PHYSICAL AND CHEMICAL PROPERTIES OF VARNISHES AND THEIR VIBRATIONAL CONSEQUENCES

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ABSTRACT: It is well known that the sound quality of stringed instruments evolves for years after their fabrication, specially during the varnish drying process. Even if essentially aesthetic and protective, the varnish has an effect on the vibrating properties of the instrument. This may be due to the evolution of its chemical structure and mechanical behaviour. The existing studies on the matter are not really concluding. From viscoelastic characterisations, we will try to understand on a simplified system what the relationship is between the physico-chemical properties of isolated simple varnishes and the mechanical characteristics of samples of varnished woods.

1. INTRODUCTION

It is generally known that the quality of violin changes with time after it has been completed. Various parameters may be responsible for this change: the drying and hardening of varnish over a few years, the change of mechanical properties of wood and varnish over a long period, and the condition of use of the violin (frequency of use, humidity, temperature). Violin makers and scientists show interest in understanding, at least from a qualitative point of view, the vibrational consequences of varnish, depending on their composition and their drying conditions. The varnishing of violin is needed for the purpose of appearance and protection of the surface. The effect on tone is not negligible, according to the experience of violin makers. On one hand, they notice that the sound of violin becomes to be duller than before varnishing while they also feel that sound from a thoroughly dried violin is steadier than that of an unvarnished one. One the other hand, violin varnish compositions and coating conditions have often been kept secret as it was assumed they were responsible for the violin tone qualities [1].

Keeping in mind the two first purposes that varnish serves (beauty and protection), and that varnish is one parameter among others in influencing the vibrational properties of instruments, tone qualities are not discussed here. In this paper, we try to compare the vibrational properties of wood coated with alcohol varnishes to those with fatty oil varnishes, showing in particular that the effect of the oil varnishes may strongly depend on frequency. Although the chemical properties of resins and oils used for varnishing have been well investigated [2], only a few studies have dealt with the viscoelastic and mechanical properties of varnishes. The long drying duration (couple of years) and the special techniques and conditions required for coating make difficult experimental set-ups. Some experimental results have been obtained for wood strips coated with basic fast-drying varnishes [3] or various complex varnishes [4]. They describe the changes in the viscoelastic properties of the coated wood strips, showing that two or three classes of varnish can be told apart, for their vibrational effects. However, the complexity of the varnishes studied has not allowed any link to be made with their chemical properties or elicited any explanation of these changes. In a recent study, the vibrational properties of wood (spruce) with lacquer coatings have been studied [5]. A simple model relating the vibrational properties of coated wood to those of wood and coating layer has been satisfactorily used [6].

In this paper, this model has been applied to violin varnish coated spruce strips, and the experimental results described in literature [4] have been interpreted, considering the different classes of varnish, and their drying conditions.

2. MATERIAL AND METHODS

The acoustical properties of a violin are determined by its eigenmodes. These eigenmodes are defined by the shape and the viscoelastic properties of the system. They result from the individual stiffness-mass-damping distribution of the constructed violin. The material for violin is varnish-coated wood. For varnish has a specific interaction with wood, its acoustic effect depends on this carrier material. The system was assumed to be a composite material composed of two thin layers thoroughly connected, with limited penetration (In practice, a thin layer of varnish, called a aprimer, is first applied to the wood to protect it from extended penetration by the following thicker layers). These assumptions allow the application of physical laws concerning composites.

The carrier material is generally spruce (or maple) which can be considered as orthotropic. The surface of the plates is defined by the along-grain (L, fiber direction) and cross-grain (R, radial direction) directions, the thickness, along the tangential direction (T) is about 2 or 3 mm. The dynamic Young's modulus (E) and the internal friction ($\tan\delta$) of these orthotropic plates can be determined by modal analysis [4,5].

The coating material is varnish. Violin varnish is a complex and variable material with properties such as gloss, colour, toughness and adhesion to wood. Varnishing consists of applying several coats of identical or different compositions, which generally are a mixture of resins in a particular solvent. Hundreds of natural and synthetic ingredients, and a lot of varnish recipes and advice about coating conditions are found in the literature [5]. The number of ingredient combinations is infinite, and it is necessary to make a classification. We assumed that the best classification to study the viscoelastic properties of varnish is the one which considers the solvent. Alcohol, essential oil and fatty oil varnishes can be distinguished, for they differ by their drying behaviour and the role of solvent in the final properties. For alcohol varnishes, the solvent quickly vaporizes off the applied layer, and the residual resin (for example shellac) is alone responsible for the properties of the layer. For fatty oil varnishes (with linseed oil for example), the drying corresponds to the polymerisation of the solvent, which also is responsible for the final properties of the film. Essential oil varnishes have intermediate behaviour.

