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Physical properties of Portuguese pinewood chemically modified

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Abstract

Maritime Pine softwood has low dimensional stability. Chemical modification is the easiest way to improve technological features of the softwood into a material with enhanced and less varied properties. In this work, physical properties of modified wood using four methods of modification were studied. Pure sapwood of the Maritime pine species (*Pinus pinaster* Ait.) was submitted at different chemical modification processes: 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), N-methylol melamine (MMF), tetra-alkoxysilane (TEOS) and wax (amid WA and montan/ lignite wax WL). The following physical properties were assessed experimentally: density and weight percent gain (WP), equilibrium moisture content (EMC), isotherms curves, anti-swelling efficiency (ASE), swelling strain and swelling coefficient. Significant changes in the material properties took place. All modification processes increased the density of modified wood in different extent: Modification with cell wall reaction (DMDHEU and MMF resin) were the most effective methods to achieve high dimensional stability (ASE) in parallel with low equilibrium moisture content (EMC). The lumen fill modification (TEOS and wax) had no effect in to different physical properties.

Keywords: chemical modification; equilibrium moisture content; anti-Swelling efficiency; shrinkage; swelling.

1. Introduction

Many of problems with wood in service are attributable to the dimensionally stability when subjected to vary humidity environments. This instability is due to the shrinking and swelling effect that results from changes in moisture content (MC) of the wood. Consequently, it is generally accepted that the chemical modification (cross-linking with reactive chemicals) changes the composition and structure of the wood material; thus, material properties related to the humidity, such as EMC and swelling behaviour, will also be changed. New methods have been investigated since Rowell [1] lectured about different chemical modifications and Hill [2] suggested the wood modification (by heat or chemical) as the best way to overcome the main wood shortcomings and turns the modified wood in a high-value of wood material. In the most case, changes are in such way that modified wood performed well related to the moisture, has low EMC and low swelling behaviour at a given relative humidity (RH), as well was observed in [2,3].

The use of resin to modify wood was a knowledge successful transferred from the textile industry. It is known that resin based modification improve the durability and the dimensional stability of solid wood [2,4-9].

All the modification methods chosen in this study, are being newly investigate in the basic physical properties, as well as his decay performances or commercially available in the north of Europe [10-17]. The technological improvement of Portuguese pinewood by chemical modification is not known.

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Nevertheless, it is expected to be obtained similar properties to other modified pines. All physical properties searched in this work is part of a whole work with the final objective to access the short- and long-term behaviour of Portuguese pine softwood species under different environment conditions. Therefore, the objective of this work was to investigate the effect of the chemical modification with different chemicals on the main reference physical properties.

2. Experimental, materials and methods

Flaw less specimens of Maritime Pine species (*Pinus Pinaster* Ait.) from pure sapwood part of the stem with 2-3mm annual ring width and range dry density between 520 to 550 kg m^{-3} were chemically modified. Before modification, all material was cut into specimens measuring the dimensions indicated in Table 1.

All specimens were dried 24 hours at 103ºC before the impregnations. A full cell process with a vacuum step of 30 minutes and a step of two-hours pressure at 12bar were used.

The wood material was impregnated with solutions of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) supplied by BASF AG (Ludwigshafen, Germany). The following concentrations were used: 0.8M, 1.3M and 2.3M using 4% magnesium nitrate relative to the mass of the DMDHEU solution as catalyst. Assigned respectively, D1, D2 and D3. After impregnation the curing process was: one week at environment temperature and 48hours at 120ºC in the oven.

Table 1. Overview of specimens size, applied standard and number of specimens (n)

Properties	LRT [mm³]	Standard	n
Density and WPG	200 · 75 · 25	DIN 52 182, [34]	70
EMC	25 · 25 · 10	House standard, Dieste [28]	10
Iso curves	25 · 25 · 10	------	10
ASE	25 · 25 · 10	Hill and Jones [20]	10
Swelling	25 · 25 · 10	------	10

N-methylol-Melamine (MMF) resin was Madurit MW 840 supplied by INEOS (Frankfurt a. M., Germany). To obtain two levels of concentrations, it was dilute with water 10% and 20% MMF solution. After impregnation, in the curing process, the oven-drier was used, specimens were allowed to dry for 48 hours at room climate before to go into the oven. Then in an oven, material was placed at 50ºC in which the temperature was raised by 10ºC every 24h until 90ºC of temperature was reached. In the curing process through the steam drier, the impregnated specimens were stacked in the steam dryer according to the description by [18]. Where the main part of the reaction process consisted to keep high temperature phase at 90ºC for 36h, which was reached by a heating and cooling phase with air RH app. 90%. The oven or steam drier curing processes led to the following assignment for melamine modification, i1o and i2o or i1s and i2s, respectively for both concentrations.

