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Original article

Consolidating properties of Regalrez 1126 and Paraloid B72 applied to wood

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ABSTRACT

This study is aimed at an assessment of the properties of two polymeric products applied to Norway spruce (*Picea abies*) and White poplar (*Populus alba*) wood species. It contributes to ongoing research experiments on the consolidating properties of two synthetic resins and their potential synergic action on wood, resulting from their different interaction with the substrate: Paraloid B72 and Regalrez 1126. Experiments were carried out on a series of samples of the two wood varieties. The consolidants were applied alone and one after the other, with one coat of Regalrez and then one of Paraloid. Porosity and variations in pore size distribution were ascertained by mercury intrusion porosimetry (MIP). Colorimetric and IR spectroscopic measurements were also taken before and after aging by solar radiation and freeze/thaw cycles, to verify the possible slowing of photodegradation of the treated wood and the consolidating resistance. Results confirm that both products penetrate the wood with a different behaviour. After double treatment with Regalrez + Paraloid, a significant advantage was observed in terms of mechanical resistance and pore size distribution, although no advantages as regards resistance to photo-oxidizing processes or colour changes were observed.

1. Research aims

One of the most important aspects of the preservation of wooden artefacts is consolidation of decayed wood which, in the majority of cases, shows structural decohesion. One of the most common and most frequently criticized restoration operations is the application of synthetic products which can penetrate into the wood and restore sufficient mechanical resistance [1].

The choice of consolidating agent is essential to recover or try to improve the physico-mechanical characteristics of a wooden artefact, especially if it falls into the category of historical and artistic cultural heritage. The consolidating product has to be selected in relation to wood characteristics of the various degrees of penetration and different location inside the wood. For instance, Castelli et al. [2] hypothesized a higher consolidating efficiency of wood when it let follow one application of Regalrez 1126, a low molecular weight resin, with another of Paraloid B72, of higher molecular weight and different mechanical properties.

The present study was focused on behavioural characterization of the two products, first applied singly and then together, on a series of wood samples of two tree species belonging to the broadleaf and conifer classes, that have been both widely used in history of art [3,4] and found as archaeological wood [5], and studying their chemical–physical characteristics in comparison with identical samples subjected to solar aging and freeze/thaw cycles [6]. It is important to emphasize that these types of aging could not reproduce a real environmental condition in which a wooden building is placed, but we have chosen to perform these tests in order to create a proper stress condition to discriminate physical and chemical behaviour of the different treatments.

Study and analysis of these characteristics are extremely useful when restoring wood, since proper consolidating action against forms of degradation can be assessed and suitable strategies for conserving the artefact can be planned at the same time.

2. Materials and methods

2.1. Synthetic resins

Paraloid B72 (Rohm and Haas) is a well-known and studied acrylic resin [7–9] which has been and still is extensively used as an adhesive and consolidant for wood composing works of art [10,11]. This polymer is composed of two monomers, methyl acrylate and ethyl methacrylate, and it has high molecular weight.

The recently marketed Regalrez 1126 (Eastman Chemical Company) [12] is a low molecular weight aliphatic resin, resulting from polymerization after addition of hydrogenated styrene monomers. Regalrez is a hydrocarbon, cyclic, saturated compound which creates a product very similar to paraffin wax.

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2.2. Wood species

The woods used for experimentation were a conifer Norway spruce (*Picea abies*) and a broadleaf white poplar (*Populus alba*). They were chosen both for their historical use in wood artefacts especially in Italy, mainly painted, and for their differing macro- and microscopic characteristics. The two woods are similar as regards density, but have different mechanical behaviour. Poplar, a diffuse porous species, has a heterogeneous structure (tracheids and vessels), straight fibrous structure, and a modulus of elasticity and shrinkage which are lower than those of spruce, which has an only slightly impregnable heartwood. Poplar decays easily and has a tendency to crack. Spruce, with an undifferentiated heartwood, has a fine structure. Its tangential modulus of elasticity and degree of shrinkage are both higher than those of poplar and its heartwood is more impregnable than that of poplar.

Both woods are easy to work, even during gluing and dying operations, although in some cases the heartwood of spruce may change the colour, due to its high contents of resin. However, as both spruce and poplar have poor natural resistance to microbiological attack, they often pose serious problems of loss of homogeneity, cohesion and mechanical resistance, compromising their original function of supports for preparatory layers and paint.

2.3. Application of products and aging procedures

Three samples, measuring 3 cm × 3 cm × 2 cm, of the two wood species were prepared and each consolidant was applied to three samples.

