

Effect of extractions on dynamic mechanical properties of white mulberry (*Morus alba*)

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Abstract Vibrational properties of wood are affected by several parameters, of which extractives can be one of the most important ones. Wood for European musical instruments has been often studied, but traditional Middle Eastern ones had been left unnoticed. In this study white mulberry (*Morus alba* L.), the main material for long-necked lutes in Iran, was extracted by five solvents of various polarities (water included). Free-free bar forced vibrations were used to measure longitudinal (L) loss tangent ($\tan\delta$), storage (elastic) modulus (E') and specific modulus (E'/γ) in the acoustic range. Their anisotropy between the 3 axes of orthotropy was determined by dynamic mechanical analysis. Native wood had a quite low E_L'/γ but its $\tan\delta$ was smaller than expected, and the anisotropy of $\tan\delta$ and E'/γ was very low. Removal of extractives caused $\tan\delta$ to increase and moduli to decrease. Acetone, the most effective solvent on damping despite a moderate extraction yield, increased $\tan\delta_L$ by at least 20% but did not modify E'/γ as much. When used successively, its effects masked those of solvents used afterwards. Anisotropy of E'/γ was nearly unchanged after extraction in methanol or hot water, while $\tan\delta$ was much more

increased in R than in T direction. Results suggest that in white mulberry, damping is governed more by nature and localization of extractives rather than by their crud abundance.

Keywords Anisotropy · Damping coefficient · DMA · Extractives · Vibrational properties · White mulberry wood (*Morus alba* L.)

Introduction

Wood has always been considered as a multifunctional material. Each of its versatile properties makes it appropriate for a particular final use. Wood historical use in musical instruments is in relation with its dynamic mechanical, or vibrational, properties, including mechanical damping (loss tangent) $\tan\delta$, storage (elastic) modulus E' and specific modulus E'/γ . As a quasi-orthotropic material at the macroscopic scale, wood has different properties in longitudinal (L), radial (R) and tangential (T) directions [1–3]. In the case of wood used for Western classical string instruments, it is generally accepted that a low $\tan\delta$ and high E'/γ in axial direction, and a high anisotropy, are convenient for obtaining a soundboard of good quality. However, few studies have addressed the vibrational properties of wood used in Middle-East instruments. String instruments in Iran can be traced back to 970 B.C. Long-necked lutes *Tar*, *Setar* and *Kamancheh* are specifically made from white mulberry (*Morus alba* L.), which is also used for the Japanese short-necked lute *Biwa* [4].

Sources of variations in dynamic mechanical properties of wood include cell arrangement and grain angle, microfibril angle within the cell wall, proportions of constitutive

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polymers, as well as the presence of additional compounds [5–9]. Although in lower quantities than cell wall constitutive polymers, extractives can have a considerable effect on mechanical and damping properties of wood. Exceptionally low damping of some musically important woods was somehow correlated with their extractives. Extractives impact can be studied either through correlations between their amounts and vibrational properties variation resulting by their removal, or by the re-injection of extracts into a “neutral” wood. Methanol extraction increased the $\tan\delta$ of heartwood by 15–37% in red cedar (*Thuja plicata*) and up to 60% in African Padauk (*Pterocarpus soyauxii*), while E'/γ slightly decreased [10, 11]. Impregnation of water-soluble extractives of pernambuco (*Caesalpinia echinata*) into spruce decreased $\tan\delta$ by a half [12]. The formation of hydrogen bonds between extractives and cell wall matrix was proposed as a possible cause of $\tan\delta$ reduction [13]. Impregnation of Sitka spruce with isolated key chemical compounds from muirapiranga (*Brosimum rubescens*), a Moraceae as is mulberry, decreased $\tan\delta$ by up to 25%, both in axial and radial directions. This was explained by motion restriction of matrix macromolecules due to extractives entering [14]. Contrary to these studies, water-soluble extractives of Reed (*Arundo donax* L.) increased both $\tan\delta$ and E' [15, 16]. Extractives can also change wood equilibrium moisture content (EMC) [17]. Higher EMC induces higher $\tan\delta$ and lower E'/γ [18, 19]. The potential effect of extractives on vibrational properties could come from their chemical structure, cellular location and relation with basic polymers [11, 13]. Removing extractives using solvents of different polarities could give a first idea about their polarity and possible cellular location.

Our work aims at evaluating the dynamic mechanical properties of white mulberry and understanding the possible contribution of extractives. Basic properties of samples from different regions of Iran were compared in a previous study [20, 21]. In the present article, mulberry wood was extracted in five solvents of different polarities. To separate the overlapping effect of various solvents, they were used both as independent extracting agents, and in a successive order on the same specimens, to determine the changes in acoustical properties along the grain. Furthermore, the effects on the anisotropy of $\tan\delta$, E' and E'/γ were also studied after extraction by the two solvents with highest yields.

Materials and methods

Material

Mulberry trees were cut in Iran and kept for 1 month in outdoor conditions. Wood was selected there by a professional instrument maker. Several $500 \times 50 \times 50 \text{ mm}^3$

($L \times R \times T$) rods were cut from the middle of the heartwood and sent to France, in three batches within 1 year. The 1st batch (used for powder samples and independent extractions on vibrational specimens) and 2nd batch (successive extractions on vibrational specimens) came from the same tree; the 3rd (specimens for DMA) came from another tree.