Tetra-ethoxysilane (TEOS) with acid ethanol (1.mol) was adding to 1.mol silane and stirred at ambient temperature for 30 minutes, assigned T2. To achieve the lowest TEOS concentration (T1), 50% of weight mass of tap water was added. After the impregnation, all samples were weighed and cured in an oven at 60ºC for 4 days.

Two types of wax were used, amid and montan wax (from lignite), assigned WA and WL respectively. The wax was impregnated at temperature of 120ºC in liquid state. After the impregnation, the excess of wax was cleaned with filter paper. All samples were weighted and left for several months in the climate room.

The density was calculated as weight per volume. The dimensions in the main directions (radial, tangential and longitudinal) were measured.

Before the EMC, isotherm curves and ASE were measured, the leaching according to EN 84 was done [19]. Between each measurement, all material was left at least six weeks in the climate chambers with the respective RH environment.

The EMC was calculated at three humidity levels (i - 30, 65 and 87%) based on the oven-dry weight (before and after the modification) and the weight at the specific climate (Eq. 1).

$$EMC_i = \frac{m_i - m_0}{m_0} \times 100[\%] \qquad (1)$$

Where m_i is the weight of the specimen at moisture content i and m_o is the oven-dry weight of the material.

The ASE was determined according to the method presented in [20]. Specimens were subject to climate cycles between dry state and saturated conditions, at four cycles, the average values were found. Before each climate change, weight and thickness in radial (R) and tangential (T) direction were measured. It was calculated by comparison of the volumetric swelling coefficients of the modified and unmodified specimens.

$$ASE = \frac{S_{unmodified} - S_{modified}}{S_{unmodified}} \times 100[\%] \qquad (2)$$

The swelling strain (ε) was calculated for both directions, R and T. The RT tree rings direction was clearly oriented perpendicular and parallel to the sawn surface of the specimens. The swelling strain in both directions RT was calculated.

$$\varepsilon_i = \frac{|I_{87} - I_{30}|}{I_{30}} \times 100[\%] \quad (3)$$

Where I_{87} is the dimension at 87% RH and I_{30} is the dimension at 30% RH.
The swelling coefficient (β) was calculated according to the following equation for both direction (R and T) where ε_i is the swelling strain (in the individual directions) and EMC_{87} and EMC_{30} are the equilibrium moisture content at 87% and 30% RH, respectively.

$$\beta_i = \frac{\varepsilon_i}{(EMC_{87} - EMC_{30})} \times 100[\%] \quad (4)$$

The statistical analyses were done using a computerized software ORIGIN 13.0. The wood performances are characterized by mean values (–), median (x) and standard deviation (through a rectangle - □), as well as the upper and lower whisker with 5 and 95 percentile. Univariate analyses followed by a t-test with a 95% confidence interval were used. The level for significance was set at $p<0.05$. For the iso-curve fitting, in the ORIGIN statistical software, where the Gauss-Newton method as the default algorithm, to find the minimum of function that is a sum of squares of non-linear functions, was used.

3. Results

The concentration of solution correlate with weight percent gain (WPG) acquired by the wood material. Before all impregnations, wood material was dried over 24h at 103ºC ($W_{unmodified}$). After impregnations and curing, wood material was dried to access the dry weight ($W_{modified}$). The weight percent gain was obtained by the difference between both weight measurements for each type of modification methods.
Fig. 1 shows the correlations between WPG and density for four methods used (DMDHEU, MMF, TEOS and wax). This analysis was conducted with specimens used for marine expositions according to EN 275 (experiment which ran in parallel) [35].