We assumed that the best model to represent the varnish in terms of viscoelastic properties is a thin film of polymer, clearly defined by a stress/strain relationship. The variable which describes this relationship is the complex term $E^*=E'+iE''$ where E' is the elastic (Young's) modulus and $\tan\delta=E''/E'$ is the internal friction. E* depends on several parameters: the glass transition temperature T_g (the temperature at which a glassy material starts to change to a flaccid material), the molecular mass M, the crosslinking rate (rate of links between high molecular weight molecules involving the inability of molecules to flow past one another), the nature and quantity of plasticizers (low molecular weight additives used to lower the effective Tg and to make stiff polymers more flexible). T_g can be measured by various methods: differential scanning calorimetry (DSC, on small pieces of polymer), dynamic mechanical analysis (DMA, on thick or thin films of polymer). E* can be determined by DMA on thick or thin films of known geometry. In these conditions, the changes of T_g and E* cannot be studied during drying. To study the polymerization and hardening of some varnishes, the liquid varnish is applied on a glass fiber cloth, used as a support. In this case, DMA gives relative elastic modulus and internal friction, for the material is a composite.

We have chosen to study two typical products, chemically described in the literature, to understand how chemical nature can influence viscoelatic properties. The first one is a natural resin called shellac, used in alcohol varnishes and in fatty oil varnishes. It is composed of a "hard resin" which corresponds to large molecules and is responsible for the T_g around 40°C and the relatively high E and low $\tan\delta$ at room temperature, and a "soft resin" which corresponds to small molecules acting as plasticizers, lowering E and increasing $\tan\delta$. The second product is linseed oil, currently used as a solvent in fatty oil varnishes. It is known that it dries by oxidation/polymerisation, forming a cross-linked material [2]. The drying of linseed oil has been studied with DMA, on glass fibre cloth. Relative E and tanδ were measured against time, at different temperatures. The T_g of the dried layers was measured by DSC. The drying of a standard varnish composed of resin and oil was studied in the same conditions.

3. RESULTS AND DISCUSSION

3.1. Viscoelactic properties of shellac, linseed oil and oil varnish standard

The T_g of a polymer determines many of the mechanical and some of the chemical properties of a polymer. As the temperature is raised, the polymer changes from a glassy state (high E and poor ability to stretch) to a flaccid one (small E and flowing for thermoplastics) or a rubbery one (for cross-linked materials). Molecular movements are enhanced and the polymer is able to adjust to stress, with a partly viscous response. This change is not sharp but occurs in a small range of temperatures. In this range, the drop of E corresponds to a peak of tanδ, i.e., the stiffness is lowered and the loss factor is high. The ability of the polymer chains to move past one another depends not only on how mobile the chains are, i.e., how much above T_g the polymer is, but also on how fast the stress is applied. The value of T_g is increased by increasing the frequency scale of the stress. There is an approximate relationship between T_g and the frequency of measurement, called the time-temperature superposition theory [7]. T_g is conventionally measured at 1 Hz. If the measurement frequency is increased to 1000 Hz, T_g will increase by 10°C to 20°C, depending on the polymer. Mechanical properties of a varnish should then depends on the stress frequency, that is to say on the frequency of the vibrational mode of the plate or the strip studied. When determining the characteristics of a polymer film as a coating for violin plates, its viscoelastic profiles must be clarified over the audio-frequency range, 20 Hz to 20 kHz.

For alcohol varnishes, as no major chemical modifications occur during drying, the properties of the film should be the same than those of the bulk thermoplastic (the mixed resins). For a mix of resins, T_g can be calculated with a linear formula involving the T_g and the weight percentage of each resin. Generally, the viscoelastic profiles for resins used in varnish recipes can be identified to those of thermoplastics (fig. 1) with a transition temperature between 25°C and 100°C and Young's modulus between 1 to 5 Gpa. When the frequency of the stress is increased, the plots are shifted along the temperature axis. For T_g is higher than room temperature, the effect on E and tanδ is weak. E slightly increases, and tanδ is unchanged, or slightly decreases when T_g (1 Hz) is near room temperature.