The two consolidants were prepared in butyl acetate. The samples were immersed in the solutions and then characterized both before and after aging. Measurements were made at least 30 days after application. For each experiment, the averages of data obtained from each single sample of each series were calculated. In the double treatment, a 5% concentration of Regalrez 1126 was applied first and a 10% concentration of Paraloid B72 afterwards. Aging procedures were as follows: solar aging: 1000 hours on a rotating plate under an Osram Ultravitalux 300W solar lamp. This form of aging was performed in order to evaluate the behaviour of treated samples in respect of the solar irradiation.

In order to evaluate the behaviour of different treatments against thermal shock, freeze/thaw cycles were performed. In particular, four cycles of 144 hours each were conducted. After being immersed in water for at least 3 hours, the samples were taken to a temperature of −5 °C for 72 hours and then placed in an oven at 60 °C for another period of 72 hours.

2.4. Characterization and experimental testing

The treated but non-aged series of samples were characterized by means of porosimetry with an Autopore IV mercury porosimeter (Micromeritics). Maximum intrusion pressure was about 800 kPa.

The samples undergoing solar aging were characterized by Fourier transform infrared spectroscopy (FT-IR) and colorimetric tests, both before and after aging. FT-IR spectra were acquired on an FT-IR Spectrum 100 instrument (Perkin Elmer), equipped with a universal ATR, with range 450–4000 cm^{-1} and resolution 4 cm^{-1}. Colorimetric measurements were made with a Konica Minolta CM-2600d instrument, values being expressed in the CIE L*a*b system.

The series of samples undergoing freeze/thaw cycles were analyzed before and after aging, by measurement of size variations taken with a calliper (sensitivity 0.1 mm) and by macroscopic analysis, to assess any damage to the constitutive structure of the wood, such as deformation and cracking.

Table 1

3. Results

3.1. Porosimetry

The literature contains many works regarding porosimetric measurements by mercury intrusion to study the porous structure of wood [13–15]. Our measurements on poplar and spruce (Fig. 1) showed clearly different trends of curves and porosity values: in the 2–100 μm interval, porosity was 25 ± 1% for poplar and 30 ± 1% for spruce.

The poplar samples treated with Paraloid B72 and Regalrez + Paraloid B72 showed a significant reduction in porosity (−6 ± 2%), with a slightly lower value in the spruce samples. In samples treated with Regalrez alone, porosity was practically unvaried in both species (0 ± 2% for spruce; −2 ± 2% for poplar). The results with Regalrez may be due to its lower molecular weight: a reason it could be that it tends to penetrate more deeply into the cell wall respect to the lumen and leaving general porosity unaltered. Instead, Paraloid B72, of higher molecular weight, could tend to concentrate in the cell lumen and thus lowers porosity, also in the double treatment.

Table 2

3.2. Fourier transform infrared spectroscopy measurements

The progressive deterioration of wood exposed to solar radiation causes a fall in the content of hydroxyls, with a consequent increase in carboxyl groups [16]. Fig. 2 shows the FT-IR spectra for spruce and poplar in untreated samples (US). The main bands were assigned as follows [17–19]: 3300 cm^{-1} stretching of OH groups, 1736 cm^{-1} stretching of the C=O bond, 1638 cm^{-1} bending of water, 1596 cm^{-1} stretching of aromatic cycle of lignin, 1500 cm^{-1} aromatic groups of lignin, 1423 cm^{-1} cellulose, 1375 cm^{-1} symmetric bending of CH_3 groups of lignin and hemicellulose, bending of OH groups of polysaccarides, 1157 cm^{-1} asymmetric stretching of bridging oxygen, and 898 cm^{-1} cellulose bond.

In this work, we examined the stretching bands of OH and carbonyl groups, to measure photo-oxidative trends in samples.

Before comparing different spectra, they were normalised, it has been assigned absorbance value equal to one to the band at 1025 cm^{-1}.

Although variations in carbonyl groups (Fig. 3) cannot discriminate the efficacy of the products, they could indicate a close correlation with variations in the corresponding OH groups. Vari-

Table 1
Treatments and aging procedures carried out on sample series.

Norway spruce/White Poplar	Analyses			
	US	R	P	R + P
Not aged	Porosimetry, colorimetry, FT-IR, size	Porosimetry, colorimetry, FT-IR, size	Porosimetry, colorimetry, FT-IR, size	Porosimetry, colorimetry, FT-IR, size
Solar radiation	Colorimetry, FT-IR	Colorimetry, FT-IR	Colorimetry, FT-IR	Colorimetry, FT-IR
Freeze/thaw cycles	Size variations	Size variations	Size variations	Size variations

US: untreated; R: Regalrez 1126; P: Paraloid B72; R + P: Regalrez + Paraloid; FT-IR: Fourier transform infrared spectroscopy.