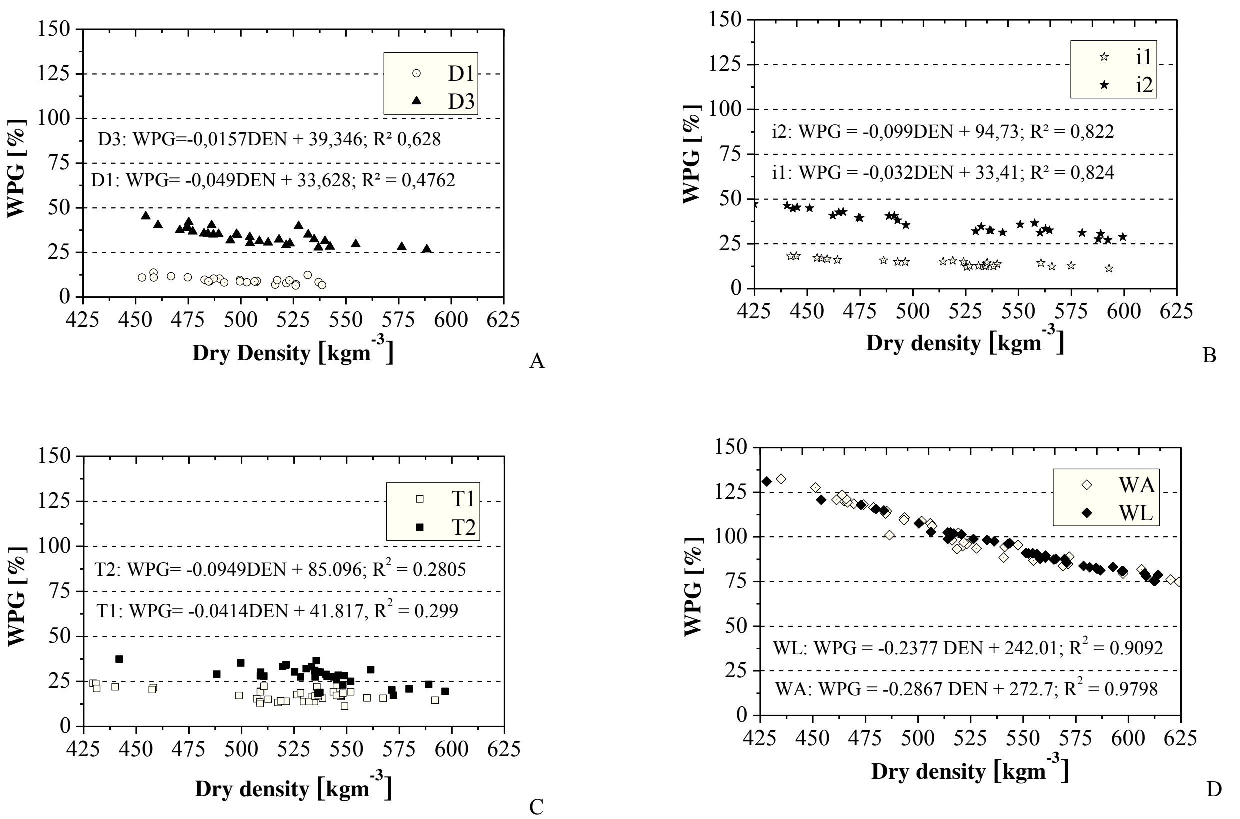

Fig. 1. Correlations between WPG and density, A - DMDHEU, B - MMF, C - TEOS and D - wax (n 38). For abbreviations see material item.

In cell wall modification (DMDHEU and MMF resin), the WPG and density correlations were significant. In DMDHEU resin with low concentrations (D1, 0.8M), a moderate correlation between density and WPG was found, R2 (0.476). The WPG took 100% of variations, between 6 up to 12%. Both concentrations of MMF resin showed high correlations between density and WPG where a range of 10 up to 50% of WPG was found.

In the lumen fill modification: TEOS has shown low correlation between density and WPG (correlation not significant, R^2 0.28). Therefore, WPG showed a range between 10 up to 40%. In both types of wax (WA and WL) a range between 75 up to 130% of WPG was found, with no difference between the types of wax (significant correlation, R^2 0.909).

Fig. 2 shows the EMC values observed in the three RH environments. Two analyzes can be made according to Dieste [28]. The calculation of the EMC based on the oven dry weight of wood material after and before modification is presented in Fig. 2A and Fig. 2B, respectively. In the former, the WPG of the wood material imparted by the modification will be overestimating the EMC. Therefore, an incorrect evaluation of EMC can be found, Fig. 2A.

For instance in Fig. 2A and Fig. 2B, comparing the EMC values in 87% of RH environment, the modification with lumen filling with wax (WA or WL) have shown approximately the double of EMC.

