back to a degraded and fragile material part of its mechanical strength in order to maintain at the highest level the authenticity of the restored object [1-12].

A common consolidation technique is consolidation with synthetic resins in solutions. Basically, a solid polymer with adequate physical, mechanical and durability properties is introduced into the degraded wood structure so as to fill, at least partially, the "extra-porosity" resulted from degradation. Diluted solutions of polymers, such as Paraloid B72, are most often employed, the process of consolidation having two phases: the "impregnation" phase, when the polymer solution is introduced into the wooden element followed by a conditioning phase when the solid polymer is fixed within the wooden structure and solvents evaporate. The techniques usually employed in a consolidation treatment are total immersion, vacuum impregnation and injection, the technique being chosen in accordance to the particularities of the object.

The development of new materials and methods of consolidation characterized by improved efficiency, potential reversibility and re-treatability is a subject of worldwide interest in conservation specific research [2, 13-17].

Previous research of the authors, including research of Paraloid B72 solutions modified with nano-ZnO additives, focussed mostly on the factors which influence the efficiency of the treatment in terms of uptake of consolidant solution, retention and distribution of solid consolidant into the wooden structure [16]. Therefore, this was conducted on small samples of sound poplar and spruce wood to ensure the uniformity of the treated material. Poplar, linden and spruce wood is the most common used in manufacturing artefacts, mainly with polychrome layers [10-12].

The present research is closer to real practical applications by employing degraded wood specimens in different conservation levels (extracted from a massive wooden gateway from the historic centre of Brasov, Romania that was restored during the year 2010), by directly assessing the effects of the consolidation treatment on the physical and mechanical properties of treated wood, as a function of the consolidant formulation and initial conservation level of the wooden material.

The main aim was to study the opportunities and limits of modifying a widely employed consolidant (Paraloid B72) by adding a nano-ZnO dispersion of 40% in ethanol. The experiments were carried out on old, degraded spruce wood samples; at different levels of degradation. The specific objectives of the research were:

-assessing the treatment efficiency of a simple technique by adequate quantitative and qualitative indicators;

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-determining the efficiency of Paraloid B72 as a consolidant for degraded spruce wood with different initial conservation levels;

-determining the influence of nano-ZnO additives upon the consolidation efficiency;

-analyzing the changes in the wood properties after consolidation, depending on the consolidant formulation and the initial conservation level of the wooden material.

The effect of the nano-ZnO additive on the efficiency of Paraloid B72 was studied in two phases characteristic to a consolidation process with resins in solution: “the impregnation” phase and the final state after solvent volatilization. The consolidant uptake and retention were considered as treatment efficiency indicators; the actual consolidation effects were related to the physical and mechanical properties of treated wood. The presence of the consolidants inside the final consolidated material was demonstrated by FTIR analysis.

Experimental part

Materials and methods

Paraloid B72 Treating Solutions

Paraloid B72 (from CTS Romania) was employed as a polymer matrix for the ZnO nano-insertions. The nano-ZnO additive was used under the form of a nano dispersion of 40% in ethanol (supplier: Sigma&Aldrich). Paraloid B72 was chosen as a polymer matrix due to its extensive use in conservation – restoration practice [13-15].

Paraloid B72 was prepared as a solution of 10% in a mixture of acetone and ethanol 1/1, coded C_4, the formulation of this basic Paraloid B72 solution (solvent type, concentration) being based upon previous experimental results [16].

The second solution was formulated from the basic solution C_4, by adding nano-ZnO in an amount of 2.5% (code C4-ZnO-2.5). In choosing the concentration of the nano-ZnO additive to be added to the basic solution, previous experimental results regarding the influence of the nano-ZnO concentration upon the consolidant uptake were taken into consideration [16, 17].

Wooden Samples

Degraded spruce wood (*Picea abies*) from two elements of an old wooden gateway from the historic centre of Brasov, replaced during its functional restoration in 2010, was employed in this research (fig. 1).

Before dimensioning the wooden elements into experimental samples, the oil paint layer was stripped off entirely by hot air. This allowed a first visual assessment of the wooden species and of the conservation state. The two elements, which had been close to soil contact were fragile and presented active insect attack at their bottom part. A better conservation state was noticed towards their upper parts which were not as close to the soil as the bottom part. Accordingly, three types of specimens were obtained as a function of their initial conservation state: specimens in conservation level I (CL I) - severely degraded samples extracted from the bottom of the rail, presenting obvious loss of mechanical strength and cohesion; specimens in conservation level II (CL II) - samples with a high degradation but with structural cohesion, extracted from the central zone of the wooden rail and specimens in conservation level III (CL III) - samples with little degradation and good structural cohesion, extracted from the upper part of the wooden element (fig. 1.b). A batch of ten specimens was obtained for each conservation level.

The samples were dimensioned at 20x20x30mm (radial x tangential x longitudinal) and conditioned under laboratory conditions, at a temperature T = 20±2°C and a relative humidity RH = 55±5% until constant weight was reached. The conditioning period before applying the consolidation treatment was around 30 days.