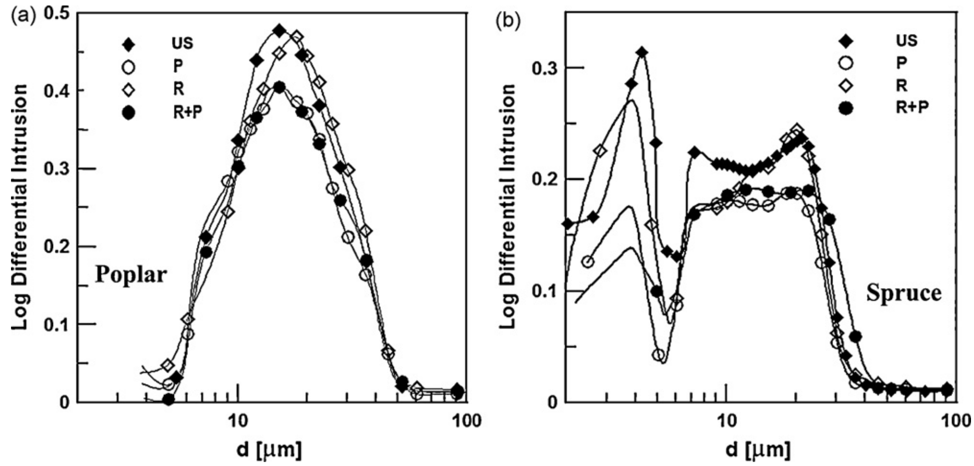

Fig. 1. Porosity curves for treated and non-treated samples of (a) white poplar and (b) Norway spruce.

Table 2
Porosity values measured on treated samples.

Spruce	Porosity (2 ÷ 100 μm) (%)	Poplar	Porosity (2 ÷ 100 μm) (%)
US	30 ± 1	US	25 ± 1
R	30 ± 1	R	23 ± 1
P	27 ± 1	P	19 ± 1
R + P	26 ± 1	R + P	19 ± 1

US: untreated; R: Regalrez 1126; P: Paraloid B72; R + P: Regalrez + Paraloid.

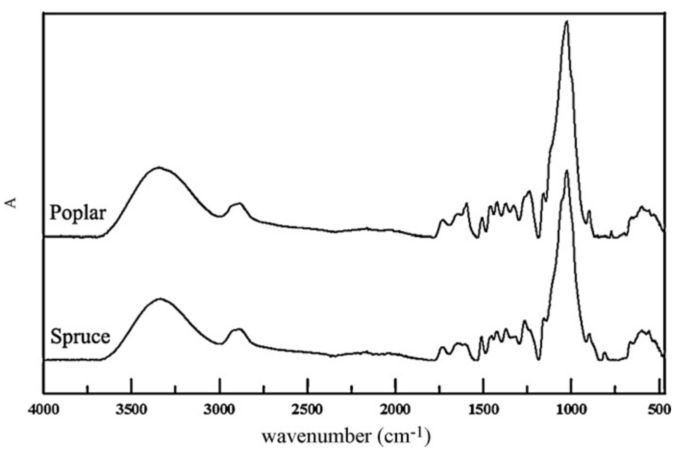

Fig. 2. FT-IR spectra of TQ poplar and spruce samples (untreated).

ations in the hydroxyl groups of samples treated with Regalrez only (Fig. 4) show higher resistance to photo-oxidation, and treatment with Regalrez + Paraloid, particularly in spruce, shows greater protection than that given by Palaroid alone.

3.3. Colorimetric measurements

Variations in colour are due to photochemical oxidation processes and the consequent formation of new chromophore groups [20]. Fig. 5 shows colour variations before and after 500 and 1000 hours of exposure to solar radiation.