A portion of each rod was ground, the fraction passing through 40 mesh and retained on 60 mesh sieves was kept for powder extractions (TAPPI standard method T207_cm) [22]. For vibrational tests, the rods were cut into approx. 200 axial specimens of dimensions $150 \times 15 \times 2 \text{ mm}^3$ ($L \times R \times T$), from which 77 specimens were kept for extractions and controls (Table 1). For dynamic mechanical analysis (DMA), specimens were cut to a cross section of $4 \times 3 \text{ mm}^2$ and a length of 42–48 mm (Fig. 1). 14 specimens were prepared in each direction of orthotropy leading to a total number of 42.

Conditioning and physical measurements

The specimens were oven dried at 60°C for 48 h. This procedure ensured that the equilibrium was reached in adsorption. Residual moisture content, as compared with oven drying at 103°C, was around $1.36 \pm 0.49\%$. Specimens were then kept for 3 weeks in controlled conditions of $20 \pm 2^\circ\text{C}$ and $65 \pm 5\%$ RH. This procedure was repeated before any mechanical measurement. Specific gravity γ (both oven dried and air dried) and EMC were recorded. EMC of native wood was of $7.9 \pm 0.8\%$.

Table 1 Specimens number and treatments for both independent and successive methods of extraction

Number of specimens	Solvent	Drying and stabilization condition	Number of cycles of drying and stabilization
12	Hexane (HX)	60°C for 48 h	2
12	Dichloromethane (DM)	followed by 20 ± 2°C and 65 ± 5% RH for 3 weeks	2
12	Acetone (AC)		2
12	Methanol (ME)		2
5	Hot Water (HW, 70°C)		2
12	HX/DM/AC/ME/ HW (100°C)		6
12	Controls		6
15 DMA (5L, 5R, 5T)	ME		2
15 DMA (5L, 5R, 5T)	HW (70°C)		2
12 DMA (4L, 4R, 4T)	Controls		2

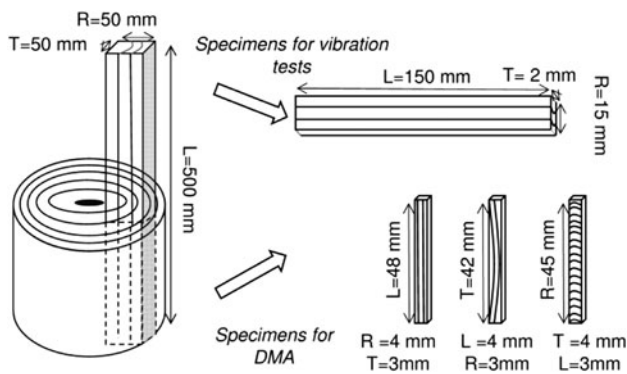


Fig. 1 Cutting plan for vibrational and DMA specimens. Variations in length of DMA specimens were due to limitations in raw material

Although mechanical measurements could not be run in a climatic chamber, mass change was small: $-0.3 \pm 0.4\%$ for native state specimens, both during vibrational and DMA tests. For treated specimens, mass change was negligible ($-0.1 \pm 0.1\%$) during vibrational tests, and less than that during DMA tests ($-0.6 \pm 0.7\%$).

Measurement of dynamic mechanical properties

Axial dynamic mechanical properties were measured both by vibrational tests and by DMA, while anisotropy was studied only by DMA.

Non-contact forced bending vibrations of free-free bars

A frequency scan was imposed through an electric magnet facing a tiny steel plate (15–20 mg, a negligible additional weight) glued at one end of each specimen. A laser triangulation sensor measured the displacement. A program developed with LabView[®] software [23] monitored vibration emission and detection. Specific elastic (storage) modulus (E_L'/γ) was calculated from the first resonance frequency by the Euler–Bernoulli formula and elastic modulus (E_L') was obtained by multiplying E_L'/γ with specific gravity (γ). Damping coefficient was measured using both bandwidth at half power in the frequency domain (or quality factor) and logarithmic decrement of amplitude in the time domain after stopping the vibration. Both measurements shall be equivalent to loss tangent $\tan\delta$, if $\tan\delta \ll 0.1$, which is the case for air-dry wood in this temperature/frequency range. Three repetitions were made for each specimen. Resonance frequencies were in the range of 200–400 Hz.

Dynamic mechanical analyzer (DMA)

The viscoelastic behavior of specimens was measured using a BOSE[®] ELF3230 DMA equipped with tension/

compression fatigue grips, a 22 N ($\pm 0.17\%$ maximum error) load cell and a high-resolution displacement sensor (1 mm range with $\pm 0.26\%$ maximum error). The specimens were fixed between two clamps with a working distance of 35 mm and tested in tension along their longest direction. The tests were done in purely alternative tension/compression loading controlled in displacement with an amplitude of ± 0.0175 mm corresponding to a maximum tension/compression strain of $\pm 0.02\%$ (i.e., within the linear viscoelastic region, see [24]). Using BOSE WinTest[®] analysis software, E^* (norm of the complex modulus), E' (storage modulus), E'' (loss modulus) and $\tan\delta$ (loss tangent) were calculated. Both moduli and $\tan\delta$ were corrected for the stiffness of the whole apparatus (around 1785 N/mm with a negligible viscous contribution), measured using a stiff steel specimen. Frequency sweeps from 0.1 to 10 Hz were run in triplicate for each specimen, native and then treated.