The Consolidation Treatment

The degraded specimens were treated with the two prepared consolidation products by total immersion at room temperature for 1 h. During the immersion treatment, the samples were fixed in a stainless steel device to keep them submerged entirely in the treating solution (permanent liquid contact to all surfaces). During the treatment, the samples were kept in airtight plastic boxes to refrain solvent evaporation. After treatment, the samples were kept in a well ventilated air cabinet to allow solvent evaporation and then they were reconditioned until constant weight, until a temperature T = 20±2°C and a relative humidity RH = 55±5% were reached.

Evaluation of Consolidation Treatment

Efficiency of the Treating Technique

Consolidant Uptake and Retention

The purpose of a consolidation treatment is to ensure a better internal structural cohesion and improved mechanical strength and, therefore, filling the voids resulted inside the wooden structure as a consequence of degradation phenomena, at least partially, is necessary. With this respect, a higher retention of consolidant and a deeper penetration are desirable.

Fig.1. The gateway before restoration: bottom wooden elements used as experimental material; division according to initial conservation levels

The efficiency of the applied consolidation treatments was evaluated quantitatively by the gravimetric method, based on samples weighing before and after the treatment, in the two phases characteristic to a consolidation process with resins in solution: "the impregnation" phase and the final state of the consolidated material after solvent volatilization. Accordingly, the solution uptake Csp [Kg/m^3] and the retention of solid consolidant WPG [%] were determined and considered as quantitative indicators of the treatment technique efficiency. It was considered that the increase in mass of the consolidated samples was the result of the consolidant uptake and retention into the wooden structure. The experimental procedure used to determine the consolidant uptake and retention as well as their mathematic formulae are those depicted in [16, 18].

Investigation of Consolidant Penetration by FTIR spectroscopy

FTIR spectroscopy was used to determine the presence and the penetration of the used consolidants applied by total immersion treatment. A Perkin Elmer spectrophotometer BX2 equipped with ATR system was employed for this investigation. The spectra were registered in reflectance mode in the range of 4000- 600 cm-^{1} at a resolution of 2 cm-^{1}; four scans were performed for each spectrum.

For this investigation, wood samples were extracted by drilling from both untreated (control) and treated samples, after the compression test, from two different areas: an area which presented good structural cohesion and a zone which presented fissures as a result of the applied compression force. The wooden powder was investigated by FTIR spectroscopy without further grinding.

Reference FTIR spectra were also recorded for the consolidation products: Paraloid B72, nano-ZnO dispersion in ethanol and Paraloid B72 with 2.5% nano-ZnO additive. For this purpose, these products were applied by brushing in a thick layer on glass lamella and left to dry (solvent evaporation) in a plastic box for two months.

Effects of the Consolidation Process

In order to study the effects of the applied consolidants and treating technique upon the physical and mechanical properties of the treated material, two tests were undergone for each conservation level. The first test was a water immersion test during which the water absorption WA [%] [equation (1)] after different periods was calculated. The second test was a compression test to determine the compressive strength parallel to the grain $\tau_{c//}$ [MPa] [equation (2)].

The water immersion test was performed on a batch of four samples (untreated and treated samples) as follows: the samples were weighed initially (m_i), submerged entirely into distilled water for different time intervals (1h, 2h, 3h and 24h) and weighed immediately after each time interval (m_{u1}, m_{u2}, $m_{u3,}$ m_{u24}). At these points, water absorption values WA [%] were computed:

$$A = 100 * \frac{(m_u - m_i)}{m_i}\ [\%] \qquad (1)$$

where:

A = water absorption of the wooden samples, in [%];
$m_{u=}$ mass of the moist sample after the consolidation treatment, in [g];
m_i = initial mass of the sample, in [g].

The mechanical and elastic characteristics of the treated samples were reflected by the compression test parallel to the grain performed according to SR ISO 3132:2008 on a ZWICK – model BT1- FB050TN.D30 machine. A batch of six specimens was used for each conservation level. The compressive strength for each sample was computed automatically by the soft of the machine according to formula from equation (2). Macroscopic investigations (visual assessment) were also performed before and after the compression test.

$$\tau_{c//} = \frac{P_{\max}}{A_{sample}} [\text{MPa}] \qquad (2)$$

where:

P_{max} = force applied to the wooden samples, in [N];
$A_{sample=}$ area of the treated sample, in [mm^2];

Results and discussions

Efficiency of the Treating Technique

Consolidant Uptake and Retention

The treatment of the degraded spruce specimens by total immersion into Paraloid B72 solutions (C_4 and C_4-ZnO-2.5) led to different values of solution absorption (uptake), expressed as Csp [Kg/m^3], as a function of the initial conservation level of the wooden sample (fig. 2.a).

It is obvious from the graph that, as expected, the most degraded samples (conservation level I) absorbed the maximum amount of consolidant solution. There were also some differences in the actual mean values of the consolidant uptake depending on the consolidant type: the highest value was registered when treating with C_4-ZnO-2.5: 457.51±51.39 [Kg/m^3] compared to 419.53±94.06 [Kg/m^3] for the simple Paraloid B72 solution, though this difference does not seem to be statistically important, considering the high standard deviations associated to this determination, explainable by the non-homogeneity of the degraded material (fig. 2.).

