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SOLVENT POLARITY AND INTERNAL STRESSES CONTROL THE SWELLING BEHAVIOUR OF GREEN WOOD DURING DEHYDRATION IN ORGANIC SOLUTION

Shanshan Chang,[a] Françoise Quignard,[b] Francesco Di Renzo,[b] and Bruno Clair [a,*]

The dimensional variations of green wood samples induced by organic solvents have been studied. The solvents used (ethanol, isopropanol, acetone, and acetonitrile) covered a wide range of polarity and were studied pure and in aqueous solutions over a wide range of concentrations. Samples of normal and tension wood of poplar were used in order to minimize the effect of hydrophobic extractives on the wood-solvent interactions. The evolution of wood volume and of tangential strain with the concentration of the organic solvents shows a behavior similar to gels, with a significant swelling for solutions of intermediate polarity. The similarity of volume obtained in water and less polar pure organic solvents strikingly contrasted the different effects of water and organic solvents on dry wood. Low-polarity solvents were extremely effective in the stress release of tension wood, as indicated by the pattern of longitudinal shrinkage. Solvent exchange does not affect the mesoporous structure of the cell walls of tension wood and is a promising way to reduce internal stress in wood products.

Keywords: Tension wood; Organic solvent; Longitudinal strain; Tangential strain; Stress release

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INTRODUCTION

The new context of the carbon disequilibrium produced by the use of petro-products in the last decades makes it important to explore all ways of carbon storage. Among them, the more sustainable issue is the massive use of wood and wood-plant based products, since the resource is renewable, cheap, and abundant. The replacement of 5% of concrete building by wood would prevent the emission of about 100 Mt/y of CO_2, corresponding to the emission of 50 million cars (Metz *et al.* 2007). The extended use of wood as a material faces new challenges at each step of the production process. A fundamental challenge is the control of the dimension changes between the water-saturated state of the living plant and the air-dried equilibrium of final product. The consequent strains, involved in several phases of the drying process, affect the quality of the products and hence their usability by producing distortions and cracks. Wood structure is mainly responsible for the pattern of shrinkage experienced by living wood when its original water is removed by drying. The variations of wood moisture content below fibre saturation point (a parameter defined as the moisture content at which free

water should be completely gone, while the cell walls are saturated with bound water) are responsible for dimensional variation in wood. Normally, the most stable dimension is in the longitudinal direction, and the least stable in the transverse direction. The departure of bound water results in anisotropic shrinkage, usually in the order of 0.1% to 0.2% along the longitudinal, 3% to 6% in radial, and 6% to 12% in tangential directions (Skaar 1988).

The shrinkage pattern also depends on the large mechanical stresses, called maturation stresses, which originate in living trees during the cell maturation process (Clair 2011). In the case of normal wood, newly formed fibers tend to contract longitudinally and to expand transversely, but this strain is restrained by their adherence to the older and stiffer wood cells. The resulting tensile stresses provide a better resistance against buckling. Adjusting this mechanism, a tree is able to create asymmetric growth stresses in inclined trees and to create a bending moment, allowing a trunk to recover verticality or a branch to maintain a given inclination. This unusually stressed wood is called reaction wood. Two kinds of reaction woods exist, depending on the kind of tree. While gymnosperms produce compression wood in the lower face of stems, angiosperms produce tension wood, generating high tensile stresses on their upper face (Wardrop 1964; Fisher and Stevenson 1981). In tension wood, longitudinal tensile stresses can reach up to 70 MPa (Okuyama *et al.* 1994). Maturation stresses are present in the living stem as internal or residual stress even without the action of external forces. During the transformation process (falling of tree and sawing), a part of the stress is released, but internal stresses still remain in the log. To reduce stress in wood product, heating treatments, such as steaming can be applied (Nogi *et al.* 2003a, 2003b). The phenomenon associated with this technique is known as 'hygrothermal recovery' (HTR, Kubler 1987; Gril and Thibaut 1994). Recently, Chang *et al.* (2009a) showed that the use of alcohol has a similar effect and releases stress

