Following of the Relaxations in a Polymer's Behavior Part II: Characterization by Quasistatic and Dynamic Forced Bending

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SYNOPSIS

The aim of this work is to quantify the internal loss in polymers, for frequencies near 1 Hz, and including the domain (100 and 3000 Hz). The quasistatic experiment used the double-pendulum method; the other experiments were forced vibrations in bending. Two materials were tested between 20 and 60°C, PMMA and wood. Owing to the anisotropy of the wood, the different mechanisms that induce internal loss are located in the matrix or in the reinforcement (fiber) of this composite. The results were plotted on the correlation diagrams, presented in the first part of this study.

INTRODUCTION

Part I of this work allows the qualification of the relaxations of two polymeric materials, PMMA and wood, at very low frequencies. The aim of this study is to complete the first part of this paper by applying higher frequency excitations. We first used "quasistatic" bending at about 1 Hz with the double-pendulum method. The rig is pictured on Figure 2. Second, we used forced bending oscillations at frequencies about 1 kHz near the two symmetrical resonance modes of the sample (Fig. 3). The experiments have been conducted from room temperature to 60°C, and from the dried state to 20% of moisture content. The results were then plotted on the correlation diagrams introduced in Part I.

EXPERIMENTATION

Metrology

The samples are of parallelepipedic shape. The width, thickness, and length are included in the following intervals ⟨18 to 20⟩, ⟨7 to 11⟩, and ⟨100 to 200⟩ mm, respectively. Taking into account the cylindrical properties of the wood material, the smallest length is associated with the radial direction. Longitudinal samples account for only a few number of age rings. Samples were cut at dried states in room conditions (about 12°C) as in Figure 1.

The density of the Douglas samples is about 0.45; and 1.19 for the polymethyl methacrylate (PMMA).

The experiment consisted of increasing the temperature of the sample over a range from 20°C, to a mean value T_{max} of about 60°C depending on the moisture content. The moisture content was regulated by the use of a special room. For a temperature higher than T_{max} a constant moisture content cannot be maintained in this room.

The samples were tested mechanically very briefly, while the temperature remained constant. These temperatures were changed by degree every 5 min. This should avoid thermo-hygro-mechanical interactions.

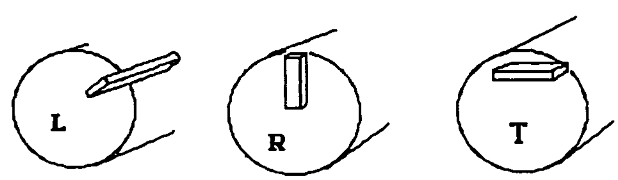

Figure 1 Three different ways of cutting the wood samples.

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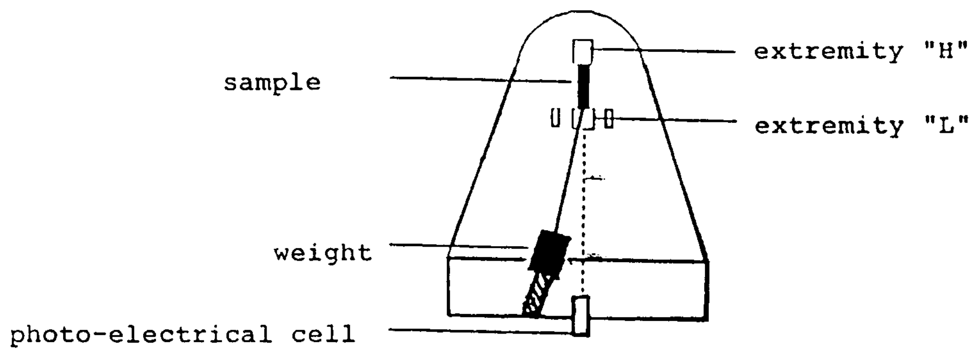

Figure 2 The double pendulum method: the internal loss of the sample was obtained by the difference between the pulsations, when the extremity "L" of the sample was fixed or free.

The Conditioning

PMMA Samples

Reported results were noted after two increases of temperature, that is, from room temperature to 70°C. We paid no attention here to the moisture content of these samples.