In contrast, the differences in terms of consolidant uptake in relation to the initial conservation state were significant. Thus, the samples extracted from the upper part of the wooden

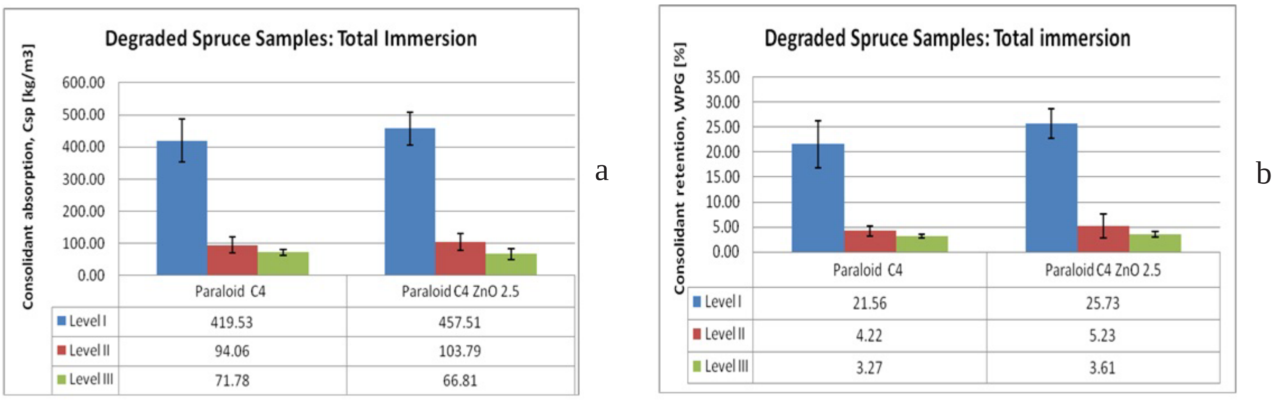


Fig. 2. Comparative consolidant uptake (a) and retention (b) of spruce degraded samples in different initial conservation levels (I, II, III) after treatment by total immersion with Paraloid B72 solutions (C_4 and C_4-ZnO-2.5): a – uptake, b – retention

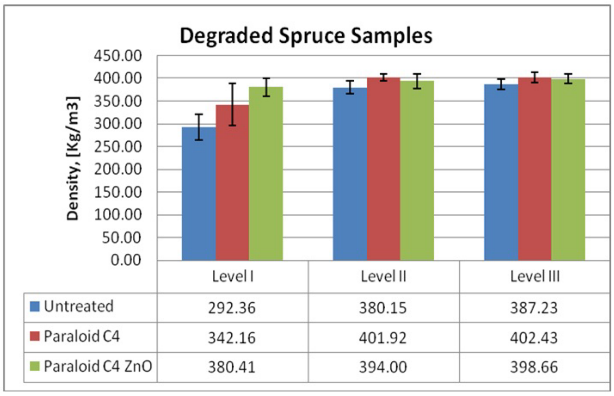
element which had the best conservation state (level III) absorbed the lowest amount of consolidant solution, regardless its formulation with or without nano-additives. A slight difference between the mean values was registered again, but this time in the favour of the solution without nano-ZnO: 71.78±9.82 [Kg/m^3] compared to 66.81±16.25 [Kg/m^3] for C_4-ZnO-2.5. For the samples from the central part of the wooden element, which presented a moderate degradation (level II), a higher mean consolidant uptake value was registered in the case of Paraloid B72 with nano-ZnO additive compared to the solution without additive, respectively 103.79±26.40 [Kg/m^3] and 94.06±24.90 [Kg/m^3].

The actual values that reflect the retention of the solid consolidant into the wooden structure and could be correlated to the expected consolidation effects are the weight percent gain WPG [%] values depicted in figure 2.b.

It is perfectly expectable that these values will depend upon the consolidant uptake (fig. 2. a); a high consolidant uptake would therefore lead to high consolidant retention. As a consequence, the most degraded samples (level I) which registered the highest consolidant uptake in the case of the two consolidants also registered the highest consolidant retention (mean values between 21.56-25.73%). Significantly lower values of WPG were obtained for the less degraded samples (level II and III). The highest WPG values were registered when treating with Paraloid B72 10% with nano-ZnO additive compared to Paraloid B72 irrespective of the degradation level (fig. 2.b). The slightly higher solids content of the Paraloid solution modified with 2.5 % ZnO could explain this situation even for the cases where a slightly higher solution uptake was registered for the samples treated with Paraloid B72 solution without nano-ZnO (samples in conservation level III).

The efficiency of a consolidation treatment may also be evaluated by the increase of density ρ[Kg/m^3] of the specimens after the treatment (fig. 3).