Specimens modified with TEOS in dry and indoor conditions (30% and 65% RH) have shown similar EMC with both concentrations, with a slight reduction up to 10%. The EMC in wet conditions (high RH, 87%) has shown a reduction up to 20%.

Notice that the EMC difference in the lumen fill modification, of 20% in TEOS and the double (100%) in wax, is roughly similar to WPG imparted by the modification.

For specimens modified with DMDHEU resin, similar EMC were found in dry and indoor conditions (30 and 65% RH) at three levels of modification (D1 up to D3). In the modified pinewood with different concentrations of DMDHEU had shown a reduction up to 30% and for high RH a reduction up to 50%. Between high and low level of modification, slight difference in EMC was found (increase app. 25%).

Both levels of modification with MMF resin at dry conditions (30% RH) showed similar EMC. In wet conditions the EMC were reduced 20 up to 40%, respectively with the level of modification.

Fig. 2B shows the EMC according to the latter method (dry mass of wood before modification).

Specimens with cell wall modification: MMF resin had a slight effect on the EMC reduction and DMDHEU resin showed a reduction up to 30%.

Specimens with lumen fill modification (TEOS and wax) had no effect in the EMC of the wood material.

Fig. 3 shows the compliance of ASE after four cycles. As higher the ASE is, higher the dimensional stabilizing effect is on the modified wood. An ASE value of 60%, for instance, means that a modified wood specimen swells 60% less than an unmodified specimen.

Specimens with cell wall modification with three concentrations of DMDHEU resin, three different ASE values were found. As high the concentration of DMDHEU resin is (D3), the high ASE value is, 60%.

At low concentration (D1, 0.8M) slight effect was shown, app 20%. Both concentrations of MMF resin have shown similar ASE, 28 and 38%.

The ASE assumed a negative value in the lumen fill modification (TEOS and wax), roughly -15%. These figures indicated that both modifications probably did not increase the swelling effect, but these lower values are result of natural variability of wood material.

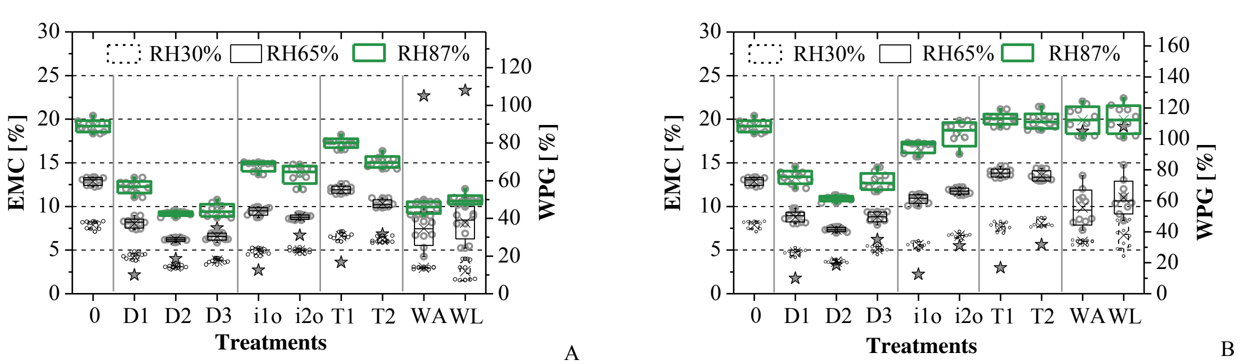

Fig. 2. EMC calculated at three RH (30%, 65% and 87%) environment with (A) - dry weight after modification and with (B) - dry weight before modification, and WPG (☆). For abbreviations see material item.

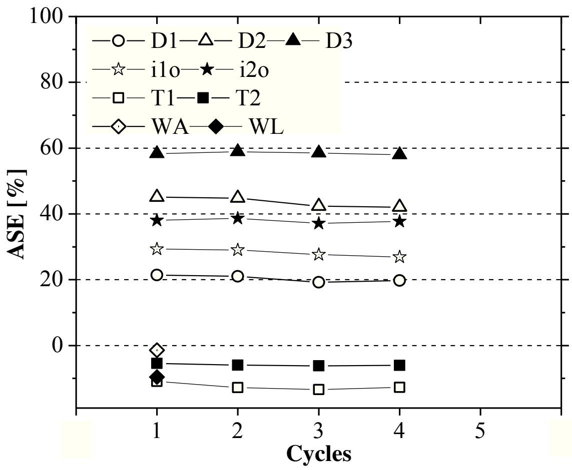

Fig. 3. Compliance ASE. For abbreviations see material item.