Extraction procedures

Extractions used solvents of increasing polarity: hexane (HX), dichloromethane (DM), acetone (AC), methanol (ME) and hot water (HW). The most used were Soxhlet extractors. Groups of specimens, with similar ranges in properties, were defined after vibrational tests in native state and subjected to different treatments (Table 1).

For extractions on powder and on solid specimens for vibrational tests, extractions were run both in an independent (or parallel) and in a successive (or serial) way. Independent extraction means that a sample is submitted to one extraction in a given solvent, and its properties are measured before and after this single treatment. In this case, hot water extraction from vibrational specimens was run (for 8 h) at 70°C (not using Soxhlet). Successive extractions means that a given group of specimens is submitted to extraction, first by the less polar solvent (HX), then oven dried (brief process: weighted, air-dry stabilized, weighted, mechanically tested, and dried again for solid wood specimens), extracted by the next solvent (DM), and so on. In this case, a “standard” Soxhlet extraction (<95°C) was run for water (complete description of conditions can be found in Table 1).

Specimens were dried before being extracted, so that less polar solvents could not enter cell walls. Control specimens underwent only physical steps (drying and stabilization) and were measured in the same time and condition as the extracted ones. For determination of extractive content, 3 g of powder were put in a cellulose cartridge, extracted for 8 h, and their oven-dry (48 h at 60°C) weight loss was measured. For solid wood, as color hardly changed during extraction, duration of 12 h was chosen. Based on the yields of extractions in vibrational

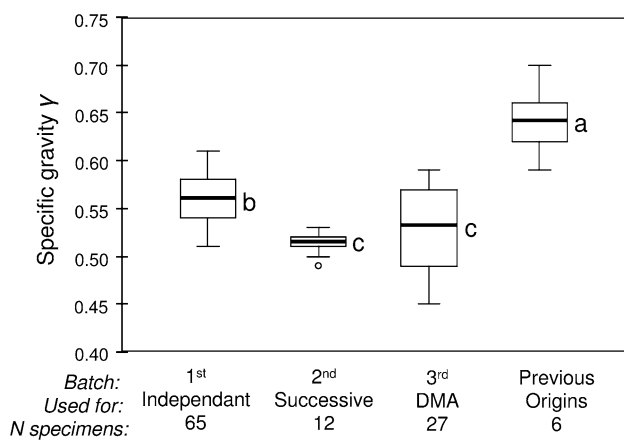


Fig. 2 Box plot of specimens specific gravity (γ) for the three batches of wood under study, and for previous data on wood from different origins [20]. *a–c* significantly different groups (one-way ANOVA)

specimens, ME and HW were applied as independent solvents on DMA specimens. For each anisotropic direction, 4 specimens served as controls, 5 were extracted in ME and 5 in HW (70°C, without Soxhlet). Although hemicelluloses may be partially depolymerized at moderately high temperatures for water-saturated wood [25, 26], treatment temperatures and duration were sufficiently low to neglect such effect.

Results and discussion

Properties of native mulberry wood

The specific gravity γ of the mulberry wood under study ranged from 0.45 to 0.61 (Fig. 2). This was significantly lighter than wood from different regions in a previous study [20]. The 1st batch (used for independent extractions) was significantly denser than the 2nd one (used for successive extractions), although they came from the same tree. The 3rd batch (used for DMA), which came from a different tree, covered a broad range, but its average γ was not significantly different from the 2nd batch. Differences in density were not clearly related to those in vibrational properties (Fig. 3).

The specific dynamic modulus in L direction of all studied batches of wood was rather low (Fig. 3) and variable (11–18 GPa). Although dispersion was quite large, $\tan\delta_L$ was negatively related to E_L'/γ . However, all batches generally had a lower $\tan\delta_L$ than the “standard trend” [5, 6], a statistical relationship obtained on 20 softwoods and 30 hardwoods that can be considered as a reference. In the 1st and 3rd batches $\tan\delta_L$ was in average 6 and 11% lower than “standard”, but with a higher dispersion than in 2nd

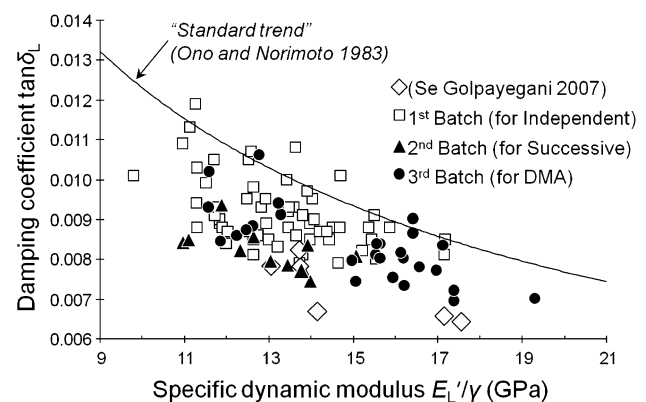


Fig. 3 Relationship between E_L'/γ and $\tan\delta_L$ for 4 batches of native mulberry wood (N specimens: see Fig. 2)

batch and in wood from a previous study [20], for which $\tan\delta$ was always within the lower range (21 and 23% lower than the standard).