The initial density of the samples reflected well the degradation level, a decrease in density being registered with the increase in degradation. Thus, if for conservation level III, representing spruce wood in fairly good conservation state, a mean density value of 387.23±10.82 [Kg/m^3] was calculated, the respective value was only 292.36±28.07 [Kg/m^3] for the mostly degraded samples categorised in the conservation level I; the degradation level is obvious from the computed data, the density of sound spruce being 440-460 [Kg/m^3]. This is because degradation was mostly due to the insects attack resulting in galleries within the wooden structure, so that more galleries meant lower density and a higher loss of mechanical resistance and cohesion as result of structural damage.



	Level I	Level II	Level III
🟦 Untreated	292.36	380.15	387.23
🟥 Paraloid C4	342.16	401.92	402.43
🟩 Paraloid C4 ZnO	380.41	394.00	398.66

Fig. 3. Comparative density data of spruce degraded samples in different initial conservation levels (I, II, III) before and after

The treatment with Paraloid B72 solution without nano-ZnO led to an increase in density of treated samples compared to the untreated samples: 402.43±11.24 compared to 387.23±10.82 [Kg/m^3] (level III); 401.92±7.42 compared to 380.15±13.50 [Kg/m^3] (level II) and 342.16±45.69 compared to 292.36±28.07 [Kg/m^3] (level I). It is obvious that this increase in density was the highest for the conservation level I, as these samples absorbed the highest amount of consolidant solution leading to the highest WPG value.

Similar results were obtained, as expectable, in the case of treatment of wooden samples in different initial conservation levels with Paraloid B72 solutions modified with nano-ZnO additive. The mean density values for the treated wood compared to untreated wood varied as follows: 398.66±10.45 compared to 387.23±10.82 [Kg/m^3] (level III); 394.00±15.89 compared to 380.15±13.50 [Kg/m^3] (level II) and 380.41±19.63 compared to 292.36±28.07 [Kg/m^3] (level I). The highest increase in density of the most degraded samples (level I) was obtained when treating with Paraloid B72 with 2.5% nano-ZnO additive.

The registered modifications in density resulted in fact from the retained consolidant within the wooden structure after the solvent evaporation, so that very good linear mathematical correlations could be obtained between the percentage density increase and the WPG values, irrespective of the initial conservation level of the wooden material before treatment, as shown in figure 4.

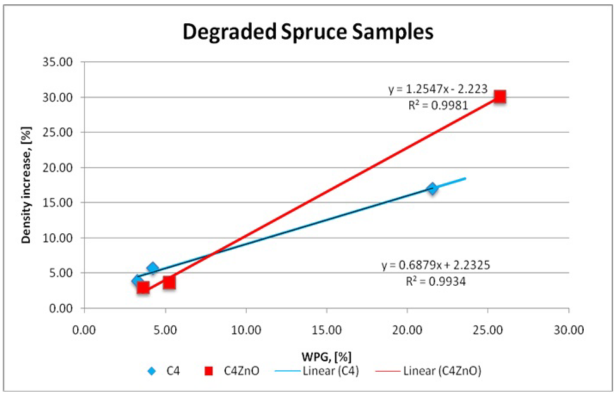


Fig. 4. Correlation between density increase of the treated samples and the consolidant retention WPG [%] (consolidants C_4 and C_4-ZnO-2.5)

Consolidant Penetration - FTIR spectroscopy

The reference spectra recorded for the consolidation products used in this research namely: the synthetic acrylic copolymer Paraloid B72 (copolymer methyl acrylate and ethyl methacrylate), ZnO nano dispersion in ethanol 40% and Paraloid B72 with 2.5% nano-ZnO additive are presented in the figure 5.

An important characteristic absorption band for Paraloid B72 is at approximately 1720 cm^{-1}. This corresponds to the ester carbonyl group, usually identified at 1730-1740 cm^{-1} and is a very important band characteristic to Paraloid B72, an acrylic and methacrylic ester [19-21]. On the other hand, this is not a band really characteristic to wood, as carbonyl groups, though present in some wooden components (e.g. hemicelluloses), are only in small amount [22-24]. Accordingly, this band is present in the wood spectra more like a shoulder than a distinct band (fig. 6). Therefore, the presence of a distinct band at 1720-1730 cm^{-1} in the FTIR spectra of treated wood would outline the presence of a carbonyl bearing compound in wood, namely of Paraloid B72 in the case of this research [19].