More generally, the treatment of wood with organic solvent is an important technological process and forms the basis of several methods of preservation and functionalisation of wood materials. In most cases, the interactions between wood and organic solvents have been studied on oven-dried wood. The degree of swelling of oven-dried wood in solvents is a direct function of the polarity of the solvent (Mantanis *et al.* 1994). Most organic solvents are less polar than water, and oven-dried wood soaked in water usually swells much more than when immersed in organic solvents. The only exceptions are observed in the case of very polar solvents, for which swelling is comparable to the swelling in water. The sensitivity to polar solvents has suggested that swelling of dry wood depends on a mechanism similar to the swelling of other hydrophilic materials, such as natural polyelectrolyte gels (Wilson and Wilson 1918; Anseth *et al.* 1996). The extent of swelling of dry wood is more limited than the swelling of polysaccharide or polypeptide gels (Draget *et al.* 1996; Pourjavadi and Salimi 2008), due to the composite nature of wood, which includes a less hydrophilic lignin fraction and presents a complex cell structure.

In this paper, we present the first study on shrinkage/swelling behavior of green (never-dried) poplar wood samples in the aqueous solutions of several organic solvents at different concentration levels. This study contributes to a more fundamental understanding of the surface properties of wood cells. Swelling and shrinkage of gels are the result of the competition of the gel surface with the solvent of the surrounding

solution. The osmotic pressure generated by the different affinity of a component of the solution for the solid adsorbent and the solvent accounts for the displacement of fluids between the gel and the solution. In the case of the interaction of some polyelectrolytes with organic solvents, it has been shown that swelling occurs only in the presence of solvents with a polarity closely matching the polarity of the polymer surface (Phenix 2002; Ono *et al.* 2007). The study of the competition between water and organics for the surface of green wood can provide information on the surface properties of wood before they are affected by drying treatments. Poplar wood was chosen for its low content of extractives, which are low-polar molecules that are able to modify the hydrophilic-lipophilic balance of the surface.

EXPERIMENTAL

Wood Samples

One tilted and bent young poplar tree with a diameter of 8 cm was sampled for various testing conditions. This species produces tension wood with a typical gelatinous layer and a longitudinal drying shrinkage up to 10 times higher than that of normal wood (Fang *et al.* 2008). Normal wood and tension wood samples were taken from the lower and upper side of the tilted trunk, respectively. The presence of tension wood was confirmed by anatomical observations, showing a large amount of fibers with a gelatinous layer and a thin S_2 layer. Care was taken to maintain samples in wet condition during storage from the time of sampling to experimentation. As a result, the moisture content of samples was always kept much higher than the fibre saturation point.

Five sets of specimens were sampled along the trunk axis; 9 specimens from pith to bark for normal wood and tension wood were obtained for each set. Specimen size was: 60 mm (longitudinal direction) × 2 mm (radial direction) × 7 mm (tangential direction). In order to compare them, the specimens in each set were located nearly at the same position.

Dehydration by Organic Solvents and Dimension Changes Measurements

Dehydrations were performed in ethanol, acetone, acetonitrile, and isopropanol. The choice of solvents was dictated by their miscibility with both water and the liquid CO_2 used for the final supercritical drying step. Some properties of the solvents are reported in Table 1. The octanol/water partition coefficient (Ghose *et al.* 1988), *viz*. the ratio of the concentrations of the solvent in octanol and water equilibrated phases, increases for decreased polarity of the solvent. The Hildebrandt solubility parameter is representative of the cohesive strength of the solvent, while the Hansen hydrogen bond parameter is the component of the cohesive force corresponding to hydrogen bonding, which tends to be higher for more polar protic solvents.

The first to fourth wood sets were dehydrated by immersion in serial solutions of increasing solvent concentration (10, 30, 50, 70, 90%, and anhydrous) during three days for each step. The fifth set was dehydrated by repeated three-day treatments with anhydrous ethanol, in order to check the effect of serial dehydration on final dimensions.

