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Microcrystalline cellulose filled composites for wooden artwork consolidation: Application and physic-mechanical characterization

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ABSTRACT

Two types of historical wood (18th century) (*Juglans regia* and *Abies alba*) presenting different degradation conditions were consolidated through acetone solutions of microcomposites consisting of a commercial polymer (Paraloid® B72) often used for wood consolidation and two different amounts (5 and 30 wt%) of microcrystalline cellulose (MCC). As a comparison, the same tests were also performed on modern samples of the same types of wood in a well preserved state.

Rheological and mass variation measurements evidenced that the introduction of microfiller did not affect the viscosity and the water sorption of the neat resin to a significant extent. Moreover, mercury intrusion porosimetry highlighted how MCC filled composites were able to decrease the pore radius of treated wood samples, reaching values close to those of modern intact wood. Remarkably, the presence of MCC within Paraloid led to a positive enhancement of the stiffness and the flexural strength of treated damaged wood in both quasi-static and impact conditions, with the increase of the flexural modulus, the maximum stress and the rise of both initial and total impact absorbed energies. Additionally, an increase of the radial and tangential surface hardness due to the treatment with MCC filled composites was observed.

1. Introduction

Wood is one of the most used constituent materials for art objects. The historical wooden heritage is huge and varied. For instance, as far as the introduction of canvas, paintings had made on wood. But this material is very sensitive to decay and several kind of degradative processes can attack it [1]. In particular biological degradation is very common for most types of wood and their restoration is generally a critical issue. In fact, there are wood species that for their microstructure and porosity type are less resistant than others to biological attacks. Moreover, the degradation operated by living organisms is not always the same. Generally speaking, xylophagous agents can generate chemical, physical and/or mechanical decay in wood and one of the main effect of these degradative actions is the reduction of its mechanical strength [2,3]. In case of a critical conservation state of wooden artworks, conservators prefer to consolidate artworks applying synthetic resins by brush, spray, injection or direct immersion in order to allow the capillarity impregnation of the consolidating solution. Low pressure and vacuum impregnation chambers can be suitable to consolidate small historical objects as well. Thanks to their physical and mechanical properties and especially their good reversibility, thermoplastic polymers are preferred over thermosetting resins [4,5]. In the last years, new materials and new methods have been investigated to consolidate wood [6–8]. Despite this, Paraloid B72 is still one of the most utilized consolidant products and the one that guarantee to conservators good consolidating performance [9]. This polymer manifests good chemical stability, yellowing resistance and photo-thermal oxidation stability in comparison to other commonly used acrylic resins for art conservation [10].

This work proposes the composite technology approach for a possible increase of the Paraloid consolidating performance for various reasons. In fact, several studies reported in the open scientific literature are focused on the improvement of the durability of wood through chemical treatments [11–14]. Moreover, cellulose based fillers are certainly attracting scientific attention in the wood consolidation [15,16]. At the same time, the economic aspect related to the industrial production of new materials for a market niche, such as the art conservation field is a key issue. For this purpose, a microcrystalline cellulose (MCC) was added to Paraloid B72 in order to obtain microcomposites to be applied as consolidants for degraded wood. MCC was selected for its well-known reinforcing properties [17–19] and even for its chemical constituents that

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are the same of wood. Additionally, MCC is easy to source, conservators can handily use it, directly adding it into consolidant solutions, because MCC does not require any other chemical process to be applied. The aim of this work is the investigation of the effect of MCC introduction on the consolidating properties of a traditional polymer for wood preservation. The final goal is the improvement of the capacity of neat Paraloid to recover the initial mechanical properties of decayed wood through the addition of appropriate amounts of MCC.

2. Experimental

A thermoplastic acrylic resin (Paraloid B72 by Rohm and Haas, Germany) was used as polymer matrix. Microcrystalline cellulose powder (MCC) (Sigma Aldrich, USA) was selected as a filler. Composites with 5 wt% and 30 wt% of MCC were prepared by melt-compounding in a Haake Rheomix® internal mixer (temperature = 160 °C, rotor speed = 60 rpm, residence time = 5 min) and compression molding in a Carver hydraulic press (temperature = 150 °C, pressure = 4 MPa, time = 5 min). These formulations were dissolved in acetone making solutions at 10 wt% of neat Paraloid and corresponding microcomposites, to be applied on two species of historical degraded wood. The wood types selected for this work were a hardwood Persian walnut (*Juglans regia*) and a softwood European silver fir (*Abies alba*). The two wood samples presented different conservation states. The Persian walnut exhibited a critical and advanced biological decay with evident holes and tunnels made by larval worms that interested also the inner part of the wood. Even in the silver fir larvae holes and galleries were visible but not so diffused as in the walnut case. These two historical woods were chose for their different taxonomic family and degradation degree, in order to prove the consolidating properties of the neat Paraloid and the resulting microcomposites in various situations. As a comparison, all tests were also performed on modern samples of the same types of wood in a well preserved state. Prismatic specimens of each wood species (5 mm wide, 5 mm tick and 80 mm long) were impregnated with consolidants solutions by means of a brush. Two cycles of application for each face of specimens were performed on a Gibertini E42 electronic balance with a resolution of 10^{-4} g. In this way, the same amount of consolidants, about 130 mg, were applied on each face. After solvent evaporation, samples for physical characterization were dried under vacuum at 105 °C until a constant weight was reached and then conditioned in a climatic chamber (ATS FAAR mod. CU/220-35) at a temperature of 23 °C and a relative humidity of 65% until a constant weight was reached. A relative humidity level of 65% is the most common wet condition for outdoor wood that, consequently, presents a moisture content at

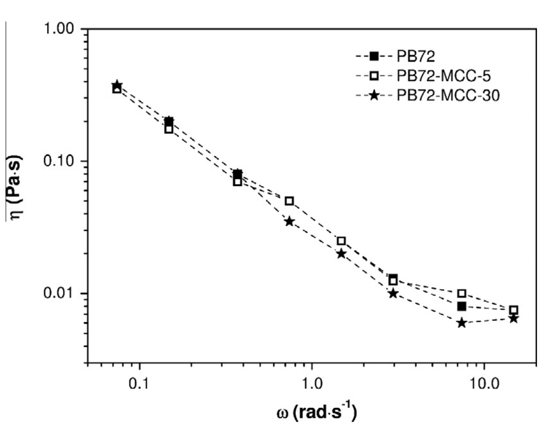

Fig. 1. Brookfield rheological curves of neat Paraloid and corresponding MCC composites.