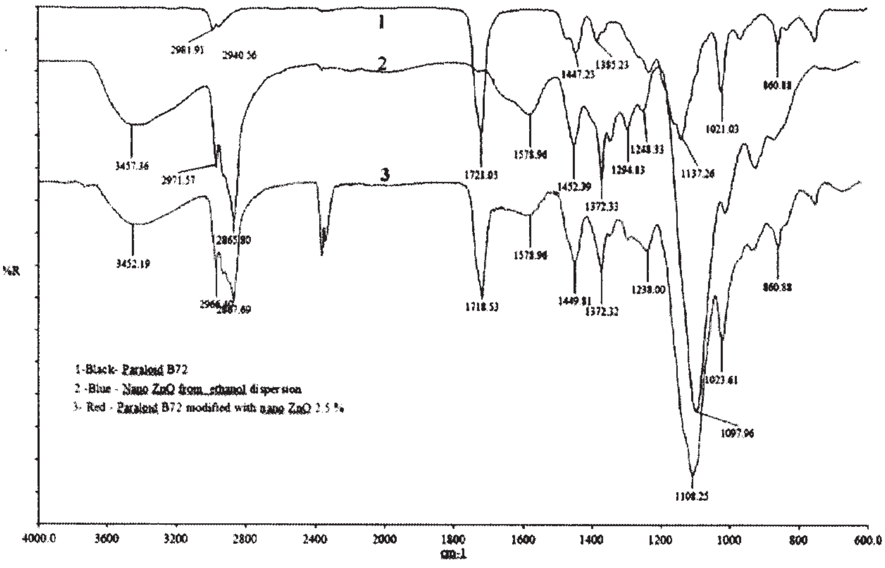


Fig. 5. Comparative reference spectra of the consolidation products employed in this research: Paraloid B72 (black), nano-ZnO from dispersion in ethanol (blue), Paraloid B72 modified with 2.5% nano-ZnO (red)

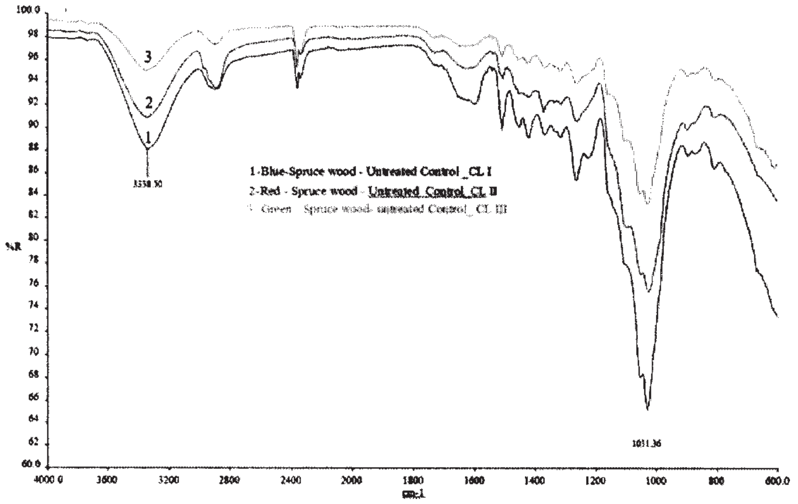


Fig. 6. Reference spectra for untreated degraded wood samples in different initial conservation levels (I, II, III)

The FTIR spectra of nano-ZnO as a film formed on a glass lamella from a nano-ZnO dispersion of 40% in ethanol is quite complex, with many absorption bands due very likely to the organic precursors employed for the preparation of nano-ZnO dispersion and to the adsorption of water at the surface of nano-ZnO particles [25-28]. Thus the broad band at 3450 cm^{-1} is characteristic to free –OH groups and organic compounds or water, while the band with a double peak at around 2970 and 2865 cm^{-1} corresponds to -CH stretching. The vibrational band at 420 -460 cm^{-1} characteristic to metal–oxygen in ZnO reported in literature [25-28] could not be registered being outside the recording domain.

In this context, the absorption band considered representative for the identification of nano-ZnO in the Paraloid B72 matrix was the absorption band with two maximum absorption peaks at 2865 and 2971 cm^{-1}. This band could be easily identified in the spectra of the Paraloid B72 modified with nano-ZnO additive, as a band with two peaks at 2867 and 2966 cm^{-1} (fig. 5). A similar band with two peaks at around 2850 and 2930 cm^{-1} was reported by Venkatachalam and Kanno (2009) on FTIR absorbance spectra of nano-ZnO thin films deposited onto glass substrate by pulsed laser.

The reference spectra corresponding to the untreated wooden specimens in the three conservation levels are presented in figure 6.

The main absorption bands of the wooden samples were assigned according to the information from literature [19, 23]. Examining the spectra of control wood (untreated) it