This experiment was stopped when the weight difference between two subsequent treatments became less than 0.3%.

Wood specimens dimensions at different dehydration stages were measured along longitudinal and tangential directions using a digital micrometer (precision 0.001 mm) on a dedicated device allowing perfect repositioning of the specimen at each measurement. Bending or warping was weak enough to be neglected. Relative dimensional changes due to organic substitution in longitudinal and tangential directions were represented as strains ε_L and ε_T, respectively, and expressed in percent. The dimensional change was calculated as the dimensional variation between each dehydrated condition and green condition, divided by the dimension in the green state. A positive value of ε_L or ε_T indicates that the sample expands, and a negative one indicates shrinkage. The volume variations of the specimens were calculated as the product of longitudinal, tangential, and radial strain, and the radial strain being assumed as half of tangential strain (Nakano 2008).

Table 1. Properties of the Solvents Used

Solvent	Boiling point / °C	Octanol/water partition coefficient (log)	Hildebrandt solubility parameter / $MPa^{0.5}$	Hansen hydrogen bond parameter / $MPa^{0.5}$
water	100	-	47.9	42.3
ethanol	79	0.07	26.4	19.4
isopropanol	82	0.39	23.5	16.4
acetone	56	0.67	20.2	7
acetonitrile	82	0.66	24.1	6.1

N_2 Adsorption-Desorption Measurement

To evaluate the effect of solvent dehydration on gelatinous layer texture, nitrogen adsorption measurements were performed on the supercritical CO_2 dried samples. Such techniques, typically used for the characterization of adsorbents or inorganic catalysts, have been applied to the study of biological materials such as wood. Before nitrogen adsorption measurements, the organic solvent in dehydrated samples was replaced by liquid CO_2, which was supercritically extracted in a Polaron 3100 apparatus. Then the dried samples were tested on a micromeritics ASAP 2010 volumetric apparatus at 77 K for adsorption measurement. This experimental technique allows the specific surface area (S_{BET}) (Brunauer *et al.* 1938) and the pore size distribution (Broekhoff and de Boer 1967) of the samples to be evaluated. The volume of pores smaller than 50 nm was measured as the volume of liquid nitrogen adsorbed at p/p° 0.98. Only tension wood samples have been measured since only the specific gelatinous layer of tension wood contains significant mesoporosity (Clair *et al.* 2008; Chang *et al.* 2009b).

RESULTS

Dimensional Deformation during Organic Solvent Exchange

Figure 1 shows the variations of longitudinal strain (ε_L) during serial organic solvents substitution. As observed previously with alcohol (Chang *et al.* 2009a), normal

wood slightly swelled during serial organic solvent substitution. For each solvent, a stable value of the strain (-0.02% to +0.1%) was rapidly attained, which was the same order as what is released with hygrothermal treatments (Clair 2011). Tension wood shrunk greatly (up to 0.5 %) and seemed to continue to shrink at the end of the substitution without reaching an asymptote.

The range of longitudinal strain was different from solvent to solvent during the substitution process. Acetonitrile gave the largest longitudinal swelling or shrinkage (around -0.5%, at the end of the substitution), and was followed by acetone. Both isopropanol and ethanol showed similar smaller strains. It also can be seen that during acetone and acetonitrile substitution, more than 50% of the final strain appeared between 0 to 30% concentrations in tension wood specimens. During ethanol substitutions, strains appeared to be proportional to the solvent concentration.