Wood Samples

These samples were hygro-sensitive. They were preconditioned before any experiment in an oven at 105°C. After that, the samples with a moisture content higher than 2% were conditioned at room temperature for 3 days with different salts. We obtained the following moisture contents: about 1.7, 6, and 10%. For moisture contents of about 15 and 20%, the samples were imbedded in an aluminum paper with water in it. The same sample was used for each moisture content. During the temperature increase, moisture content measurement was made by weighing a reference sample continuously. It turned out that the variations $H(T)H(\text{initial})$ were always lower than 2.8%, and generally lower than 1%.

Models Used

A completed presentation of these models can be found in Ref. 1.

For the double pendulum, the equations were developed by Plenard, and rewritten by Guitard.[2] This model does not take into account either the shear stresses or the orthotropic properties of the material. Discussion on this point can be found in Ref. 1.

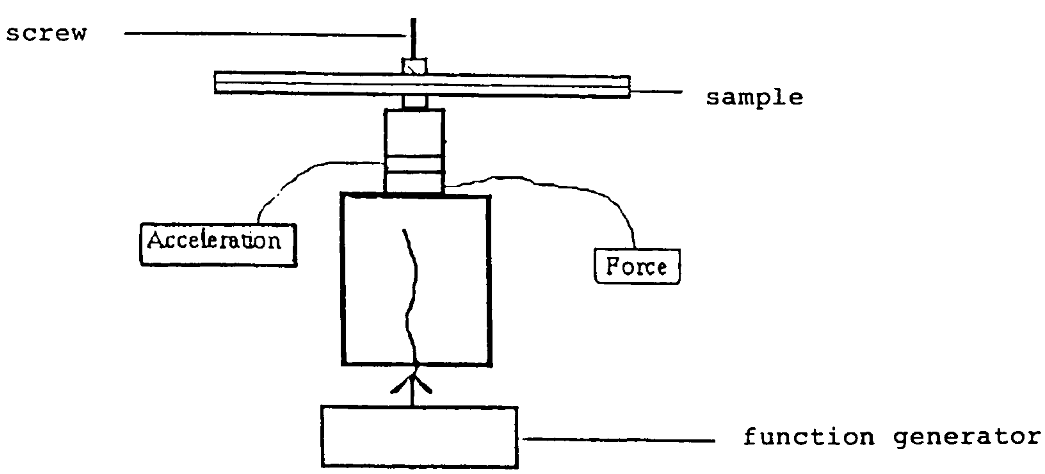

Figure 3 The dynamic bending experiment gave acceleration and force at the middle of the sample. A measurement of the internal loss was obtained at the two first resonances of the sample.

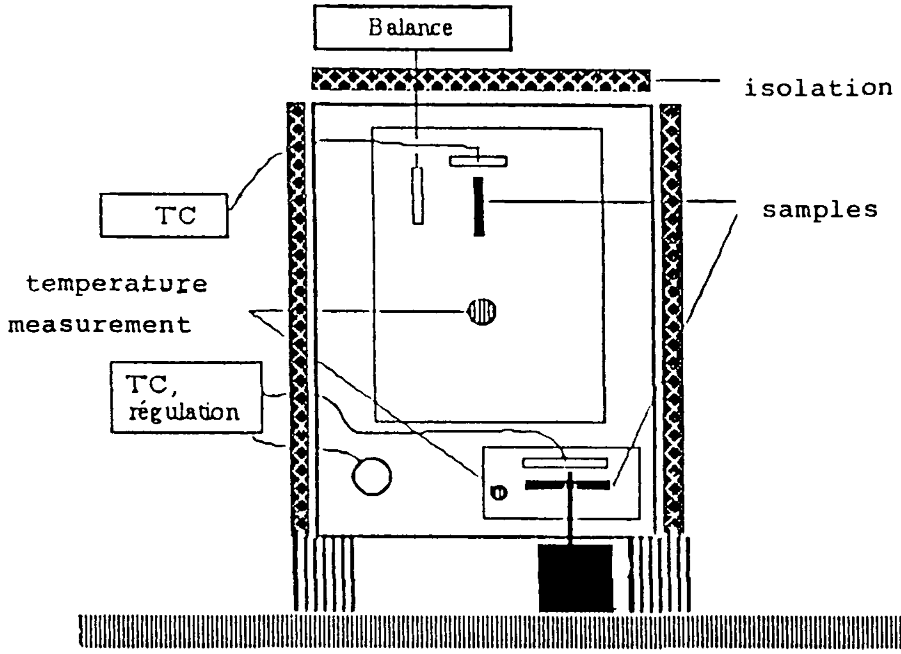

Figure 4 The dynamic and quasi-static samples were tested simultaneously in a controlled atmosphere.