Fig. 4 shows the sorption and desorption isotherms curves for unmodified and chemically modified pinewood. The compliance curve depends of the RH environment. The sorption and desorption isotherms curves were different for modified and unmodified wood.

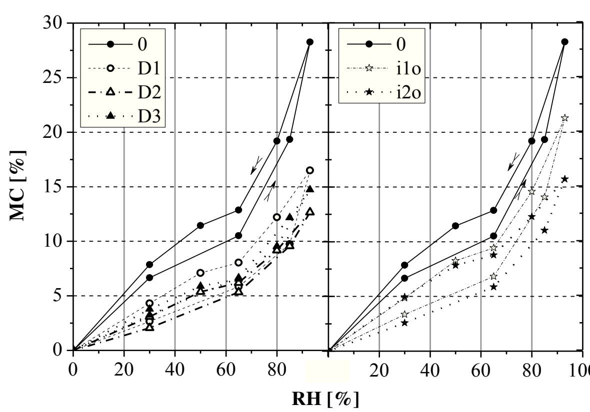

Fig. 4. Isotherms curves determined with app. T 21ºC (Moisture content - MC and relative humidity - RH), (↙) downward desorption and rising adsorption (↗), for cell wall modifications - DMDHEU and MMF.

To fit the compliance isotherm curves, several models can be found in the literature and briefly summarized in [21,22]. In this analysis, the Hailwood-Horrobin model was used according to the following equation and described in [23].

$$MC=\frac{1.8}{W}\times\frac{k_1\times k_2\times RH}{1+k_1\times k_2\times RH}+\frac{k_2\times RH}{1-k_2\times RH}[\%] \qquad (5)$$

Where the W is the molecular weight of the dry cell wall in kg per mole of sorption sites, k_1 is the equilibrium constant for the hydrated cell wall with the dry cell wall and dissolved water, and k_2 is the equilibrium constant for dissolved water with the external vapour pressure.

Table 2 shows the constants of the Hailwood-Horrobin model (k_1, k_2 and W) calculated using dry mass material by fitting the function from the last equation to experimental data obtained. All parameters were initialized W=0,28; k_1=5,5; k_2=0,75 as suggested in [21].

This study has shown significant differences in the sorption/desorption behaviour between unmodified and resin based modification. DMDHEU exhibited the lowest level of hysteresis compared with MMF or unmodified wood. For both types of resins (DMDHEU and MMF), the medium and high level of modification did not show significant different behaviour. In the DMDHEU with low concentration (D1, 0.8M), albeit significant difference to the control was found, no significant difference to the others concentrations was been shown.

Fig. 5 shows the swelling strain (ε) in the radial and tangential directions (RT), in Fig. 5A and B respectively. Specimens modified with high concentration of DMDHEU resin (D3, 2.3M) have reduced the swelling strain (ε) in both directions RT, with significant effect in the tangential direction.

Specimens modified with MMF resin have showed significant effect only in T direction with high concentration. Lumen fill modification (TEOS and wax) had no effect in swelling strain (ε).

The Portuguese unmodified pinewood has shown similar results as found in the literature [24,25], with swelling behaviour greater in the T than in R direction, roughly 1:2 - RT. The same tendency (1:2, RT) was kept for modified wood with resin.

Table 2. Coefficients of fitting isotherm curves in sorption (So) and desorption (Ds) behaviour for cell wall modification (DMDHEU and MMF resin)

Modification	0 [*ctrl*]		D1 [9,33]		D2 [18,6]		D3 [34,6]		i1o [14,7]		i2o [38,5]	
and WPG[%]	**So**	**Ds**	**So**	**Ds**	**So**	**Ds**	**So**	**Ds**	**So**	**Ds**	**So**	**Ds**
W	0,40	0,29	0,61	0,37	0,62	0,47	0,59	0,57	0,68	0,35	0,65	0,32
k_1	79633	69	11,2	6,5	2,3	5,3	5,0	54,0	19,2	7,7	5,1	8,1
k_2	0,90	0,84	0,90	0,77	0,85	0,77	0,83	0,85	0,96	0,82	0,90	0,71