Table 1
Gravimetric analysis results of undamaged and damaged walnut and fir wood samples before and after consolidation with neat PB72 and corresponding composites.

Sample	*M*% (wt%)	ρ_0 (g cm^{-3})	ρ_{12} (g cm^{-3})	*S* (%)
Walnut				
UW	12.23 ± 0.13	0.677 ± 0.008	0.694 ± 0.009	7.82 ± 0.18
DW	11.20 ± 0.09	0.602 ± 0.015	0.574 ± 0.013	7.29 ± 0.35
DW-T0	8.27 ± 0.30	0.631 ± 0.011	0.655 ± 0.025	3.43 ± 0.59
DW-T5	8.46 ± 0.45	0.627 ± 0.020	0.656 ± 0.019	3.69 ± 0.25
DW-T30	8.98 ± 0.32	0.658 ± 0.016	0.683 ± 0.030	3.60 ± 0.43
Fir				
UW	12.50 ± 0.56	0.364 ± 0.004	0.388 ± 0.010	7.36 ± 0.13
DW	14.65 ± 0.15	0.351 ± 0.009	0.371 ± 0.012	8.65 ± 0.55
DW-T0	10.49 ± 0.45	0.398 ± 0.010	0.419 ± 0.007	3.84 ± 0.57
DW-T5	10.70 ± 0.26	0.390 ± 0.006	0.414 ± 0.013	4.11 ± 0.69
DW-T30	10.94 ± 0.40	0.415 ± 0.012	0.440 ± 0.015	4.23 ± 0.15

M%: Moisture content at the equilibrium point.
ρ_0: Ovendry density.
ρ_{12}: Density calculated at 65% of relative humidity and 23 °C of temperature.
S: Volumetric swelling.

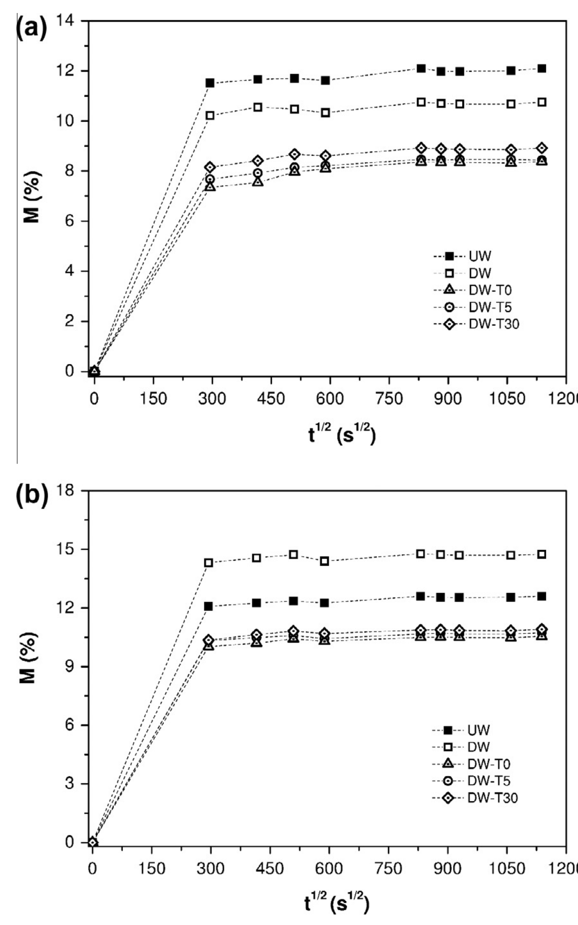

Fig. 2. Moisture absorption kinetic curves of undamaged and damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

equilibrium of about 12–15% [20–22]. Samples for mechanical tests were conditioned at 23 °C and 55% of relative humidity in a chamber with a super-saturated solution of $Mg(NO_3)_2{\cdot}6H_2O$ until a constant weight was reached. This is the indoor humidity level recommended for the optimal artwork conservation and fruition. Composites samples were denoted indicating the matrix (PB72), the filler (MCC) and its weight concentration. Wood samples were identified through their conservation state (UW represents the

Table 2
Results from mercury intrusion porosimetry analysis of undamaged and damaged walnut and fir wood before and after consolidation with neat PB72 and corresponding composites.

Sample	P_{TOT} (%)	Pore radius (nm)
Walnut		
UW	40.89	350.3
DW	26.98	1614.3
DW-T0	37.24	711.8
DW-T5	35.99	356.9
DW-T30	33.76	318.5
Fir		
UW	62.22	136.4
DW	60.84	292.4
DW-T0	55.77	191.2
DW-T5	47.30	144.9
DW-T30	40.56	141.1

P_{TOT}: Percentage of total porosity.

undegraded modern wood; DW is the degraded historical wood), and the type of formulation used for the consolidation treatment (T0 refers to neat Paraloid, T5 and T30 refer to Paraloid based composites with 5 wt% and 30 wt% of MCC, respectively).