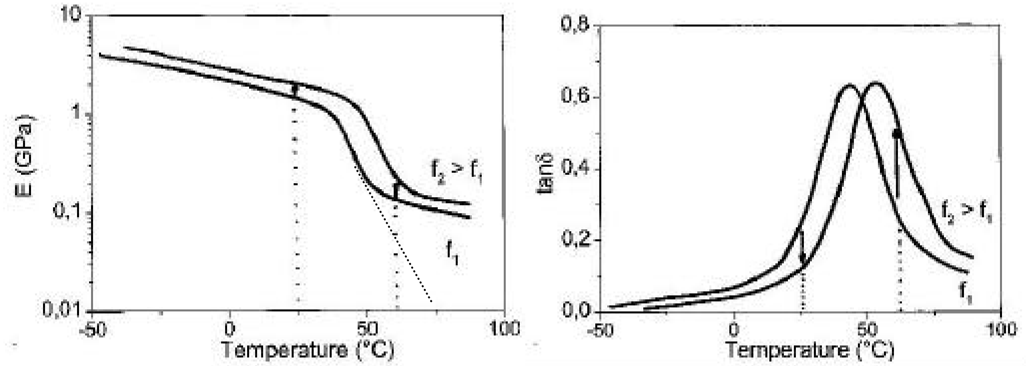

Figure 1. *Temperature variations of dynamic Young's modulus (E) and internal friction (tanδ) for a cross-linked polymer (Tg (1 Hz)=40°C). For thermoplastics (- -), E falls to very low values with raising temperature.*

For fatty oil varnishes, T_g and E* depend strongly on the varnish preparation and the coating conditions, as polymerisation occurs during drying. The chemical properties of linseed oil have been well investigated, as it is supposed to have been widely used for violin varnishing. The drying and aging of linseed oil is an oxygen-mediated process. The chemical changes of the unsaturated oil backbone during this process can be summerized as follows: degradation of antioxidant molecules delaying the oxygen attack on unsaturated molecules (induction period), formation of conjugated carbonyl compounds and peroxy radicals induced by oxygen attack, and extended crosslinking, fall in the crosslinking rate an stabilisation of the molecular network, thermal or photo-fragmentation inducing the loss of volatile molecules (aging). The viscoelactic changes during drying are comparable to those for a polymerization of a synthetic resin (fig. 2). The gelation process, i.e., the development of a network by crosslinking reaction, corresponds to an increase of viscosity (and of E) and a peak of tanδ. During vitrification, corresponding to a damping peak, the crosslinking rate drops, and the increase of E is slowed down. A gel time and a vitrification time can be defined.

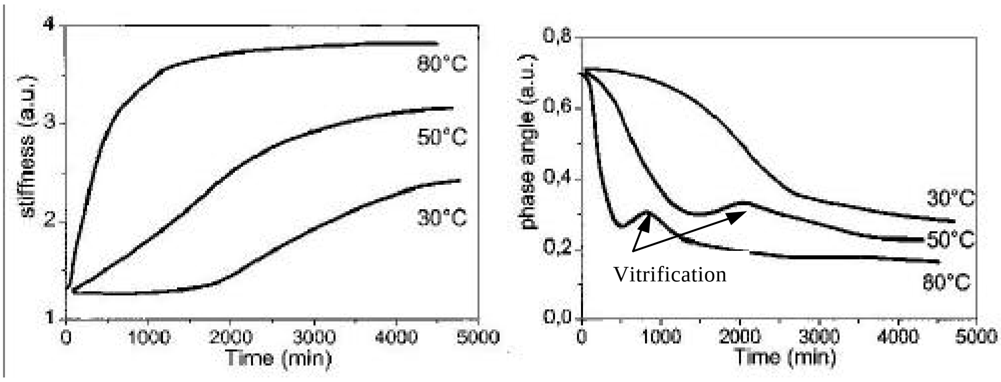

Figure 2. *Viscoelastic changes (arbitrary units) during drying for linseed oil.*

For linseed oil, the gel time corresponds to the end of the induction period. It is generally long (200 h for raw oil at room temperature), but it can be reduced to a few hours by raising the temperature or using catalysers (UV). It is not visible on the plot of E and tanδ because DMA measures were performed just after the gel time (when the viscosity was high enough for the liquid to be coated on the glass fiber cloth). The vitrification time, and the loss factor obtained after this process decrease with temperature, while the stiffness obtained after vitrification increases with temperature. The soft film obtained has a glass transition temperature around – 50°C. Its viscoelastic properties at room temperature and low frequency are those of a rubber, whose final elastic modulus and loss factor depend on the drying conditions. When applying fatty oil varnish on wood, the thickness of layer should be as well an important parameter, as the drying process needs the presence of O_2. If the applied layer is too thick, the surface of the film will polymerize first, keeping the rest of the film from contact with O_2 and from oxydation-polymerization. The resulting E and tanδ will be respectively lower and higher.