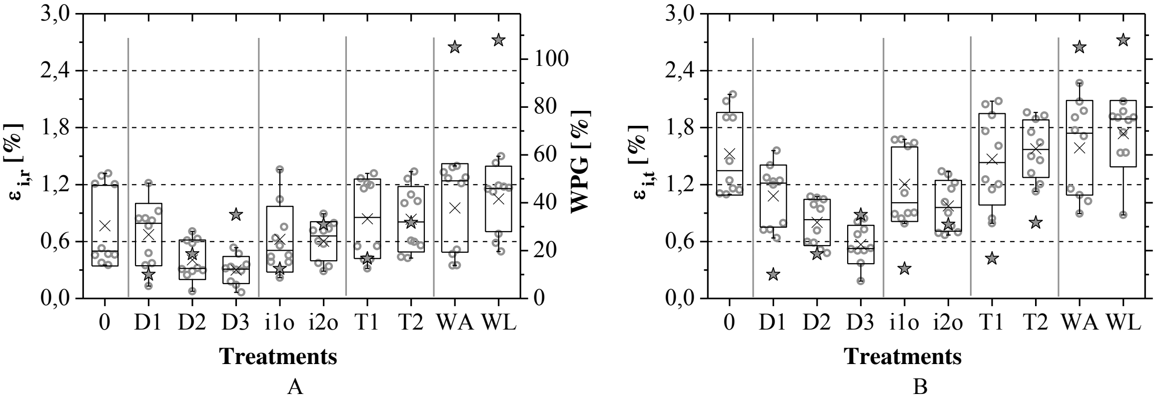

Fig. 5. Swelling strain (ε) between 30% and 87% RH for two directions RT, respectively, A - $\varepsilon_{i,r}$ and B - $\varepsilon_{i,t}$, and WPG (☆). For abbreviations see material item.

Fig. 6 shows the swelling coefficient for different modification in both directions R and T. Cell wall modification (DMDHEU and MMF resin) have shown no significant effect in low and medium level of concentration. However, high concentration showed a significant reduction in both directions RT.
For both directions, lumen fill modification (TEOS and wax) did not show any effect.
Specimens with cell wall modification (with DMDHEU and MMF resin) showed variable changes in swelling coefficient - β. Even so, not all changes were significant in the R direction. In the T direction, high concentration of resin is required to reach significant reduction in the swelling coefficient.

4. Discussion

Wood is a hydroscopic material, which means that the hydroxyl groups contained in the cell wall polymers attract and form hydrogen bonds with environmental moisture [26].
In the wood modification, the cell wall wood reacted with resin an acid catalyst results in cross linking between two hydroxyl groups in the cell wall polymers [27]. The less effect of MMF resin on the physical properties regarding the resin DMDHEU may be explained by the acidic hydrolysis of the polysaccharides as a result of the use of magnesium nitrate as catalyst.
In the lumen filling modification only a delay in the capillary water uptake at wax modification was shown by Scholz [17], whilst all others physical properties remain unaffected.
Wood modification is the best way to enhance physical properties of softwood species [4,7,8,9,12,28]. Similar improvements with heat modification with Portuguese maritime pine was found: Similar EMC at three RH environments (dry, indoor and wet conditions with 30, 65 and 87% of RH, respectively) [29].
Chemical modification with DMDHEU resin in Scots pine and European Beech species have shown similar EMC reduction, up to 30% [4,9].