Rheological measurements were performed on unfilled and filled Paraloid acetone solutions in a Brookfield RVT coaxial viscosimeter, with an inner diameter of 17 mm and an outer diameter of 19 mm, at a temperature of 25 °C controlled by a thermostatic chamber. A shear rate interval between 0.1 and 15 rad s^{-1} and a sample volume of 8 mL were used.

Weight and volume changes of at least 5 specimens for each type of wood were performed by using a Gibertini E42 electronic balance with a resolution of 10^{-4} g and a Mitutoyo digital caliper, respectively. The moisture content (M%), the oven-dry density (ρ_0), the density at 65% of relative humidity level (ρ_{12}) [20,23], and the volumetric swelling (S) [7], were calculated at the equilibrium point according to the following equations:

$$M\% = 100\frac{(W_t - W_0)}{W_0} \quad (1)$$

$$\rho_0 = \frac{W_0}{V_0} \quad (2)$$

$$\rho_{12} = \frac{W_t}{V_t} \quad (3)$$

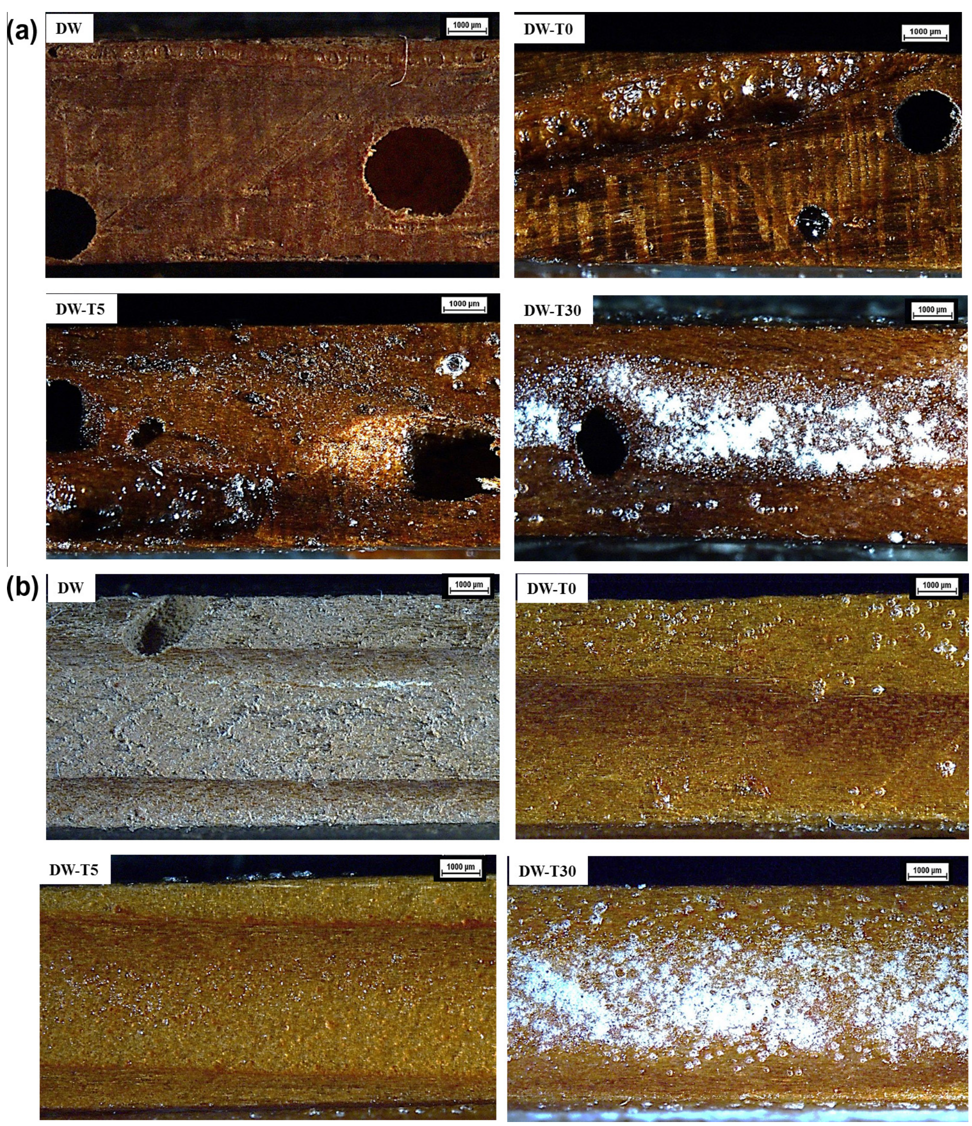

Fig. 3. Optical microscope images of surfaces of damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