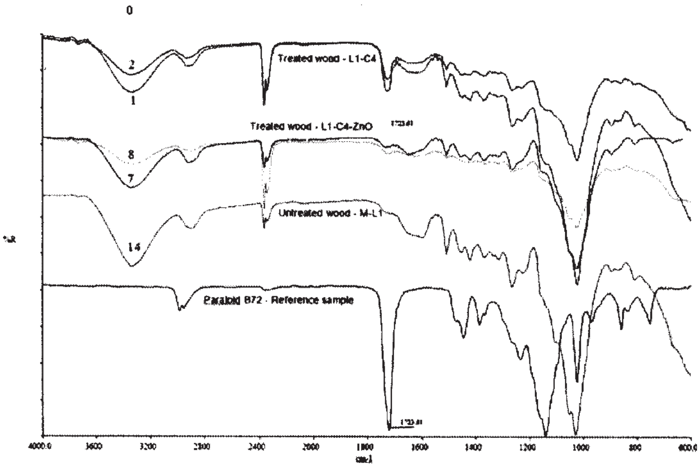
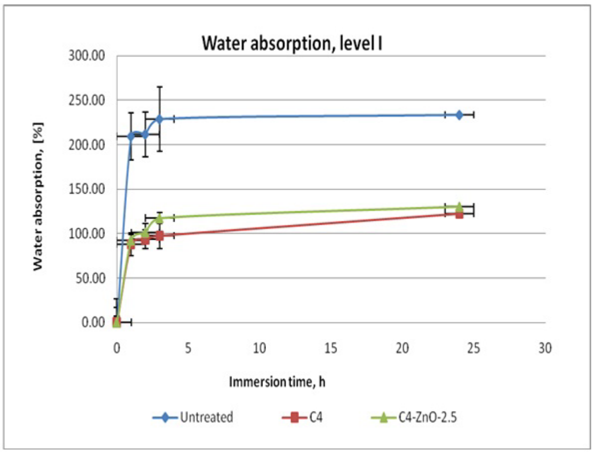
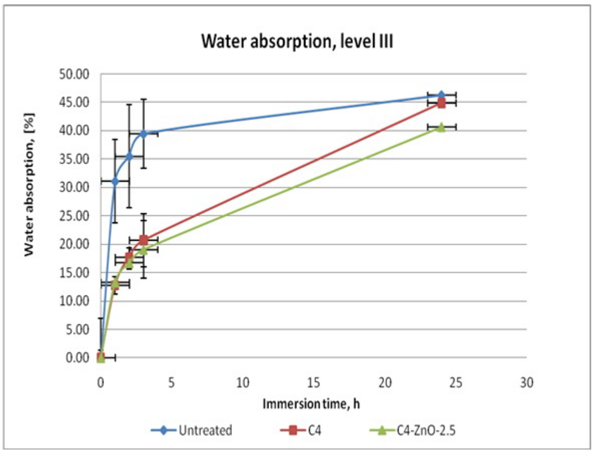


Fig. 7. Comparative spectra of untreated, degraded spruce wood (conservation level I) and specimens treated with Paraloid B72 - solutions C_4 and C_4 ZnO 2.5





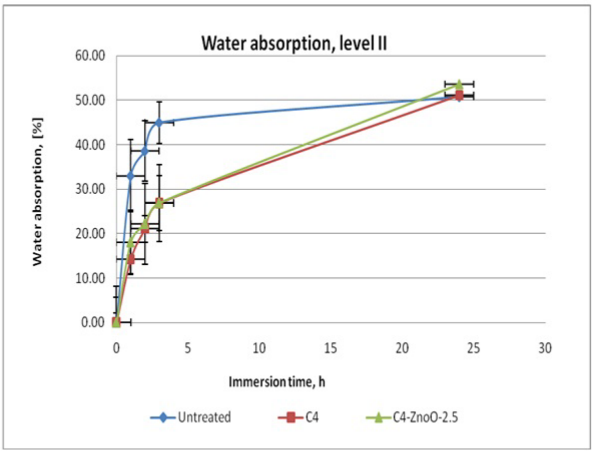


Fig. 8. Comparative water absorption curves for degraded untreated and treated spruce samples in Paraloid B72 solutions (C_4 and C_4-ZnO-2.5); a - conservation level I; b - conservation level II, c - conservation level III

can be observed that the strongest absorption bands are those at ~3338 cm^{-1} attributed to the -OH groups and ~1021 cm^{-1} attributed to cellulose (C-O in pyranose ring), which are important and abundant characteristic structural elements of wood.

The comparative spectra of degraded untreated wood and treated wooden specimens alongside those of the reference treating products are presented in figure 7, for samples with initial conservation level I (the most degraded ones). Similar spectra were obtained for the untreated and consolidated wood with initial conservation level II and III.

The analysed wood dust (powdered sample extracted by drilling) from the areas with good structural cohesion are marked with 2 (treated with C_4) and 8 (treated with C_4-ZnO-2.5) while the dust extracted from broken areas are marked with 1 (C_4) and 7 (C_4-ZnO-2.5). The spectra 1 and 2 clearly show the presence of Paraloid B72 in the powdered samples extracted from the treated wood specimens by the distinct evidence of the absorption band at ~1723 cm^{-1}. In the case of the samples treated with Paraloid B72 with nano-ZnO additive (spectra 7, 8 in fig. 7) a similar band at ~1723 cm^{-1} is less evident but still present, which could suggest a diminished amount of Paraloid B72 in the analysed sample. It has to be remarked however, that this was not a quantitative analysis and the manner of extracting the powdered sample for FTIR by drilling from surface to inner of the test samples could result into a non uniform material in terms of consolidant content, as more consolidant is expected to be on the surface of the samples compared to the inner part and more in the areas with insect galleries than in the more compact areas of the wooden samples.