$\tan\delta_L$ measured with DMA method was higher than that measured with free–free vibration. However, it exhibited a decreasing trend against frequency, so that the difference could be attributed to the higher frequency of the free–free vibration. This decrease of $\tan\delta$ with frequency was also observed in other directions, as well as a slight increase of elastic moduli. However, the anisotropic ratios remained constant in the observed frequency range. In the following analysis, only the values measured at 10 Hz will be used. Ordering of the different $\tan\delta$ in the 3 principal directions was the same as previously reported, i.e., $\tan\delta_T > \tan\delta_R > \tan\delta_L$ [27]. However, damping anisotropies between the three main directions were small: $R/L \approx 1.03$, $T/L \approx 1.34$, and $T/R \approx 1.30$. These values were lower than those collected from several studies by Brémaud et al. [3] in which the average ratios were of 2.7 (R/L), 2.9 (T/L) and 1.14 (T/R) for hardwoods. Similarly, the anisotropy of E' agrees with well-known relationships, i.e., $E_L' \gg E_R' \geq E_T'$, but actual values of ratios ($L/R \approx 4$, $L/T \approx 8$ and $R/T \approx 1.9$) were in the lower range of anisotropy compared with literature reviews (e.g., [2, 28]). It can be noted that mulberry has a low longitudinal E'/γ and a very reduced anisotropy when compared with resonance spruce that is used for top plates of Western string instruments, and is closer to maple (used for back and sides) in this respect.

Yield of extraction

In wood powder (Fig. 4a), approximately the same cumulated amount of extractives was removed when applying solvents independently or successively. In solid wood (Fig. 4b), on the contrary, cumulated weight losses differed between these two extraction procedures, suggesting some

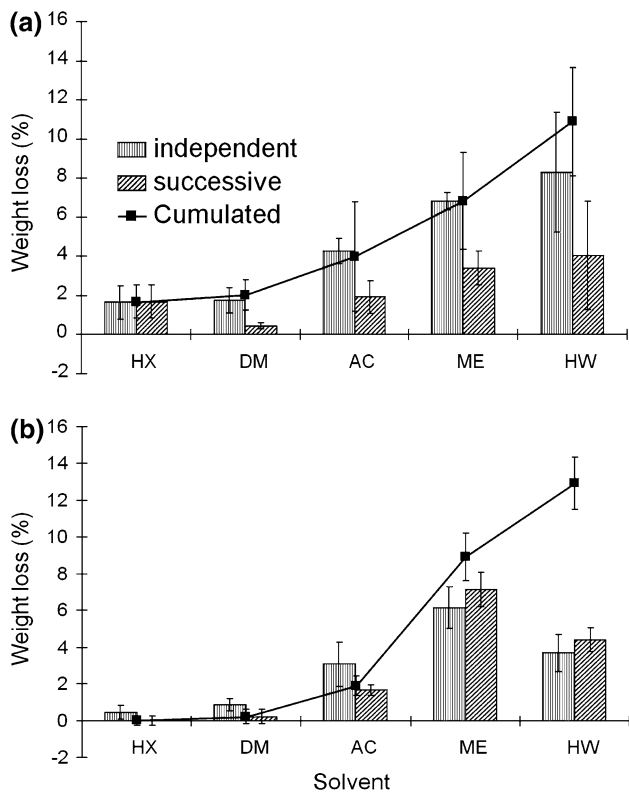


Fig. 4 Comparison of weight loss due to independent and successive extraction in **a** powder and **b** solid (vibrational) specimens. “Successive” weight losses are relative to the previous step; “independent” and “successive-cumulated” are relative to native oven-dry weight

structural effect on the accessibility to various solvents. This was supported by different extraction yields from axial, radial and tangential DMA specimens: 9, 14 and 18%, respectively for ME.

Less polar solvent HX and DM, which should reach only the lumen, removed small and comparable amounts (1.6 and 1.7%) when used independently on powder. Their yields were much smaller in solid wood. When DM was used after HX, its yield was very low, suggesting that HX had already removed most of extractives accessible to apolar solvents. Similarly, AC had a smaller yield when used after HX and DM, suggesting that when used independently, it also removed compounds from lumens. Although AC and ME are thought to be able to solubilize similar types of compounds, ME caused the most exhaustive extraction from solid wood: 6.2% when used independently. Its efficiency was even increased when used after AC (7.14% from solid wood). On the contrary, in powder, HW had the highest yield (8.31%) when used independently, while it had a much smaller yield on solid. This suggests that in solid wood, polar extractives are more easily removed by ME than by HW, as the final cumulated yields were, however, similar between powder and solid.