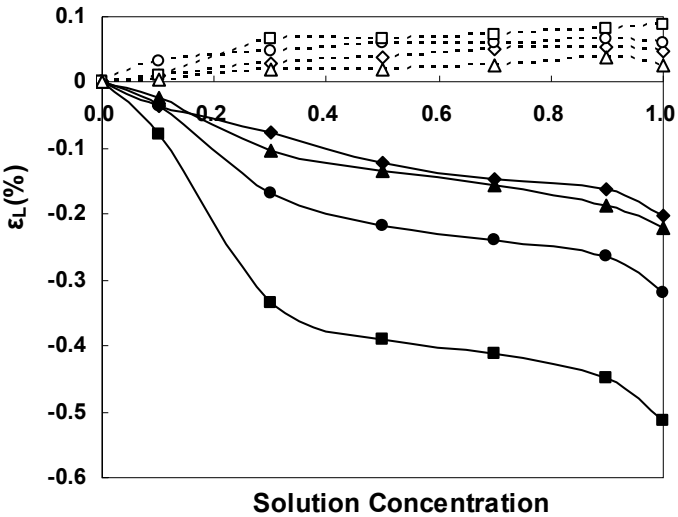

Fig. 1. Mean longitudinal strain (ε_L) after serial organic solvents substitution in poplar normal and tension wood. Filled lines (filled symbols): tension wood; broken lines (void symbols): normal wood; square: acetonitrile; circle: acetone; triangle: isopropanol; diamond: ethanol

Along the tangential direction (Fig. 2a), the value of tangential strain (ε_T) was positive both in normal wood and tension wood, which means that the specimens expanded in tangential direction in all the organic solutions in the same order as what was measured after hygrothermal treatment (Clair 2011). As the solvent concentration increased from 0 to 70%, the specimens swelled and reached a maximum swelling. These maximum strains of tension wood at 70% concentration largely depended on the nature of the solvent and varied from around 0.5% in ethanol to 1.4% in acetonitrile. At higher concentration, from 70 to 100%, the specimens shrank back and the swelling ratio gradually decreased to reach an average value of 0.35% in pure organic solvents. Independently of the nature of the solvent, normal wood always presents a smaller swelling than the corresponding tension wood. When samples were dehydrated in anhydrous ethanol directly, the deformation values (both in longitudinal and tangential

directions) were similar to the final state reached after increasing ethanol concentration by steps (data not shown).

The volume variation as a function of the concentration of the organic solvent is given in Fig. 2b. It was found that at 70% acetonitrile, tension wood increased in volume by 1.6% and normal wood by 1.3%. At 100% acetonitrile, both types of wood were back to the original volume plus or minus 0.03%. In presence of the other solvents, volume variations followed a similar pattern, with a lower swelling maximum at intermediate concentrations and a small retention of swelling in pure organic solvent.

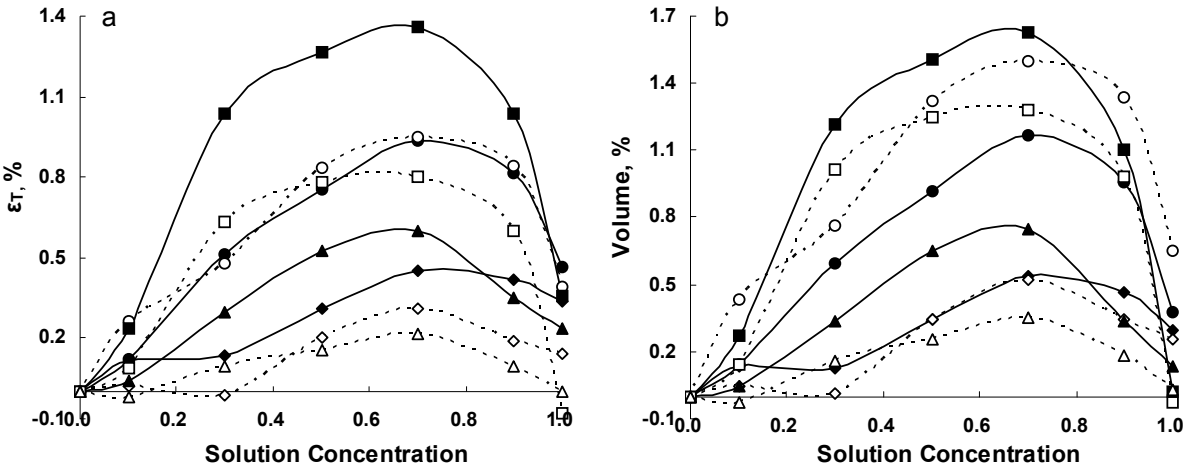

Fig. 2. (a) Mean tangential strain (ε_T) and (b) estimated volume strain during serial organic solvents substitution in poplar normal and tension wood. Filled lines (filled symbols): tension wood; broken lines (void symbols): normal wood; square: acetonitrile; circle: acetone; triangle: isopropanol; diamond: ethanol