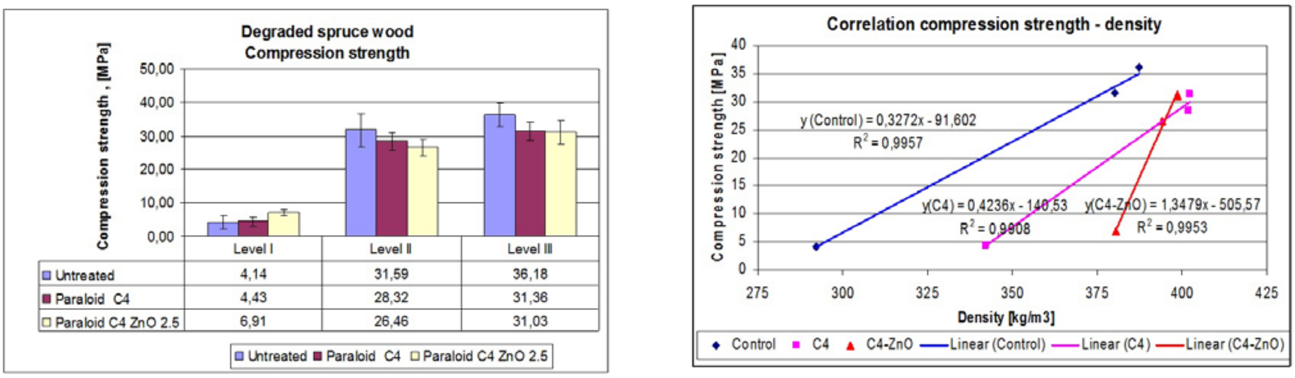
The presence of nano-ZnO additives could not be detected by the FTIR spectra of the samples treated with Paraloid B72 modified with nano-ZnO. The band with double peak aspect at ~ 2865 – 2971 cm^{-1} which was evident on the spectra of reference treating products for nano-ZnO and Paraloid B72 modified with nano-ZnO (see fig. 5) could not be detected on the spectra of treated wood. The small concentration on nano-ZnO in the treating product corroborated to the small amount of Paraloid B72 in the treated wood could be an explanation. Moreover, that double peak band is not really characteristic to ZnO but to the organic materials present on the surface of nano-ZnO as result of its preparation from organic precursors, and, perhaps, a registration of FTIR spectra down to 400 cm^{-1} could have proved the presence of ZnO by the characteristic absorption band at 420-460 cm^{-1}.

However, it has to be noted as a positive aspect that in all the cases (all conservation levels) the FTIR spectra proved the presence of Paraloid B72 inside of the treated wood, as a result of the penetration of consolidants solution into the wood structure.

Effects of the Treating Technique

Water Absorption Test

A target effect of a consolidation treatment is a better behaviour in presence of water. To evaluate the effect of the applied consolidation treatments upon the water resistance of the treated samples, a water immersion test was performed and the water absorption after different immersion times was determined. The effect of the consolidation treatment on the water behaviour of spruce wood in the three different initial conservation levels is well illustrated by the curves in figure 8. These curves are plotting the water absorption as a function of the immersion time. For the specimens with a better initial conservation level (levels II and III) which absorbed and retained less consolidant, the treatment led only to a delay in water absorption during the first 3h of immersion, after 24 h of immersion in water the specimens absorbing almost the same amount of water as the untreated ones.



	Level I	Level II	Level III
Untreated	4,14	31,59	36,18
Paraloid C4	4,43	28,32	31,36
Paraloid C4 ZnO 2.5	6,91	26,46	31,03

Fig. 9. Compression test parallel to the grain - untreated versus treated degraded spruce samples: a - Comparative data of compressive strength, b - Correlation between the compressive strength and the density of the samples

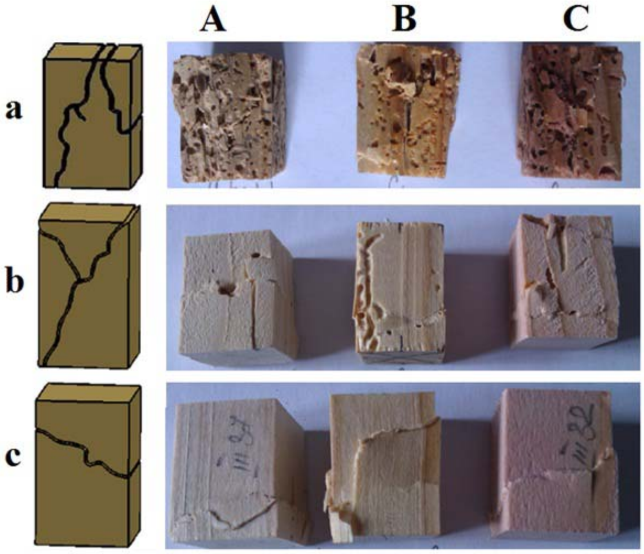


Fig. 10. Cracking models of the untreated versus treated samples resulted at compressive strength test: A – untreated samples; B –sample treated with Paraloid C_4; C –sample treated with C_4-ZnO-2.5: a – CL I, b – CL II, c – CL III

As the effect of the addition of nano-ZnO is concerned, it can be said that ZnO did not improve the water behaviour of the treated samples, the following data being registered after 24h immersion time: 122.57 [%] (C_4) compared to 130.35 [%] (C_4-ZnO-2.5) for CL I; 51.10 [%] (C_4) compared to 53.57 [%] (C_4-ZnO-2.5) (CL II) and 44.86 [%] (C_4) compared to 40.66 [%] (C_4-ZnO-2.5) for CL III (fig. 8).