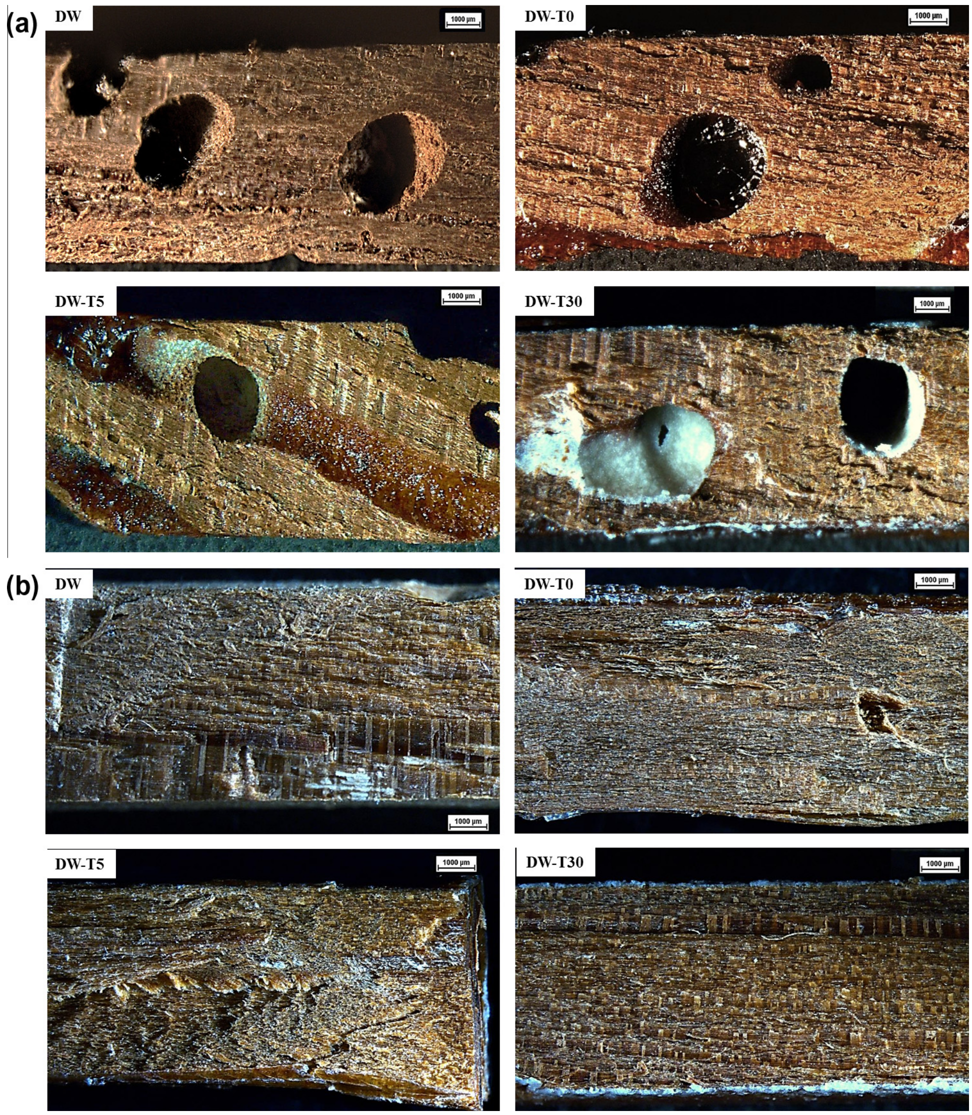

Fig. 4. Optical microscope images of long cross-sections of damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

$$S = 100\frac{(V_t - V_0)}{V_0} \quad (4)$$

where W_t and V_t are the wet weight and wet volume of specimens at the equilibrium point and W_0 and V_0 are the initial dry weight and the initial dry volume of specimens, respectively.

The percentage of total porosity (P_{TOT}) and the radius of macro- and micropore of all examined wood were detected by a Mercury Intrusion Porosimeter 2000 (FISONS Instruments). Samples of about 0.2 g were immersed in the non-wetting mercury. The increase of the pressure in the capillary allowed the intrusion of mercury in the cavities of samples. The pore radius (r) was estimated through the Washburn equation (Eq. (5)), that gives the relationship between the analysis pressure and this parameter. The total porosity (P_{TOT}) of each sample was determined as the ratio between the volume of mercury intruded into the sample at the highest analytical pressure and the initial external volume of the sample [24,25].

$$r = -\frac{2\gamma \cdot \cos\theta}{p} \quad (5)$$

where r is the pore radius, γ is the surface tension of mercury (0.48 N/m), θ is the wetting angle of mercury (141.3°) and p is the applied pressure.

In order to assess the penetration degree of all consolidating solutions, surfaces and long cross-sections of decayed wood samples, before and after treatments, were analyzed by an optical microscope NIKON SMZ25 and a FTIR spectrometer Varian 4100 (Excalibur Series) equipped with a Golden Gate diamond (Graseby Specac) for ATR analysis. A scanning range from 4000 to 400 cm^{-1} was utilized.

Three points flexure tests (ASTM D143) on at least 20 rectangular wood specimens (width = 5 mm, thickness = 5 mm, span length = 70 mm) for each set of samples were conducted by means of an Instron® 4502 universal testing machine, equipped with a 1 kN load cell. A crosshead speed of 1.3 mm/min was adopted. The flexural modulus (E_f), the maximum flexural stress ($\sigma_{MAX,f}$) and the maximum flexural strain ($\varepsilon_{MAX,f}$) were evaluated.

Charpy impact tests were conducted by a Ceast instrumented impact pendulum on at least 20 rectangular wood specimens (width = 5 mm, thickness = 5 mm, span length = 40 mm). A striker

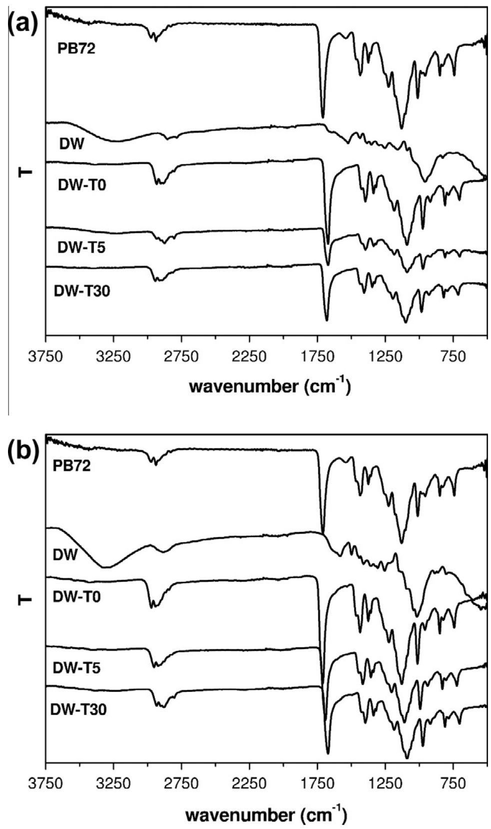

Fig. 5. FTIR spectra of surfaces of damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

mass of 1.187 kg, an initial impact angle of 84° and a data acquisition rate of 2000 points per second were utilized. Samples were impacted at a speed of 2 m s^{-1} with a maximum impact energy of 2.37 J. Through the integration of force–displacement curves it was possible to estimate the specific energy adsorbed at the crack initiation (U_i), corresponding to the energy adsorbed up to the maximum load, the specific energy adsorbed during the crack propagation (U_p) and the total specific absorbed energy (U_{TOT}), that is the sum of U_i and U_p. Additionally, the ductility index (DI), was calculated as the ratio between U_i and U_p to determine the energy absorption capability of wood samples before and after treatments, during fracture propagation [26].