Mesoporosity of Tension Wood Samples

Isotherms for the adsorption and desorption of nitrogen at 77K on solvent-substituted poplar tension wood aerogels are given in Fig. 3. The shape of the isotherms was very similar for samples exchanged with different solvents. According to the IUPAC classification (Sing *et al.* 1985), the isotherm of all samples are type IV with a H3 type hysteresis loop, indicating the presence of slit-shaped pores with a non-uniform size. The characteristic termination of hysteresis at p/p° 0.45 corresponds to the threshold of stability of N_2 menisci (Trens *et al.* 2005). The pore surface areas as measured by the B.E.T. method were 18.1, 14.8, 11.7, and 8.8 m^2 g^{-1} for tension wood samples under acetone, ethanol, acetonitrile, and isopropanol substitution, respectively. The surface area data were strongly correlated with the mesopore volume. The volume of pores smaller than 50 nm was 50, 46, 38, and 30 mm^3 g^{-1} for samples treated with acetone, ethanol, acetonitrile, and isopropanol, respectively. These volumes of pores are not significantly different considering the natural variability of amount of gelatinous layer from sample to sample.

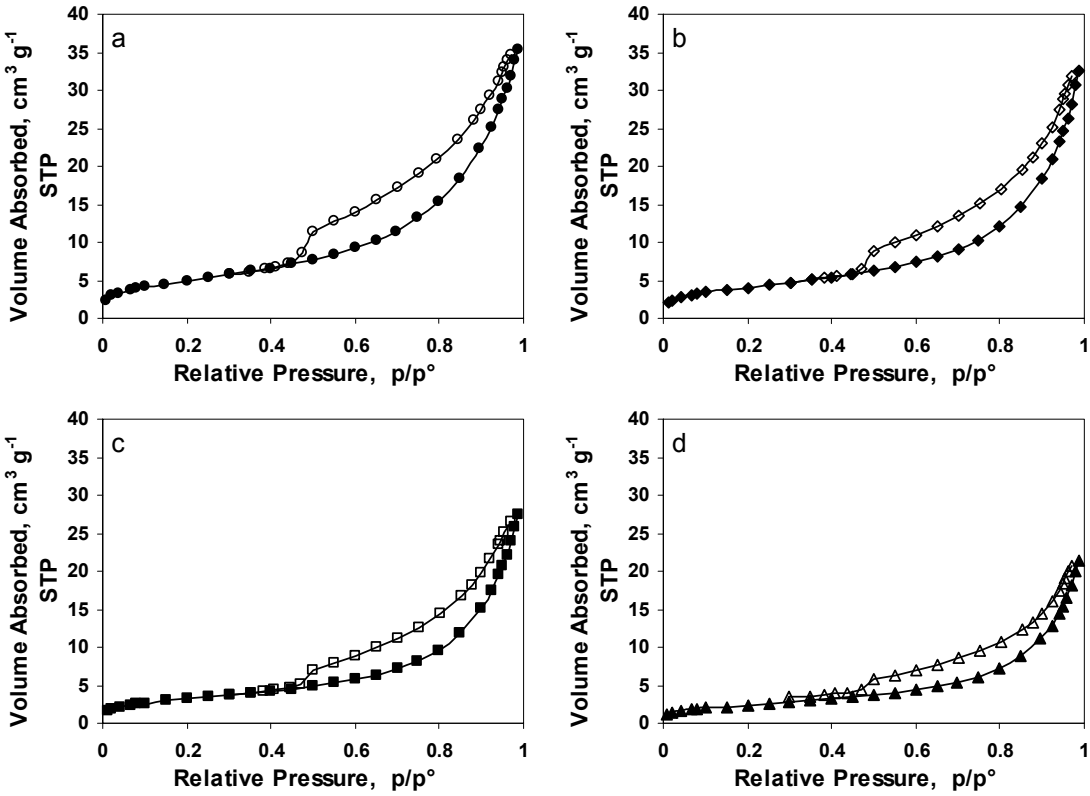

Fig. 3. Nitrogen adsorption-desorption isotherms at 77K of solvent-substituted poplar tension wood. (a) acetone; (b) ethanol; (c) acetonitrile; (d) isopropanol. Filled shape: adsorption; void shape: desorption

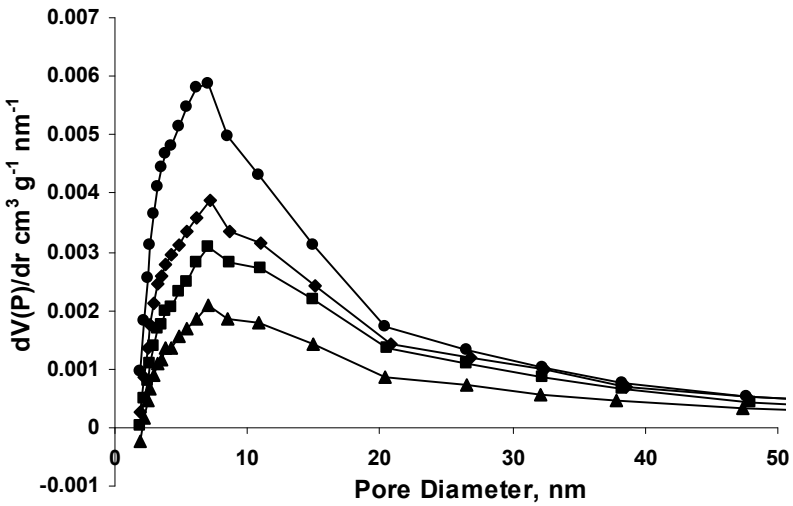

Fig. 4. Pore size distribution of solvent-substituted poplar tension wood. Square: acetonitrile; circle: acetone; triangle: isopropanol; diamond: ethanol