Linseed oil and other fatty drying oils are not used alone as varnishes. They are used as a solvent for resins, or as a binder in essential oil varnishes. DMA results for a standard oil varnish composed of drying oil and resin showed that the drying was faster, and that the resulting elastic modulus was higher, and the loss factor lower. The glass transition temperature of the dried film was around 30°C. More generally, when using resins in drying oil, the T_g of the resulting film can be changed from the oil transition temperature (≈ - 50°C) to the resin transition temperature (≈ 50°C), depending on the fraction of resin and the drying conditions. Moreover, if the resulting T_g (1 Hz) is lower or around room temperature, the dependency on frequency of the viscoelastic characteristics will be important (fig. 1). For example, if T_g (1 Hz) is slightly higher than room temperature, E increases with frequency and tanδ decreases with frequency. If T_g (1 Hz) is slightly lower than room temperature, E increases with frequency and the peak of tanδ is shifted in the playing frequency range. These considerations involve that the vibrational effects of this type of varnish on the vibrational modes of strips and plates of wood will strongly depend on the frequency of the mode. Some of the modes whose frequency corresponds to the peak of tanδ will then be damped. Some other modes will be emphasized. It is beyond our capabilities to establish a target for the desired loss factor and stiffness. Violin makers must decide which tonal characteristics to emphasize and which to reduce. It is worth to point out that drying oil varnishes and essential oil varnishes offer much more opportunities to modify the vibrational modes in a non linear way.

3.2. Properties of wood/varnish composites

A paper [6] has proposed a model to determine the influence of varnish on the vibrational properties of wood. It has been recently used to study the effects of oriental lacquers on the vibrational properties of coated spruce used for the soundboards of piano and harp [5]. The coated wood specimen is regarded as a composite plate consisting of the coating layer and uncoated wood (fig. 3). When the e_v/e_w is small enough to ensure $(e_v/e_w)^2 << 1$, the dymanic Young's modulus (E_c) and internal friction $\tan\delta_c$ of coated wood are approximately expressed by

$$E_c \approx E_w\left[1+3\left(\frac{E_v}{E_w}-1\right)\frac{e_v}{e_w}\right] \quad (2) \qquad \text{and} \qquad \tan\delta_c \approx \tan\delta_w \frac{1+3\frac{E_v}{E_w}\frac{e_v}{e_w}\frac{\tan\delta_v}{\tan\delta_w}}{1+3\frac{E_v}{E_w}\frac{e_v}{e_w}} \quad (3)$$

where v, w and c indicate the varnish layer, the uncoated wood, and the coated wood, respectively. This model agrees with experimental values if the penetration of the coating into the wood is limited.

In order to compare the results of this model to experimental results described in the literature, we considered orthotropic strips of spruce of thickness ranging between 2 and 3 mm, and isotropic films of polymer of thickness 20 to 100 µm. The vibrational modes of spruce strips are bending modes concerning longitudinal waves along L or R. The involved modulus are E^*_{wL} and E^*_{wR} for the wood, and E_v^* for the varnish.

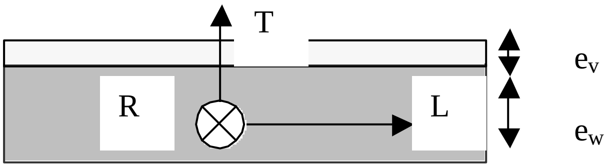

Fig 3. *Cell model for coated wood*

We have used this model to interpret experimental results obtained by Martin Schleske [4] on coated spruce strips. He measured variations of velocity of sound v ($E_{wL} = \rho v^2_{wL}$, $E_{wR} = \rho v^2_{wR}$) and loss factor $\tan\delta$ of spruce strips, induced by the coating of various compositions representing the three classes of varnishes. Some results (e_w = 2 mm) are collected in table 1.

	Alcohol varnish	Fatty oil varnish
$\Delta v_{wL}/v_{wL}$	0 % → - 3 %	- 4 % → - 7 %
$\Delta Q^{-1}_{wL}/Q^{-1}_{wL}$	0 % → 25 %	40 % → 90 %
$\Delta v_{wR}/v_{wR}$	12 % → 25 %	- 2 % → 12 %
$\Delta Q^{-1}_{wR}/Q^{-1}_{wR}$	0 % → 100 %	150 % → 230 %

Table 1. *Experimental results obtained by M. Schleske for coated spruce strips (4 years drying)*

Results for essential oil varnishes are comparable with those for alcohol varnishes or fatty oil varnishes, depending on the composition of the varnish. Aging is also studied. M. Schleske has measured the changes against the untreated wood for four years and nine years after varnishing. Aging involves a decrease of $\Delta\tan\delta/\tan\delta$ along-grain and cross-grain, an increase of $\Delta v_{wR}/v_{wR}$, and a decrease of the absolute value of $\Delta v_{wL}/v_{wL}$.