Compression Test

The compression test parallel to the grain outlined that the consolidants employed did not actually impart an increase in the compresion strength (fig. 9.a). This may be explained by the insufficient treating degree (one immersion) and relatively moderate to low WPG values. It could be assumed that the repetition of treatment (repeated immersions) or a more efficient treating procedure (long time immersion, vacuum impregnation) would lead to higher strengths. Secondly, the compression test ussually asks for larger batches of samples; the reduced number of specimens however limited the test to small bathces. Last but not least, the anisotropy of degradation leading to a very non –uniform material, with differences in terms of degradation and density even among the samples from a certain initial conservation level, must have influenced the results of mechanical tests.

In order to have an insight on how much the differences in density between the tested samples might have influenced the results of compression test, the actual compression strength values were plotted against the density of the tested samples (from all the three conservation levels) for the three series of samples: untreated controls, samples treated with C_4 and samples treated with C_4-ZnO-2.5 (fig. 9.b). Very good mathematical correlations compression strength – density were obtained for all the three series of samples. It has to be remarked that in the mathematical correlation relations the slope of the regression lines compression strength- density increases from control samples to samples treated with C_4 and to samples treated with C_4-ZnO-2.5. This could actually suggest a real effect of consolidation and even a positive effect of nano-ZnO. However, more research on larger batches of samples is necessary for a final conclusion (fig. 9).

The cracking models of the untreated and treated specimens matched the patterns depicted in the standard SR ISO 3132:2008: longitudinal cracks in one or several tilted planes were mostly present (fig. 10.a-c.). This phenomen is best noticed at the treated samples, conservation level I; crushing also occured alongside cracks and fissures (fig. 10).

On the other hand, even though no increase in compression strength was registered, the cohesion of the consolidated samples proved to be better than that of the untreated samples; the improved cohesion of the samples is due the partial filling of the voids by the consolidant.

Conclusions

The research studied comparatively the application treatment efficiency and effects of one consolidation procedure, total immersion, when treating old spruce specimens with synthetic consolidants of Paraloid B72 type without and modified with nano-ZnO additives.

The application treatment efficiency was evaluated by determining the consolidant uptake Csp [Kg/m^3] and retention WPG [%] and the actual effects of the consolidation procedure were evaluated by the water absorption in a total immersion test and compressive strength parallel to the grain $\tau_{c//}$ [MPa]. As a result of consolidant uptake and retention into the wooden structure, density modifications ρ [Kg/m^3] were also registered. FTIR investigation was undertaken to prove the existence and investigate the penetration depth of consolidants within the wooden structure.

The conservation degree (degradation level) influenced the consolidant uptake Csp [Kg/m^3], higher values being registered for the most degraded specimens (level I) and lower values for the samples that had very little degradation (level III). Similarly, the highest consolidant retention WPG [%] was registered at the samples which were severely degraded (level I), the lowest values being registered at the samples with little degradation (level III).

The density of the samples reflected well the degradation level, a lower density being registered for the more degraded samples. The consolidant uptake and retention led to an increase of density as a result of the partial filling of internal voids.

All the applied treatments improved the resistance to water of the treated samples. Still, at the samples which had a better initial conservation level, samples II and III, the applied treatment and consolidants only delayed the water absorption during the first 3h of immersion, after 24 h of immersion in water the specimens absorbing almost the same amount of water as the untreated ones. The samples which were severely degraded, level I, absorbed a small amount of water even after a 24h immersion time, the applied treatment and consolidant solutions being efficient.

The compressive strength parallel to the grain $\tau_{c//}$ [MPa] outlined that neither the consolidant formulation nor the treating technique applied in this study did actually impart an increase in the compresion strength. This may be explained by insufficient treating degree, only one immersion or the relatively moderate to low WPG values. It is therefore assumed that the repetition of treatment (repeated immersions) or a more efficient treating procedure (long time immersion, vacuum impregnation) would lead to higher strengths. Moreover, the non-uniformity of the degraded material and the differences in the actual density of the tested samples might explain these results. With this respect, very good mathematical correlations as regression lines compression strength - density were obtained for the three series of samples: untreated controls, treated with Paraloid B72 solution and Paraloid B72 solution modified with nano-ZnO. The different slopes of these regressions could actually suggest a real effect of consolidation and even a positive effect of nano-ZnO. However, more research on larger batches of samples is necessary for a final conclusion.

Finally, the FTIR spectra demonstrated the penetration of Paraloid B72 solutions into the treated specimens for all the conservation levels and both treating solutions. However, the presence of nano-ZnO additives could not be detected in the FTIR spectra of the samples treated with Paraloid B72 modified with nano-ZnO. The small concentration on nano-ZnO in the treating product corroborated to the small amount of Paraloid B72 in the treated wood, corroborated to the FTIR registering domain (4000 – 600 cm^{-1}) not including actually the region 420-460 cm^{-1} most characteristic to ZnO could explain this fact.

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