The higher chemical stability of Regalrez to photo-oxidation is also shown by the colour gradients of the spruce samples, which show lower variations than US samples, those treated with Paraloid alone, and those receiving the double application. It is interesting to note that, after only one week of exposure, aged spruce samples already clearly showed variations in surface colour. Instead, poplar samples were more stable, as confirmed by colorimetric

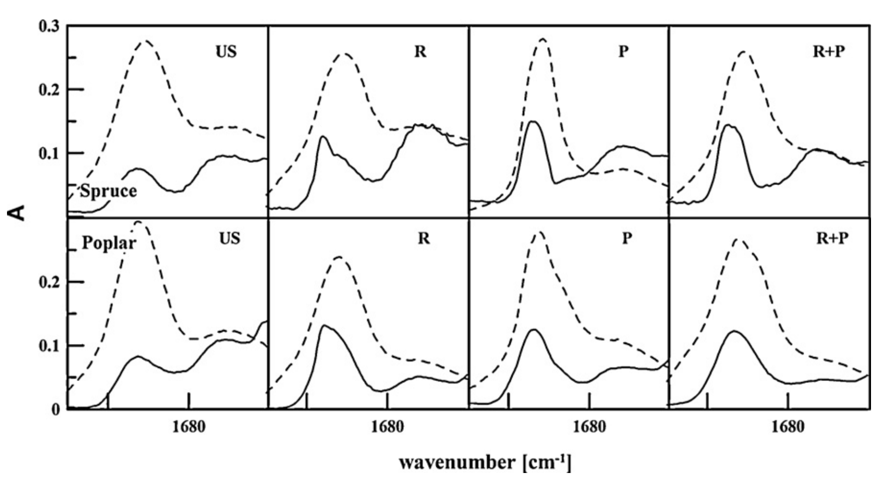

Fig. 3. Portions of FT-IR spectrum of carbonyl groups in samples of non-aged (continuous lines) and aged (dotted lines) spruce and poplar.

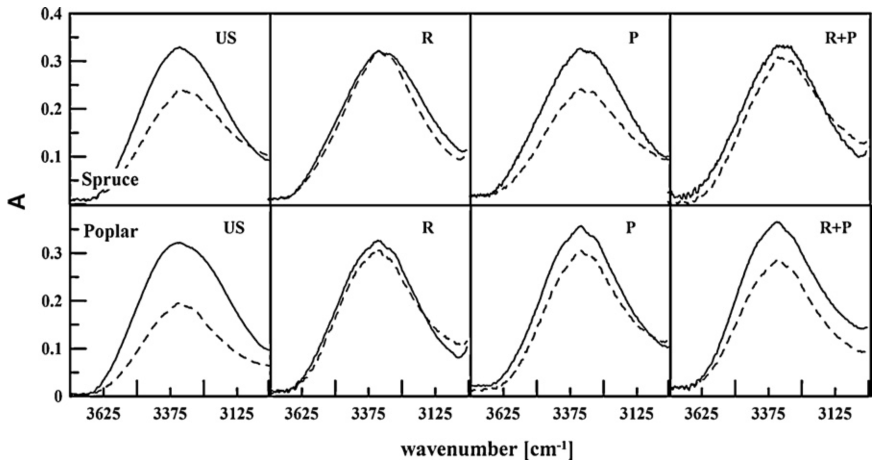

Fig. 4. Portions of FT-IR spectrum of hydroxyl groups in samples of non-aged (continuous lines) and aged (dotted lines) spruce and poplar.

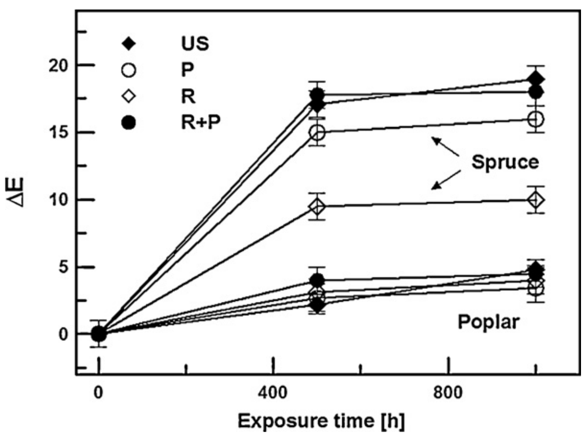

Fig. 5. Colour variations according to time of exposure to solar radiation, in treated and untreated samples.

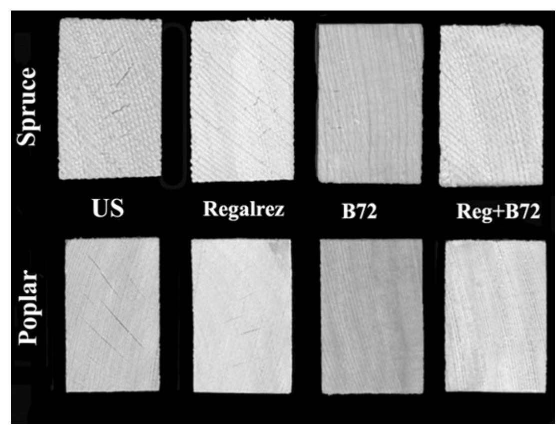

Fig. 7. Mechanical damage to samples after four aging cycles.

measurements, which did not show any significant variations in surface colour, either in US samples or any samples treated, including those receiving Regalrez. This different behaviour is attributed to the presence in conifers such as spruce of resiniferous channels containing easily oxidizable material, which can cause greater variations in colour, and reveals more accurately how applied products behave than is the case in poplar.