The surface hardness of wood specimens was determined through an ATS FAAR Shore D hardness tester. According to ASTM D2240 three penetrations on each face of all wood specimens already tested by flexural tests were carried out. Radial and tangential surfaces were analyzed.

Microstructural analysis of fracture surfaces of impact tested wood samples were carried out by a NIKON SMZ25 optical microscope. Thanks to the instrument software, 3D profiles of failure surfaces of each group of wood were investigated.

3. Results and discussion

The level of penetration of the consolidating material into the artwork is one of the most important parameters for a successful wood consolidation. In fact, these restoration operations involve more often the substrate of wooden paintings or sculptures, therefore, it is very important that the viscosity of consolidant polymers is enough to penetrate into the wood, but not too much to reach also the paint film destroying the artwork. Thanks to its optimal viscosity, Paraloid B72, in concentration range of 3–10 wt%, is one of the most used consolidant resin for wood [1]. In order to assess the possible effect of MCC introduction on this property, Brookfield rheological tests on neat Paraloid and its resulting MCC composites in acetone were carried out (Fig. 1). It is worthwhile to observe that, even at the highest amount of MCC, the viscosity of the polymer matrix does not change to a significant extent. Another positive feature of this resin for the intended application is its low tendency to water uptake. Generally speaking, degraded wood tends to absorb more water than modern intact wood [1,27] and the consolidation with Paraloid is able to reduce the moisture sorption of the damaged material. In Table 1 the main results from gravimetric analysis are reported. Fig. 2a and b shows moisture absorption kinetic curves of undamaged and damaged walnut and fir wood before and after treatments with pure PB72 and PB72/MCC composites. Comparing the physical behavior of the two types of decayed wood, it is possible to notice that both of them manifest a decrease of dry and wet densities, ρ_0 and ρ_{12}. Moreover, damaged walnut wood samples tend to absorb less moisture, *M*%, than intact wood and are characterized by a lower value of volumetric swelling, *S*. Ancient fir wood samples register higher values of *M*% and *S* in comparison to modern fir samples. This could be related to their different conservation states. In fact, degraded walnut wood shows holes and larval tunnels that are not so numerous in degraded fir samples. Maybe, the critical biological decay of walnut reduced the wooden matter able to interact with the environment, producing a decrease of the moisture content. For as the effects of consolidation treatments is concerned, the application of all formulations leads to a decrease of about 25% of the moisture sorption for both wood species. In particular, a slight increase of the absorbed water for degraded wood samples treated with filled PB72, proportional to the MCC loading is

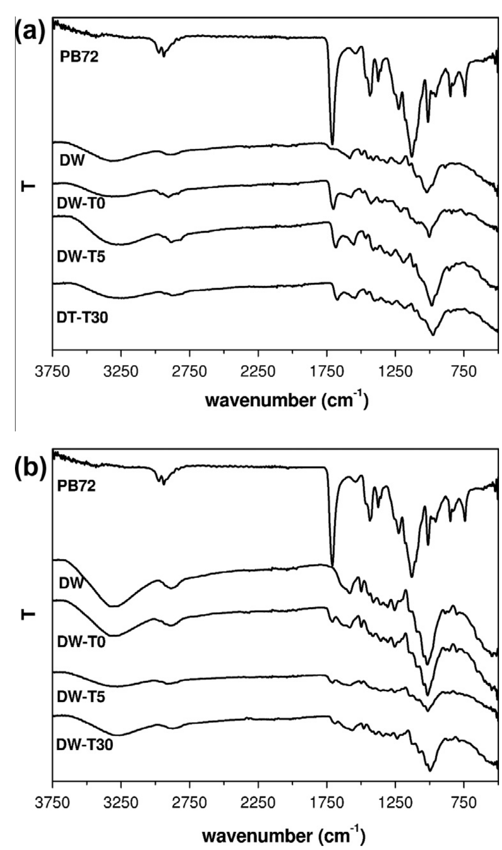

Fig. 6. FTIR spectra of long cross-sections of damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

Table 3
Results of 3-points bending tests on undamaged and damaged walnut and fir wood samples before and after consolidation with neat PB72 and corresponding composites.

Sample	E_f (GPa)	$\sigma_{MAX,f}$ (MPa)	$\varepsilon_{MAX,f}$
Walnut			
UW	6.97 ± 0.46	115.41 ± 6.12	0.115 ± 0.011
DW	4.92 ± 0.37	49.72 ± 1.32	0.060 ± 0.011
DW-T0	4.57 ± 0.66	53.88 ± 0.25	0.068 ± 0.009
DW-T5	5.37 ± 0.29	62.65 ± 4.47	0.068 ± 0.008
DW-T30	5.45 ± 0.44	63.94 ± 3.92	0.066 ± 0.006
Fir			
UW	7.87 ± 0.59	71.62 ± 4.00	0.058 ± 0.004
DW	5.99 ± 0.40	56.36 ± 4.03	0.061 ± 0.005
DW-T0	5.99 ± 0.17	68.57 ± 1.56	0.074 ± 0.005
DW-T5	6.34 ± 0.33	65.24 ± 3.42	0.071 ± 0.007
DW-T30	6.43 ± 0.24	66.26 ± 1.10	0.071 ± 0.006