The peculiar shape and typical hysteresis loop of these curves are indicative of a highly mesoporous adsorbent. The pore size distributions determined from the nitrogen

adsorption data by the method of Broekhoff and de Boer (1967) are plotted in Fig. 4. The majority of the accessible pores exhibited diameters between 2 and 50 nm, with the maximum in the distribution curves occurring at a diameter of 7 nm for all samples. The pore size distribution was not at all affected by the changes of the nature of the solvent (Fig. 4).

DISCUSSION

Tangential and Volume Strain in Organic Solutions

The curves of volume swelling shown in Fig. 2b are quite similar to the curves of tangential swelling in Fig. 2a and are relatively unrelated to the longitudinal swelling data shown in Fig. 1. This is in agreement with the relative extent of the two kinds of strain, much larger in the case of tangential strain, as observed in virtually all kinds of woods. The swelling of dry wood in organic solvents was extensively studied, and it was observed that most non-polar or weakly polar solvents induced a swelling of oven-dried wood significantly smaller than the swelling induced by water or strongly polar solvents (Mantanis *et al.* 1994; Morisato *et al.* 2002). If extrapolated from dry-oven wood to green wood, these data would suggest that replacement of water by non-polar solvents should bring about a tangential shrinkage of wood. Such behaviour does not correspond to the observed swelling of green poplar wood in mixed water-organic solvents (Fig. 2). This indicates that permanent modifications induced by drying affected the accessibility to solvents of some parts of the wood structure.