Extraction effects on E_L'/γ

As extractions change the mass and specific gravity (Tables 2, 3) of wood specimens, E_L'/γ values should be corrected for the contribution of extractives to γ :

$$\left(\frac{E_L'}{\gamma}\right)_c = \left(\frac{E_L'}{\gamma}\right)_{ap} \times \frac{\gamma_{ap}}{\gamma_{ef}}, \quad (1)$$

where $(E_L'/\gamma)_{ap}$ and γ_{ap} are the apparent measured values, and $(E_L'/\gamma)_c$ is the corrected value taking into account the specific gravity γ_{ef} after the most effective extraction (ME). $(E_L'/\gamma)_c$ should be more representative of an “extractives-free cell wall” modulus, and appeared 0.01 to 1.2 GPa higher than the apparent one (Tables 2, 3).

Corrected E_L'/γ gradually decreased due to extractions. HX, DM, AC, ME and HW modified E_L'/γ by 0.2, -0.6, -5, -11 and -1.8%, respectively, after independent extractions (Fig. 5a). Cumulated changes (i.e., relative to native state) after successive extractions followed a similar trend but with a bigger amplitude (Fig. 5b). E_L' shows a similar gradual decrease. Decrease in E_L'/γ appears nearly proportional to weight loss for different solvents (Fig. 5b), which suggests that extractives removed by AC, ME and HW bulked the cell wall matrix, and affected elasticity independently of compounds removed by these various solvents.

Changes in $\tan\delta_L$ related to weight loss

Figure 6 shows relative changes in $\tan\delta_L$ caused by each solvent either used individually or after others (successively). Apolar solvents (HX and DM) removed small amounts (approx. 1%) of extractives, probably from the lumens, resulting in small changes in $\tan\delta_L$. In successive extraction, however, DM increased $\tan\delta_L$ by 14%, which might be linked to previous exposition to HX. On the other hand, in another species (Padauk), DM was able to slightly attain cell wall and increase $\tan\delta_L$ of approx. 20% for approx. 3% extracts removed [11].

More polar solvents (AC, ME and HW) are expected to remove higher proportions of cell wall extractives, more susceptible to alter $\tan\delta_L$. However, the highest change in $\tan\delta_L$ resulted from AC extraction ($\approx +20\%$ independently or used after DM, $\approx +38\%$ for cumulated successive effect), although its weight loss was moderate. ME and HW, despite their higher yields, had smaller effects on $\tan\delta_L$ both in independent and in successive-cumulated order. When used after AC, ME even reduced $\tan\delta_L$ lower than the value for the previous state (AC-extracted, Fig. 6b). On the contrary, in other species, methanol extractives often have a high “anti-damping” effect in wood [10, 11, 14]. Acetone has also been used recently in

Table 2 Basic statistics for differences in properties between groups submitted to independent extractions and to one cycle of drying/re-stabilization (=control)

Treatment	EMC (%) ^d		Specific gravity γ		E_L'/γ Corrected (GPa) E_L'/γ Apparent (GPa)		$\tan\delta_L$ (10^{-3})	
	Native	Treated	Native	Treated	Native	Treated	Native	Treated ^f
Control ^e	9.2 ± 0.5 8.2 ± 0.4 ^a	9.2 ± 0.2 ns 8.2 ± 0.2 ^{a, b}	0.556 ± 0.027 ^a	0.553 ± 0.030 ns ^{a, b}	15.0 ± 2.2 14.0 ± 1.6 ^b	15.2 ± 2.4 ns 14.2 ± 1.6 ^a	8.6 ± 0.3 ^a	7.9 ± 0.5 ^{a, g}
Extracted								
HX	9.1 ± 0.2 8.1 ± 0.2 ^a	8.9 ± 0.4 ns 7.9 ± 0.4 ^a	0.570 ± 0.031 ^a	0.566 ± 0.030 ^{b, g}	13.5 ± 2.0 12.3 ± 1.4 ^a	13.7 ± 2.0 ^g 12.5 ± 1.4 ^a	10.2 ± 0.6 ^b	9.6 ± 0.6 ^{b, c, g}
DM	9.0 ± 0.3 8.0 ± 0.3 ^a	9.6 ± 0.4 ^g 8.6 ± 0.3 ^c	0.560 ± 0.031 ^a	0.557 ± 0.031 ^{b, g}	14.3 ± 2.2 13.2 ± 1.6 ^{a, b}	14.3 ± 2.2 ns 13.3 ± 1.6 ^a	9.6 ± 1.0 ^b	9.3 ± 0.8 ^{b, c, h}
AC	9.1 ± 0.4 8.1 ± 0.3 ^a	9.4 ± 0.4 ^h 8.6 ± 0.3 ^c	0.567 ± 0.026 ^a	0.550 ± 0.025 ^{a, b, g}	14.6 ± 1.6 13.3 ± 1.1 ^{a, b}	13.9 ± 1.6 ^g 13.2 ± 1.1 ^a	8.7 ± 0.4 ^a	9.8 ± 0.6 ^{c, g}
ME	9.2 ± 0.4 8.2 ± 0.4 ^a	8.7 ± 0.2 ^g 8.3 ± 0.3 ^{b, c}	0.554 ± 0.026 ^a	0.520 ± 0.025 ^{a, g}	14.4 ± 2.2 13.5 ± 1.4 ^{a, b}	12.9 ± 2.0 ^g 12.9 ± 1.4 ^a	8.9 ± 0.5 ^a	9.5 ± 0.5 ^{b, c, g}
HW	9.2 ± 0.3 8.2 ± 0.3 ^a	9.0 ± 0.2 ns 8.3 ± 0.1 ^{b, c}	0.550 ± 0.015 ^a	0.530 ± 0.017 ^{a, b, g}	14.1 ± 1.7 13.3 ± 1.3 ^{a, b}	14.0 ± 1.9 ns 13.7 ± 1.7 ^a	8.5 ± 0.5 ^a	8.6 ± 0.6 ns ^{a, b}