By defining $X = e_v/e_w$, $Y = E_v/E_w$ and $Z = \tan\delta_v/\tan\delta_w$, equations (2) and (3) become

$$\frac{\Delta E_w}{E_w} \approx 3(Y-1)X \qquad \text{and} \qquad \frac{\Delta\tan\delta_w}{\tan\delta_w} \approx \frac{3XY(Z-1)}{1+3XY}$$

The relevant ranges of X, Y and Z are summarized in table 2.

	e_v (µm)	e_w(mm)	X	E_v (Gpa)	E_{wL}(Gpa)	E_{wR}(Gpa)	Y_L
Sup. lim.	100	3	0.05	5	12	3	0.5
Inf. lim	20	2	0.006	1	10	1	0.08
	Y_R	Q^{-1}_v	Q^{-1}_{wL}	Q^{-1}_{wR}	Z_L	Z_R	
Sup. lim.	5	0.1	0.007	0.021	20	5.9	
Inf. lim	0.3	0.02	0.005	0.017	2.8	0.95	

Table 2. *Ranges for the model parameters, from the literature or experimental results*

Cross-grain elastic modulus and internal friction changes are plotted against (X,Y), and (XY, Z) respectively (fig. 4). These calculated results (those for L direction are not represented) agree qualitatively with those of M. Schleske and those describing oil and alcohol varnishes viscoelastic properties.

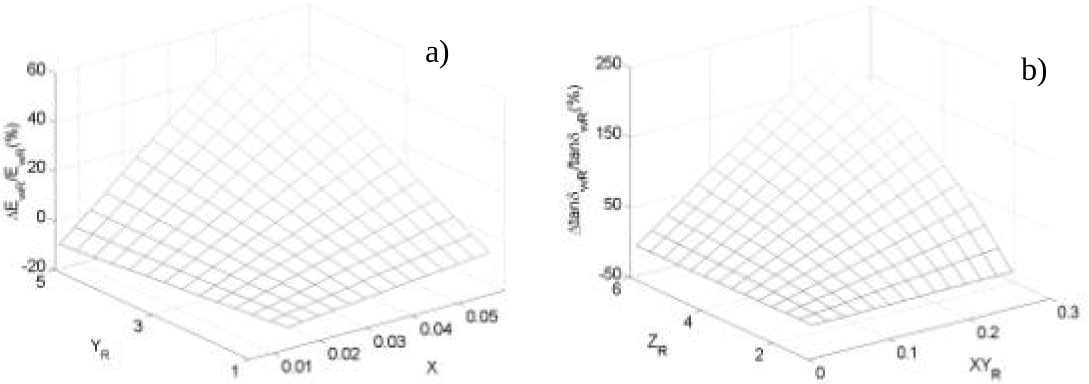

Figure 4. *Elastic modulus changes (a) and internal friction changes (b) along R direction.*

4. CONCLUSION

The effects of violin varnishes on the vibrational properties of wood were discussed. The viscoelastic properties of the two main classes of varnishes were compared, and their drying were described. The effects of coatings on the vibrational properties of wood were expressed by a model consisting of two layers, wood, and coating. These results showed good agreement, qualitatively, and suggest that it would be usefull to obtain more experimental results about the viscoelastic characteristics of resins and oils that are commonly used for varnishing.

Moreover, the model can be improved, by taking into consideration that varnishing consists in applying several layers of sometimes various compositions (two at least: a primer and a varnish) and that the penetration of the first layer into the wood is not negligible. However, if the viscoelastic properties of each applied layer is known, it is possible to determine qualitatively which layer, or which composition has the major effect. To accomplished the acoustical desired result on his instrument, the violin maker will have to control several parameters: the viscoelastic properties and the penetration of the primer layer, the viscoelastic properties, the thickness, the number of coats and the drying conditions of the varnish.

The acoustic consequences of varnish are not the secret of violin tone. There is no secret recipe. The class of oil varnishes may be richer for the choice of desired effects, but the varnish must be adapted to the instrument. One can then understand that changing the varnish of an old instrument can change the response or have no effect at all, but using the very well adapted varnish of a violin on a cello may lead to a bad tonal quality instrument.

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