E_f: flexural modulus.
$\sigma_{MAX,f}$: maximum flexural stress.
$\varepsilon_{MAX,f}$: maximum flexural strain.

detected. This may be due to the lower amount of Paraloid in composite solutions, but this variation is less than 0.5% even for formulations with the highest amount of filler. For both investigated wood types the increase of the MCC loading produces a systematic reduction of the volumetric swelling and an enhancement of dry and wet densities values, that for worm-eaten walnut samples, treated with PB72-MCC-30, almost reach those of intact wood, while values detected for damaged fir samples exceed the reference ones. Table 2 reports the values of the total percentage of porosity, P_{TOT}, and the pore radius for the different groups of wood. Also in this case, one can notice a different degradation level for the two species. Before treatment, walnut samples display a stronger decrease of the total porosity in comparison to the modern wood, while degraded fir samples present a value of P_{TOT} similar to that of the corresponding intact wood. Ancient walnut samples show a much more significant increase of the pore radius than fir. This can be explained considering the metabolism action of woodworm larvae that, making galleries and holes, enlarges the pore size of wood and thus reduces the percentage of closed porosity. For both damaged wood types, the consolidation with MCC composites induces a progressive reduction of the pore radius that becomes much closer to that one of intact wood, and, only for fir, a progressive decrease of the total porosity. For walnut, the neat PB72 application increases the P_{TOT}, filling the worm tunnels and increasing

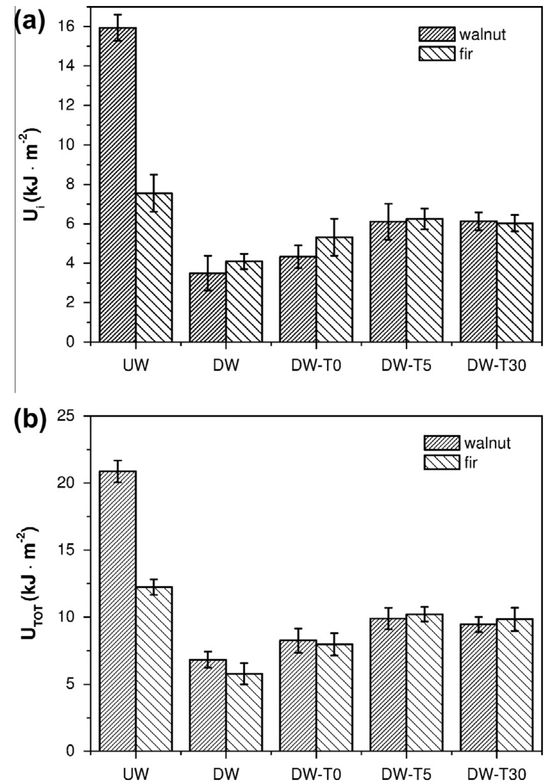

Fig. 8. Main impact flexural properties of undamaged and damaged walnut and fir wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Specific energy adsorbed at the crack initiation, U_i and (b) total specific absorbed energy, U_{TOT}.

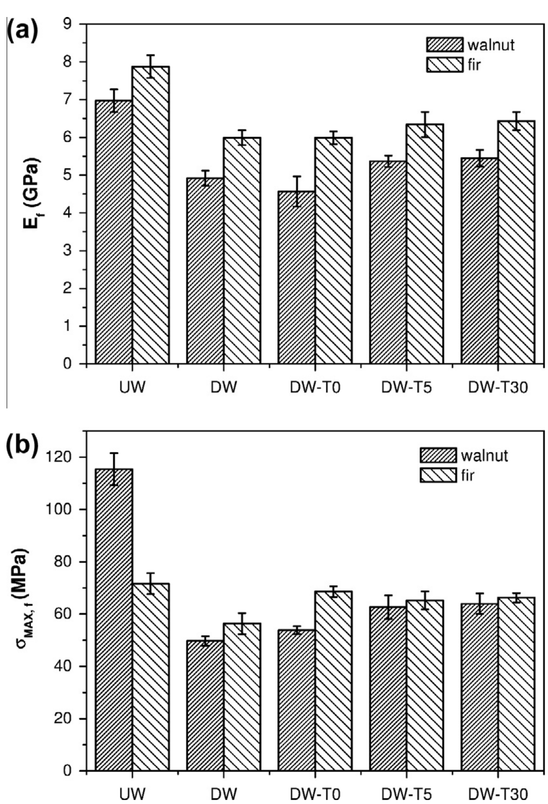

Fig. 7. Main quasi-static flexural properties of undamaged and damaged walnut and fir wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Flexural modulus, E_f and (b) maximum flexural stress, $\sigma_{MAX,f}$.

Table 4
Charpy tests results of undamaged and damaged walnut and fir wood samples before and after consolidation with neat PB72 and corresponding composites.