“Apparent” stands for measured values; “Corrected” take into account the contribution of extractives to weight (for EMC) and specific gravity (for E'/γ)
 ns Not significant

^{a, b, c} Homogenous subsets in one-way ANOVA at a level $\alpha:0.05$ (=comparison between groups in a given column, based on measured values)

^d EMC relative to 103°C oven drying. “Apparent” are measured values; “Corrected” is calculated by taking into account the total extractive content (cumulated % on powder) from 1st batch of wood [17]

^e “Treated” state for controls stands for values measured after one cycle of oven drying followed by air-dry re-stabilization

^f $\tan\delta_L$ are raw values, whereas $\tan\delta_L$ variations in Fig. 6 are corrected for controls

Differences between untreated and treated properties of a given group (based on corrected values whenever applicable) in t test for paired samples. Significant at ^g $\alpha: 0.01$, ^h $\alpha: 0.05$

Table 3 Basic statistics for the successive ranges in properties for the group of specimens submitted to successive extractions

Treatment	EMC (%) ^a Corrected Apparent	Specific gravity γ	E_L'/γ Corrected (GPa) E_L'/γ Apparent (GPa)	$\tan\delta_L$ (10^{-3})
Untreated	7.0 ± 0.3 6.1 ± 0.3	0.515 ± 0.011	13.72 ± 1.47 12.99 ± 1.25	8.2 ± 0.5
HX	7.1 ± 0.3 ns 6.2 ± 0.2	0.512 ± 0.016 ns	13.46 ± 1.68 ns 12.82 ± 1.35	7.9 ± 0.4 ^b
DM	9.2 ± 0.2 ^b 8.0 ± 0.2	0.515 ± 0.012 ns	13.51 ± 1.26 ns 12.78 ± 1.07	9.3 ± 0.6 ^b
AC	9.0 ± 0.4 ns 8.0 ± 0.3	0.515 ± 0.016 ns	13.53 ± 1.64 ns 12.79 ± 1.30	11.3 ± 0.8 ^b
ME	8.6 ± 0.1 ^b 8.2 ± 0.1	0.505 ± 0.014 ^b	12.69 ± 1.38 ^b 12.24 ± 1.13	10.6 ± 0.6 ^b
HW	8.8 ± 0.1 ^b 8.8 ± 0.1	0.488 ± 0.011 ^b	11.85 ± 1.23 ^b 11.84 ± 1.05	10.2 ± 0.5 ^c

“Apparent” stand for measured values, “Corrected” take into account the contribution of extractives to weight (for EMC) and specific gravity (for E'/γ)

ns Not significant

^a EMC relative to 103°C oven drying. “Apparent” are measured values; “Corrected” is calculated by taking into account the total extractive content (cumulated % on solid specimens) from 2nd batch of wood [17]

Differences between each successive extracted state in relation to the previous phase of treatment (based on corrected values whenever applicable) in t test for paired samples. Significant at ^b $\alpha: 0.01$, ^c $\alpha: 0.05$

this kind of study, on two tropical species [11, 23]. It was more efficient than ME in one species, and less in the other. The contrasted effects observed in mulberry could be explained by different hypotheses: (1) AC reached all extractives able to alter damping, leaving only “inactive”

compounds for subsequent ME or HW extractions. As drying cycles could reduce $\tan\delta_L$ by $\leq 8\%$, changes in $\tan\delta_L$ after ME and HW in successive order could partly reflect drying history of specimens. However, a smaller effect on $\tan\delta_L$ of ME and HW than that of AC was also observed for independent extractions, without cumulated drying cycles. This brings us to the second hypothesis; (2) Two kinds of extractives compounds would co-exist in cell walls, some decreasing, and some increasing, $\tan\delta_L$ in native wood. AC would have removed the first ones, so that the extraction of remaining, “ $\tan\delta_L$ raising”, compounds by ME and HW would decrease again the $\tan\delta_L$ of solid wood.