The tangential swelling of the green poplar studied here was very similar in normal and tension wood (Fig. 2a); hence it is not related with the microfibrils angle or the presence of G-layer. This is confirmed by the lack of significant modifications of the mesoporosity of the tension wood samples (Fig. 3), a typical property of the gelatinous layer but is in good agreement with tangential strain measured during stress release (Clair 2012). The observed tangential swelling is solvent-related and it is more important for less polar solvents, as easily deduced from the comparison of the swelling data of Fig. 2 and the solvent properties reported in Table 1. This trend is completely opposite to the trend observed for the swelling of dry wood in organics (Mantanis *et al.* 1994; Morisato *et al.* 2002) and confirms the difference in surface properties of green and dry wood. The bell-shaped dependence of swelling with the concentration of organics (Fig. 2) is especially relevant, as it indicates a non-linear dependence from the composition of the solvent. Mantanis *et al.* (1994) discussed data of Hasselblatt (1926) and observed that the swelling of several woods in organic solvents was larger if the solvents contained some water. Hiroki *et al.* (2001) for polypeptide gels and Nishida *et al.* (2003) in the case of polymeric lignin gels observed a maximum swelling at intermediate alcohol concentrations and a return to the unswelled volume for higher alcohol concentrations (Hiroki *et al.* 2001). This non-linear behavior, typical of the swelling of many polymeric systems with solvents, suggests that an optimized solvent treatment can further open the wood structure and increase its accessibility to preservation treatments. Such an effect can also present some interest in the treatments needed for the separation of wood components as a first step for the production of second-generation bio-based chemicals in

biorefineries. When different solvents were tested, swelling was only observed for solvents with values of the solubility parameter corresponding to the nature of the polymer. Lower or no swelling was observed for lower or higher values of the solvent solubility parameter for materials as different as coal (Jones *et al.* 1991), paints (Phenix 2002), polyelectrolytes (Ono *et al.* 2007), and partially-dried larch wood (Loskutov and Aniskina 2008).

The order of the amount of swelling for the aqueous solutions of different solvents is acetonitrile > acetone > isopropanol ~ ethanol. This order is unrelated to the molecular volume or the density of the solvents and it is not strictly related to the values of the solubility parameter. However, it is in excellent agreement with the order of the octanol/water partition coefficient, representative of the lipophilic/hydrophilic balance of the solvent, and with the Hansen hydrogen-bonding parameter, representative of the hydrogen-bond component of the cohesive force of the solvent. It seems clear that the extent of swelling of green wood increases when the wood surface interacts with more lipophilic solvent and it is related to the decrease of the force of hydrogen bonds which connect wood sub-structures. However, the dependence of swelling on the lipophilicity of the solvent is not monotonous.

The swelling curves of Fig. 2 indicate that green wood exchanged with pure solvents presented a volume similar to its volume in pure water. This suggests that water and organic solvents of solubility parameter between 20 and 26 are at the equilibrium with a similar conformation of poplar green wood. The bell shape of the swelling curves corresponded to a significant swelling for mixed solutions of water and organics. This suggests that the most interacting solvent for undried poplar wood would present a solubility parameter intermediate between 26 (the value for ethanol, the most polar organic used) and 47 (the value for water).

Longitudinal Strain and Stress Release in Organic Solutions

Longitudinal strain follows a pattern of evolution with the concentration of organic solvents very different from the pattern observed by tangential strain, as evidenced by comparison of Figs. 1 and 2a. Previous results (Chang *et al.* 2009a) have suggested that the evolution of longitudinal strain with alcohol concentration is related to the structure of the cell walls. The cell wall is composed of a middle lamella, which is the highly lignified joint between two cells, then a primary wall and a secondary wall divided in three layers named S_1, S_2, and S_3 from the border to the centre of the cell. Whereas primary wall, S_1, and S_3 are reinforced by crystalline cellulose microfibrils nearly perpendicular to the fiber axis, the S_2 layer is the thickest and the angles of the microfibrils are around 10° to 30° relative to the cell axis. The longitudinal shrinkage is known to be related to the microfibrils angle in the S_2 layer. Microfibrils angle is large in juvenile wood or compression wood, leading to higher longitudinal shrinkage than in normal wood where microfibrils angle is lower. In tension wood of some species, the peculiar gelatinous layer replaces the S_3 layer and part of the S_2 layer. In gelatinous layer, the microfibrils angle is close to 0, but a paradoxical high longitudinal shrinkage (up to 1.2%, Chow 1946; Clair and Thibaut 2001; Clair *et al.* 2003; Yamamoto *et al.* 2005) occurs due to the collapse of its gel-like structure (Clair *et al.* 2008). This excessive