3.4. Size changes and macroscopic observations

Thermal shock of samples (freeze/thaw cycles) aimed at subjecting the structural components of wood to stress and at the same time causing high chemico-physical tension in the applied polymers. The resulting deformations thus do not correspond to the normal volumetric shrinkage caused by the hygroscopic gradients which affect the contents of saturated water in cell walls. In order to assess the effects caused by this type of mechanical stress, the samples were measured before and after aging, and a qualitative comparison of their resistance was made, as shown by cracking or other mechanical damage. It is important to note that freeze/thaw cycles, which cause not only volumetric changes but also give rise to the formation of cracks, may cause an apparent size increase in samples at the end of the aging cycles, as shown in the case of the poplar US samples. This is due to the macroscopic characteristics of this wood, which tends to crack more than spruce.

Fig. 6 shows size changes in the three anatomic directions (longitudinal, radial, tangential) of the two woods after four aging cycles. The lower degree of shrinkage in all treated samples was

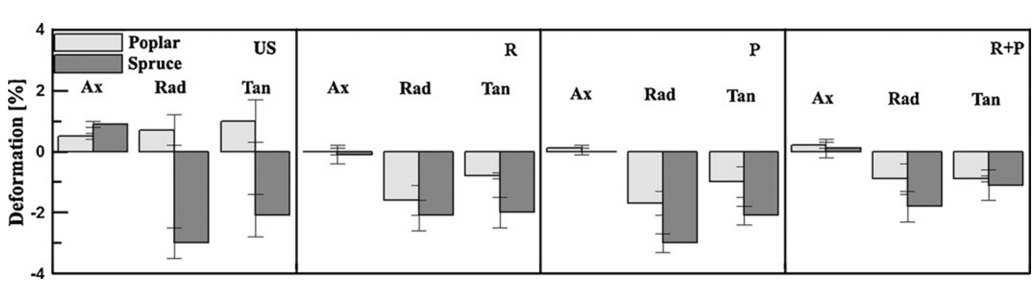

Fig. 6. Size variations in three anatomic directions (axial, radial, tangential) of treated and untreated samples after four aging cycles.

considerable with respect to US samples. In particular, treatment with Regalrez produced less physical deformation than that in samples treated with Paraloid alone. It was also interesting to note that the samples receiving two applications of consolidants showed less deformation than those treated with only one.

Macroscopic analysis of mechanical damage clearly showed that the untreated samples had more cracks, and that those treated with Regalrez were more prone to structural cracking (Fig. 7) than those treated with Paraloid, which provides greater mechanical resistance and structural cohesion. The double-treated samples also showed good behavior.

4. Conclusions

Porosimetric results seem to confirm how Regalrez does not change the porosity of white poplar or Norway spruce. Instead, Paraloid causes a significant reduction in porosity and thus acts more directly inside the cell lumen. These results seem to confirm the advantages of double application, with a different functional selectivity. FT-IR and colorimetric results (characterization of the two products on samples subjected to solar aging) show that Regalrez is more resistant to photo-oxidation than Paraloid, particularly in spruce, and that the former does not cause surface colour variations to such an extent as the latter. Double treatment does not show significant advantages in protecting the wood against photo-oxidation.

In the samples subjected to thermal shock (freeze/thaw cycles), Regalrez treated and Regarez–Paraloid treated samples give better results, with a reduction in porosity variations with respect to samples treated with Paraloid alone. This could be correlated to the greater penetration and thus consolidation of Regalrez in cell walls. In assessing the mechanical damage which thermal stress exerted on the samples, Paraloid treatment showed higher resistance and protection than that with Regalrez, partly due to its greater adhesion to the wood fibers. Double treatment shows a good level of protection against thermal aging.

In the light of these initial results and the need for further in-depth studies, double treatment – first with Regalrez 1126 and then with Paraloid B72 – shows that the two resins penetrate in different parts of the wood, with evident synergic advantages of reduced porosity variation and less mechanical damage (cracking and micro-fractures). Conversely, double treatment reveals lower resistance to oxidative processes and colour changes.

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