In various woods, methanol is reported to take out non-structural carbohydrates and phenolics [29]. White mulberry has quite important content of phenolic extractives [30]. In some woods, polyphenols can form part of the fiber cell wall matrix [31], while in some other woods, they may be either preferentially in vessels, parenchyma walls [32], or too much condensed to enter the cell wall substance [33]. In the later hypothesis, ME might have removed some lumen deposits, resulting in a lower ratio between changes in $\tan\delta_L$ and extraction yield. However, decreases in E_L'/γ after ME or HW suggested cell wall location. Thus, ME could have removed compounds such as sugars or simple phenols, which presence will increase $\tan\delta_L$ [15, 34]. A decrease in $\tan\delta_L$ is also observed after ME extraction of *Thuja plicata* sapwood—which should contain non-structural carbohydrates—whereas a completely opposite effect is observed in the heartwood of the same species [10]. In mulberry, extraction in HW, following ME, did not bring additional changes in $\tan\delta_L$, although it further removed $\approx 4\%$ extractives. In *Caesalpinia echinata*, water-soluble extractives decrease $\tan\delta_L$ in wood, which was first ascribed to their ability to form hydrogen bonds with cell wall components [12]. But other extractives, without hydroxyl

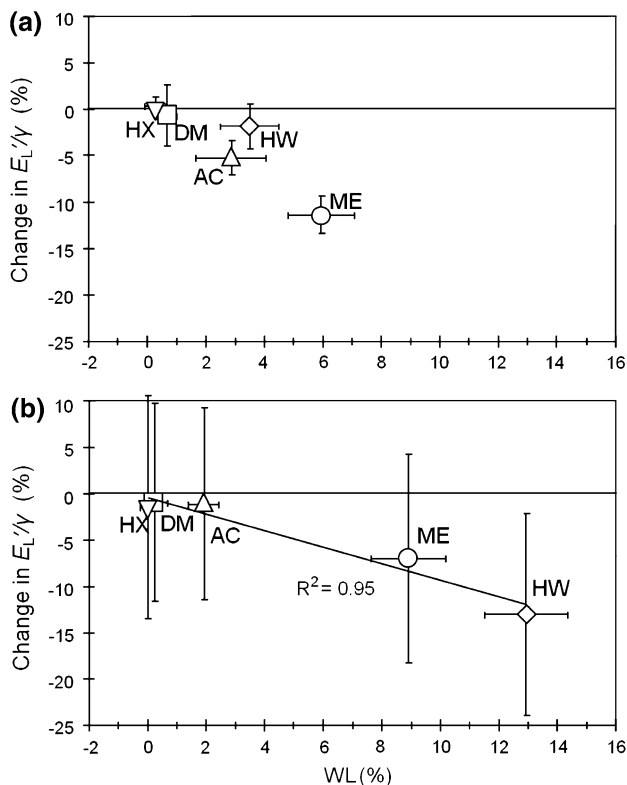


Fig. 5 Relationship between weight loss (%) and relative change of E_L'/γ (%) after **a** independent extractions and **b** successive extractions where changes are relative to initial state of native specimens (i.e., cumulated changes). E_L'/γ was corrected for contribution of extractives to γ

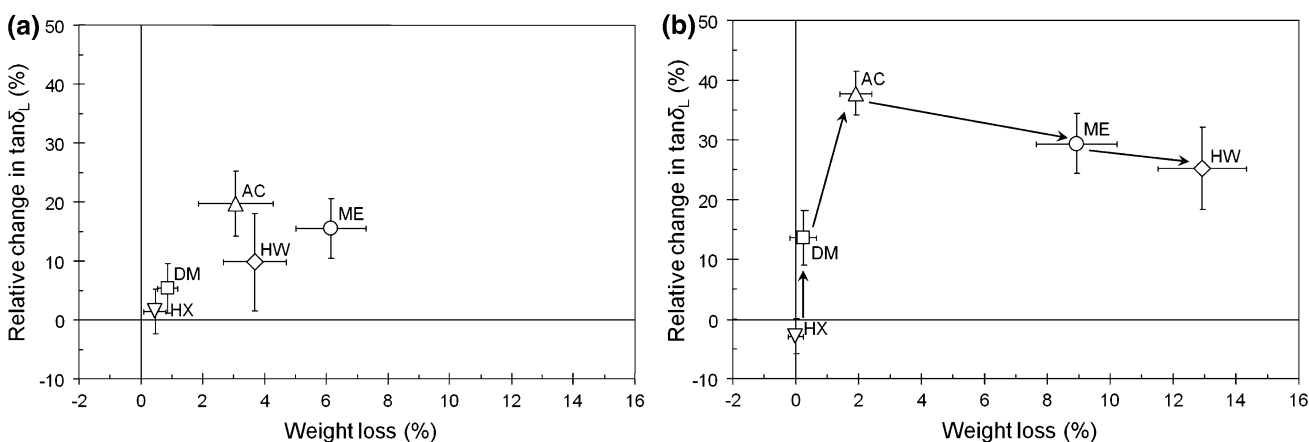


Fig. 6 Relative changes (%) in $\tan\delta_L$ plotted against weight loss (%) for **a** independent and **b** successive extractions. Changes are relative to initial state of native specimens (independent and successive-

cumulated). Arrows indicate the order of successive extractions. Values of $\tan\delta_L$ in independent extractions are corrected for controls

groups and/or insoluble in water, also reduce $\tan\delta_L$ [11, 14]. Finally, differences in $\tan\delta_L$ might be related to changes in wood moisture content [19, 35, 36]. However, changes in EMC due to independent extractions were small (Table 2). In successive extractions (Table 3), with higher cumulated yields, EMC was more significantly increased after ME and HW. This, however, should lead to an increase in $\tan\delta_L$, instead of the observed decrease for successive use of ME and HW.