shrinkage causes problems in wood utilization, including longitudinal crooking and bowing, and thus reduces the potential economic value of the material.
Previous results (Chang *et al.* 2009a) have shown that the longitudinal swelling of normal wood under organic solutions mainly depends on the microfibrils angle of the S_2 layer in the cell wall. A swelling was observed in the normal wood of poplar, whereas a large shrinkage was observed in poplar tension wood, in which the gelatinous layer presents a microfibrils angle close to zero. The behavior of tension wood, which shrunk in all organic solutions, is consistent with what was observed for tension wood shrinking in ethanol (Chang *et al.* 2009a). Since the variations of shrinkage of tension wood are very different from the changes in porosity of the gelatinous layer measured by nitrogen adsorption-desorption, the longitudinal strain in tension wood is not induced by a collapse of the gelatinous layer as during the evaporative drying, but would be the expression of the release of residual tensile stress, a basic feature shared by all types of tension wood. The formation of tension wood is characterized by the development of considerable maturation stresses (Wardrop 1964; Okuyama *et al.* 1994). Even after the release of macroscopic stress resulting from wood sample cutting, some residual stresses remain in the microstructure. At the cell wall level, the gelatinous layer is under tension (Clair *et al.* 2005, 2011) and this tensile stress is supported by the other layers, which are subjected to compression stress. During wood-solvent interaction, the water-solvent molecule exchange may provoke the increase of molecular mobility within the amorphous substance of the cell wall, *i.e.,* the matrix. Thus, molecular mobility affects essentially the other layers which are compressive stressed, and then a negative strain occurs.

The results shown in Figs. 1 and 2 reveal that the less polar solvents, acetonitrile and acetone, induced greater strains both in longitudinal and tangential directions. The larger volume swelling observed for less polar solvents contributes to more extended molecular fluxes inside the samples.

CONCLUSIONS

The mechanical behavior of normal and tension poplar green wood immersed in organic solvents and their aqueous solutions were investigated, and the solvent-induced strains were measured. The following main conclusions can be drawn:

1. In the longitudinal direction, normal wood moderately swells during solvent substitution; however, tension wood shrinks by an amount depending on the polarity of the solvent. The longitudinal strains of tension wood are not due to the presence of a given solvent but to the release of pre-existing internal stress during the exchange process. The less polar the solvent, the greater the strain observed, suggesting that disruption of hydrogen bonds within the amorphous substance of the cell wall is an important mechanism of stress release.
2. Organic solvents, as well as water can keep apart the secondary structure of green wood and prevent any significant tangential shrinkage. Moreover, mixed organic-water solvents bring about a significant non-linear swelling of green wood, which is typical behavior of organic gels.

3. Among the four organic solvents selected (ethanol, isopropanol, acetonitrile, and acetone), the more polar ones (ethanol and isopropanol) bring the lowest effect on the dimensional deformations both in longitudinal and tangential directions. Ethanol, which is still the primary solvent for sample preparation in research activities, provides a gentle process that can better keep the structure of samples and also can be readily carried out practically. On the other hand, the less polar solvents, especially acetonitrile, are highly effective for stress release of tension wood, a pre-condition for the use of this kind of wood in structural applications. In general, solvent exchange could be a promising way to reduce internal stress in wood product, similar to hygrothermal recovery induced by heating treatments. The development of effective methods of wood treatments will require a more detailed knowledge of the way in which solvents interact with each part of the wood structure.

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