Sample	U_{TOT} (kJ m^{-2})	U_i (kJ m^{-2})	U_p (kJ m^{-2})	DI
Walnut				
UW	20.86 ± 0.82	15.94 ± 0.66	4.92 ± 1.20	0.31 ± 0.05
DW	6.83 ± 0.60	3.50 ± 0.89	3.33 ± 0.70	0.95 ± 0.17
DW-T0	8.26 ± 0.89	4.33 ± 0.57	3.93 ± 0.45	0.91 ± 0.20
DW-T5	9.91 ± 0.80	6.11 ± 0.91	3.79 ± 0.52	0.62 ± 0.13
DW-T30	9.45 ± 0.57	6.13 ± 0.45	3.32 ± 0.33	0.54 ± 0.15
Fir				
UW	12.95 ± 0.58	7.55 ± 0.94	5.40 ± 1.40	0.72 ± 0.22
DW	5.79 ± 0.80	4.09 ± 0.39	1.71 ± 0.54	0.42 ± 0.11
DW-T0	7.97 ± 0.83	5.32 ± 0.93	2.65 ± 0.88	0.50 ± 0.17
DW-T5	10.21 ± 0.54	6.24 ± 0.53	3.97 ± 0.52	0.64 ± 0.15
DW-T30	9.84 ± 0.87	6.03 ± 0.42	3.23 ± 0.57	0.54 ± 0.18

U_{TOT}: Total specific fracture energy.
U_i: Specific energy for crack initiation.
U_p: Specific energy for crack propagation.
DI: Ductility index (ratio between U_p and U_i).

Table 5
Radial and tangential hardness values of undamaged and damaged walnut and fir wood samples before and after consolidation with neat PB72 and corresponding composites.

Sample	H_r	H_t
Walnut		
UW	69.25 ± 0.63	63.51 ± 0.17
DW	65.56 ± 0.81	62.78 ± 0.64
DW-T0	65.70 ± 0.70	62.88 ± 0.80
DW-T5	67.44 ± 0.59	64.33 ± 0.79
DW-T30	69.03 ± 0.46	67.70 ± 0.42
Fir		
UW	42.02 ± 0.59	45.65 ± 0.76
DW	35.54 ± 0.80	37.69 ± 0.86
DW-T0	39.28 ± 0.45	41.83 ± 0.76
DW-T5	39.13 ± 0.65	42.25 ± 0.75
DW-T30	39.09 ± 0.43	41.82 ± 0.60

H_r: Radial hardness.
H_t: Tangential hardness.

the closed porosity, but, there is a slight decrease of this property as the MCC content increases, probably related to the lower amount of PB72 in composites solutions. Optical microscope images of surfaces and long cross-sections of damaged wood samples of walnut (Figs. 3a and 4a, respectively) and fir (Figs. 3b and 4b, respectively) before and after consolidation, prove the different degradation state of these two wood types, with evident larval holes and galleries on the surfaces and in the inner of just walnut samples. All formulations create a surface transparent coating on each type of wood. Only samples treated with the composition at the highest amount of MCC present a visible exterior deposit of this microfiller. Interestingly, just for walnut samples it is possible to assess the presence of consolidants in the long cross-sections, and how PB72 and, especially, MCC are able to partially fill the defects made by larvae worms. While, in the inner sections of fir samples the consolidants penetration is not perceivable. According to optical observations, FTIR spectra of surfaces of treated degraded wood samples of walnut (Fig. 5a) and fir (Fig. 5b) confirm the formation of a surface transparent protective layer, through the presence in all FTIR curves of the main stretching peak of carbonyl groups at about 1750 cm^{-1} typical of PB72. Additionally, Fig. 6a and b report the FTIR spectra of long cross-sections of treated decayed walnut and fir samples, respectively. A stronger carbonyl group peak in the walnut wood spectra underlines the higher penetration degree of unfilled and filled Paraloid consolidants within this wood, through worm holes and galleries that become preferential ways of penetration. For fir samples a very low carbonyl signal was detected, proving the essentially surface nature of PB72/MCC consolidation treatments for this degraded wood. In Table 3 the main flexural properties in quasi-static condition are listed, while in Fig. 7a and b the values