Therefore, the present results suggest the co-existence of some “ $\tan\delta$ lowering” and of some “ $\tan\delta$ raising” compounds in the heartwood of white mulberry. The first ones are extractable by ME but also with AC and HW, consequently independent extraction with those solvents had always resulted in an increase in $\tan\delta_L$. The latter compounds, being probably hydrophilic, are not extractable by HX, DM or AC. Thus, a successive extraction using ME and HW had reduced $\tan\delta_L$, as the “ $\tan\delta$ lowering” had been already removed by previous solvents and there were only the “ $\tan\delta$ raising” components left. The methodology using both independent and successive series of extraction might reveal similar trends in other species.

Changes in anisotropic properties due to extractions

Figure 7 shows the variations in E'/γ and $\tan\delta$ in the three principal directions of orthotropy after extractions with HW and ME or 2 drying cycles (controls). Variations in E'/γ after ME extraction were similar in all three directions: -18 to -20% , although weight losses were different (9, 14 and 18 for L, R and T specimens, respectively). Hot water caused both lower weight losses (6–8% in L, R and T), and smaller decrease in E'/γ along L and R directions, while it was similar to ME in T direction.

Concerning $\tan\delta$, uncertainty was high in L direction, as clamping of specimens may crush wood in the softer

transverse direction. Even controls showed important variations, which cannot be ascribed to physico-chemical changes. However, after ME extraction, change in radial $\tan\delta$ was at least twice more important than in L (DMA estimations and changes in vibrational tests) and T directions (Fig. 7).

The quasi-isotropic effect of extractions on E'/γ is quite surprising. In previous works, extractives stiffened the transverse moduli [14, 37], but not the axial one, in which the influence of the microfibrillar reinforcement predominates [5–7]. However, mulberry wood has a low longitudinal E'/γ , suggesting high microfibril angle, and is characterized by a very low anisotropy in native state. Effects of extractions on $\tan\delta$ were clearly different in radial and tangential directions. This is interesting, as there are relatively few works on the $\tan\delta_R/\tan\delta_T$ anisotropy and sources of variations. Backman and Lindberg [1] stated that, for softwood, in tensile test latewood contributes mostly to the response in tangential direction while most of the strain occurs in early wood in radial direction. In mulberry, a ring-porous hardwood, the response in radial tension tests would more involve vessels and rays, whose cell walls are thinner, but are also susceptible to contain higher proportions of extractives [31, 32, 38]. Thus, the very high change in $\tan\delta_R$ after ME extraction ($\approx 50\%$) could express a bigger modification of rays and vessels, than of fibers.

Conclusion

Dynamic mechanical properties E'/γ , $\tan\delta$, and their anisotropic ratios in the 3 principal axes were measured on white mulberry wood (*Morus alba* L.), a representative raw material for musical instruments in Iran. They were compared before and after extractions by different solvents to investigate extractive effects. Results could be synthesized as follows:

- Mulberry wood has a quite low E_L'/γ but its damping factor ($\tan\delta_L$) is lower than expected. The anisotropy of these two properties is also much lower than average.
- Combining two methods of extractions—using each solvent as an individual agent and using solvents in a successive order on a single sampling—could suggest the importance of extractives nature compared to their amount.
- The highest changes in $\tan\delta_L$ were not due to the most polar solvents, with highest extraction yields, but to acetone. Nevertheless, acetone did not alter E_L'/γ with the same intensity, suggesting that the extracted amounts or compounds were not essential for wood stiffness.

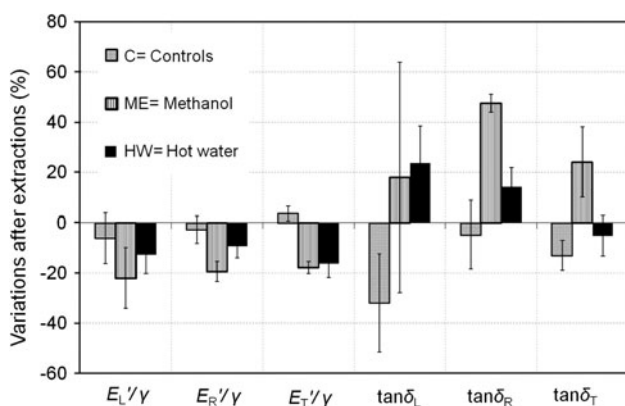


Fig. 7 Variations in mechanical properties after extractions measured by DMA at 10 Hz. Values for controls were not deduced from treated ones

- The different effects of methanol extraction on $\tan\delta_L$, between individual extraction and when used successively after acetone, suggest the existence of two types of $\tan\delta$ altering compounds in white mulberry. Some would be able to increase, some other would be able to reduce the damping, and both types would be accessible by acetone and methanol independently.
- Changes in E'/γ were nearly isotropic between the 3 principal axes of orthotropy, may be due to the very low anisotropy of mulberry in native state. On the contrary, $\tan\delta$ was much more modified in radial than in tangential direction, suggesting different responses to extractions of rays and vessel walls as compared to fiber ones.

It should be noted that even though extractives are found to definitely affect vibrational properties of *Morus alba* L., it would be enlightening to identify the most important compounds present in those extractives and how they cause changes in vibrational properties.

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