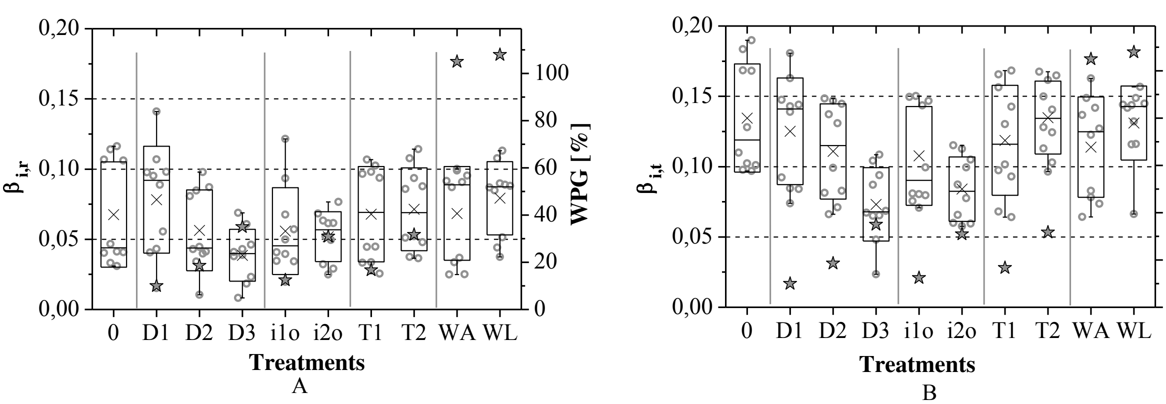

Fig. 6. Swelling coefficient for two RT directions between dry and wet conditions (30% and 87% RH), A - $\beta_{i,r}$ and B - $\beta_{i,t}$, and WPG (☆). For abbreviations see material item.

Specimens of Scots pine species modified with MMF resin with low level of concentration have shown a reduction of EMC up to 15% at indoor conditions [12]. However, unexpected results for MMF resin with a slight increase of EMC were found by Epmeier [11]. The difference to our results might be associated with the EMC calculation methodology. If the dry mass before the modification were used, similar results were found.

Specimens of Scots pine species modified with DMDHEU (25% WPG) at indoor conditions have shown a reduction of the EMC up to 20% [12].

The modification with TEOS or wax for lumen fill did not show any effect on EMC. Specimens of Scots pine modified with TEOS as well as wax at indoor conditions did not show any effect on EMC [10,12].

Specimens of Scots pine modified with DMDHEU and MMF resin showed similar results for ASE of this study [18].

Low figures or slight effect of ASE (comparatively to the control behaviour) in the lumen fill modified specimens with wax were also found by Weigenand and Santos in [14,31]. However, a slight different and moderate value for ASE was showed by Beech modified with TEOS solution, app. 30% by Donath [10].

Partly the swelling strain of Scots pine modified with low concentration (7.5%) of MMF resin was found [30]. Specimens of Beech wood species modified with DMDHEU have shown similar results of this study with pine, nevertheless the wood species was different, retention of 30% up to 40% of swelling strain for RT directions, respectively, were found [8].

Between different levels of wood modification with cell wall reaction (DMDHEU and MMF resins), the EMC did not show significant reduction. Similar behaviour was found in other different properties: Like the fitting values of the iso-curves as well as the swelling coefficients. This result has an important meaning in the modified wood with chemicals. Faced with wood beams with large cross sections of solid wooden, the thickness of the specimen assumes an important role in the distribution of chemical. A gradient of 50% (app.) with uneven chemical distribution in the cross section (great than 50 mm) was found [32] and mentioned in [33] for the process of acetylation and furfurylation, respectively. However, to achieve the featured dimension stability of modified wood no high level of modification is needed.

Normally, physical properties are used as an attempt to understand the material behaviour and support some changes imparted by the modification method in others properties, mechanicals (stiffness stabilization) e.g.. However, no correlation between short-term mechanical properties (MOE or MOR) or long-term performances in the mechano-sorptive creep effect was suggested by Epmeier [11,30]. In the latter effect and in the same line, new variable ACE (anti-creep efficiency) similar to ASE was suggested [3] and analyzed [36].

Since there are many variables that influence the EMC (chemical, catalyser, curing temperature, wood species, etc…), it is hard to compare scientifically the most reported results. However, this study point out that modification of Portuguese pine species can enhance its physical properties in the same way than others modified softwood species.

5. Conclusions

The chemical modification can turn the wood into an engineered building material. The most prospective modification methods are those that provide high dimensional stability (i.e. a large reduction in the EMC leading to high ASE). This, however, seem to be not possible to achieve with the lumen fill modification methods studied here (TEOS and wax).

All different modification (1,3-dimethylol-4,5-dihydroxyethyleneurea-DMDHEU and N-methylol melamine-MMF resins, tetra-alkoxysilane-TEOS and wax) imparted an increase of density in a different extend translated by weight percent gain (WPG). Except for specimens modified with TEOS, the remaining modification methods (DMDHEU, MMF and wax) have shown a significant correlation between WPG and density.

The cell wall modification with resin based was the most effective methods to achieve high dimensional stability (ASE), low EMC and low swelling effect. However, DMDHEU was more effective than MMF resin.

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