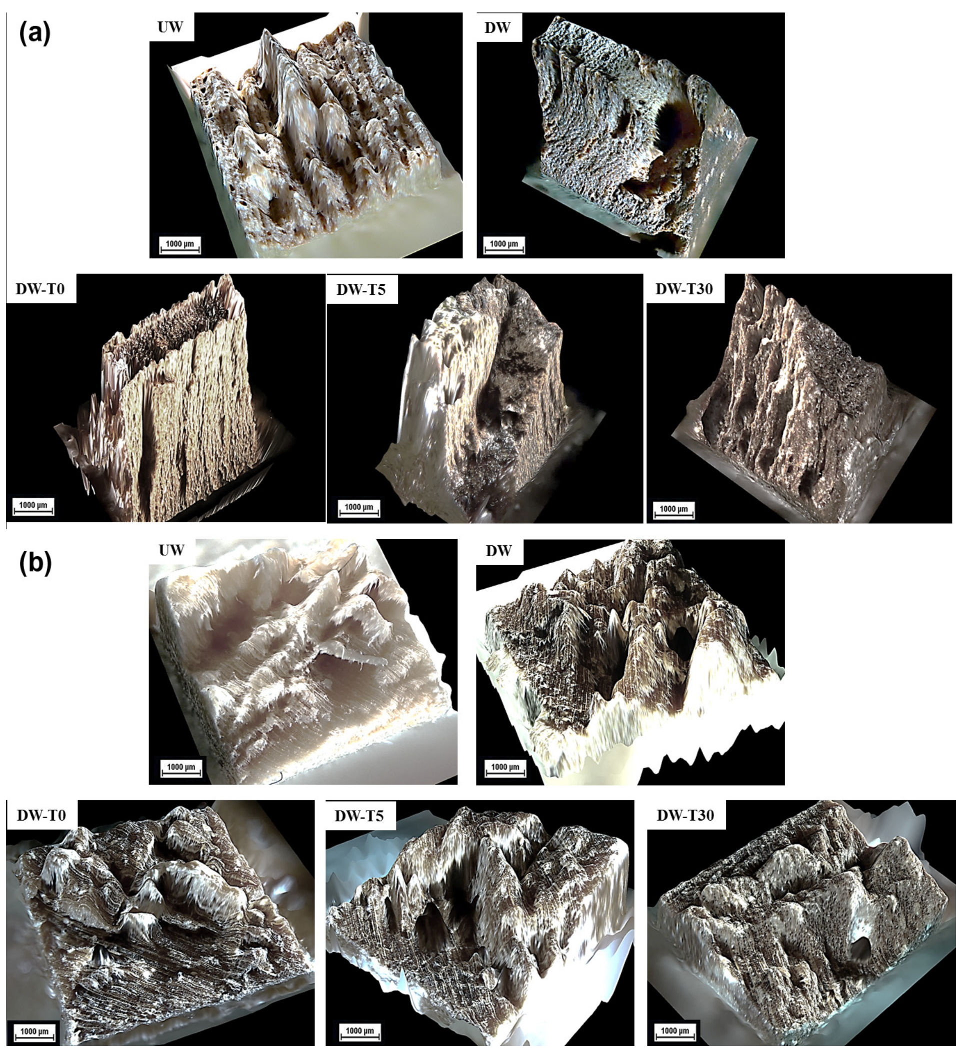

Fig. 9. 3D profiles of impact fracture cross-sections of damaged wood samples untreated and treated with neat Paraloid and corresponding MCC composites. (a) Walnut and (b) fir.

of flexural modulus (E_f), and maximum flexural stress ($\sigma_{MAX,f}$), for each group of tested walnut and fir samples are plotted. The first thing that one can notice is the drastic drop in properties for both species due to the decay process. In particular, worm-eaten walnut samples register the highest fall of flexure properties, with a reduction of about 50% of $\sigma_{MAX,f}$ with respect to damaged fir samples that register a $\sigma_{MAX,f}$ decrease of about 20%. The neat PB72 based treatment is able to raise both maximum flexural stress and strain of the two types of wood, but has not effect on the elastic modulus, E_f. Remarkably, all wood samples treated with microcomposites show a systematic increase of E_f as the MCC content increases, and just for walnut a progressive enhancement of $\sigma_{MAX,f}$ is registered. The maximum stress value of walnut samples consolidated with PB72-MCC-30 is about 20% higher than the experimental $\sigma_{MAX,f}$ value of samples treated with the unfilled PB72. MCC introduction has not significant effects on the maximum flexural strain of walnut wood. On the other hand, after consolidation with microcomposites, decayed fir samples exhibit a slight decrease of both $\sigma_{MAX,f}$ and $\varepsilon_{MAX,f}$, probably related to the almost null penetration of consolidants in this wood and the lower concentration of Paraloid in composites solutions.

The most important results from Charpy impact tests are showed in Fig. 8a and b while, in Table 4 the values of U_{TOT}, U_i, U_p and the ductility index are summarized for each group of walnut and fir samples. These results highlight the much lower impact strength values of historical over modern woods, with a drop in the main impact properties of about 70% for walnut and about 50% for fir. Moreover, if degraded fir registers a decrease of the ductility index, the DI value of worm-eaten walnut is much higher than that one of intact walnut, probably because of larval holes and galleries which modify the crack propagation path. Even under impact conditions, the consolidation with the neat matrix improves the flexural strength of the two wood species, with the increase of both U_i and U_{TOT} and the consequent decrease of U_p and DI. Interestingly, all degraded wood samples treated with MCC composites exhibit higher values of U_i and U_{TOT} in comparison to wood consolidated with neat PB72. The best results are obtained from samples consolidated through the formulation with 5 wt% of MCC. Walnut samples treated with only PB72 exhibit, with respect to the corresponding untreated samples, a higher value of the energy absorbed during the damage propagation and a similar value of the ductility index. Walnut samples consolidated with microcomposites show a progressive reduction of the U_p and, therefore, a decrease of DI as the MCC amount increases, because Paraloid and MCC can better fill decay defects in these materials. While for fir samples, the introduction of MCC leads to a proportional increase of both U_p and DI, because of the surface nature of all treatments that being not able to penetrate, make only a ductile film on fir samples. Another positive effect of the MCC presence is the improvement of both radial and tangential surface hardness values of treated decayed walnut wood (Table 5) which are progressively higher than those register by wood samples treated with neat PB72. For fir it is not possible to notice any relevant difference between samples consolidated by the neat matrix and those consolidated by MCC composites.

In order to assess if MCC particles modify the fracture mode of treated wood, microstructural analysis of failure surfaces of flexure tested samples were carried out. In Fig. 9a and b it is possible to observe the 3D profiles of cross-sections of each group of walnut and fir, respectively, after impact failure. It is evident that all consolidants do not change the fracture behavior of the two decayed wood species. However, the images of walnut samples (Fig. 9a) show how defects made by larvae worms in the samples completely change the fracture mode of walnut from a brittle clean fracture surface to a cross-grain one [28]. It is also interesting to notice the inner walls of worm tunnels with the wooden matter totally degraded and, in case of treated samples, the deposit of the neat matrix or of polymer and microfiller together.

4. Conclusions

A physic-mechanical investigation of the effect of 5 and 30 wt% of MCC on the consolidating properties of Paraloid B72 was conducted. Historical walnut (*J. regia*) and fir (*A. alba*) wood samples were treated with neat and filled Paraloid. Interestingly, the usage of microcomposites as consolidating agents for decayed wood produced a progressive reduction of the pore radius that in samples treated with formulations at the highest amount of MCC reached values similar to those of the corresponding intact wood. The presence of MCC allowed the improvement of the stiffness and the flexure strength of consolidated woods under quasi-static and impact conditions, with the flexural modulus, the maximum flexural stress and both initial and total impact absorbed energies increased with filler loading. Moreover, a systematic improvement of the radial and tangential surface hardness almost up to the intact wood values was observed on woods consolidated with MCC-based composites. Concurrently, MCC addition did not change the viscosity of the neat matrix and especially its good water repellency. In fact, for all treated wood samples a similar reduction of the moisture content and the volumetric swelling was observed.

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