For the forced bending, the model looks very much like Timoshenko's one for nonviscoelastic solids, but it includes:

1. Inertia and rigidity of the point on which the sample is fixed with the gauge.
2. Shear effects.
3. Internal losses that are described by the complex modulus ($E^* = E_r + iE_i$) and the shear complex modulus ($G^* = G_r + iG_i$); we used: $\nu = E_i/E_r$ and $\gamma = G_i/G_r$.
4. The rigidity of the fixing part.

To facilitate computation, we assume the two following points:

1. Conservative modulus should not change with frequency in a range from some 100 to 2000 Hz.
2. ν and γ should be equal.

By fitting the experimental data with the computated values, we obtain the conservative modulus E_r, the ratio E_r/kG_r (k, the shear coefficient), and the internal loss coefficients for the first and second modes: ν_1 and ν_2.

The computation does not take into account any orthotropic contribution of the solid.

RESULTS

Isotropic Material: PMMA

At Room Temperature

In order to verify the proposed model, PMMA samples are tested at room temperature. The results (Young modulus, internal friction) have to be compared with those published before.

Table I Results on the Young Modulus of the PMMA at Low Frequencies and Room Temperature

Frequency (Hz)	T (°C)	Author	Modulus E (MPa)	Excitation	Tan (δ) (%)
Static	Ambiant	Seichepine[3]	3740	Compression of a cube	
0.84	20	Pabiot[8]	3300	Traction	
0.85	20	Vautrin[4]	4100	Oscillated traction	9.7
1	Ambiant	Guerrin[1]	3300	Bending	6.4

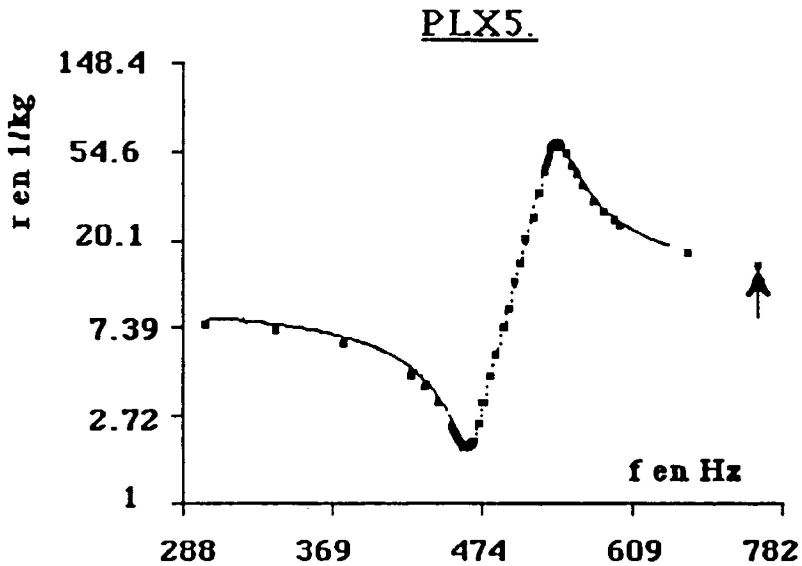

Figure 5 Evolution of the experimental ratio acceleration/force near the first resonance (dots) for a PMMA sample. The model is able to simulate the experimental answer (curve).

Quasistatic Bending (Figure 2)

The optimized rheological parameters are compared in the Table I, with values obtained with other experiments.[3,4]

The internal loss is lower than the value found by Vautrin.[4] That can be explained by the proximity of a maximum of the internal loss (Fig. 7).

Dynamic Bending (Figure 3)

Figures 5 and 6 show a good agreement between computed and measured values. The rheological values are described in Table II.

The material variability was appreciated by testing a second sample PLX1 of PMMA with the same geometry as PLX5. Relative variations of the values,

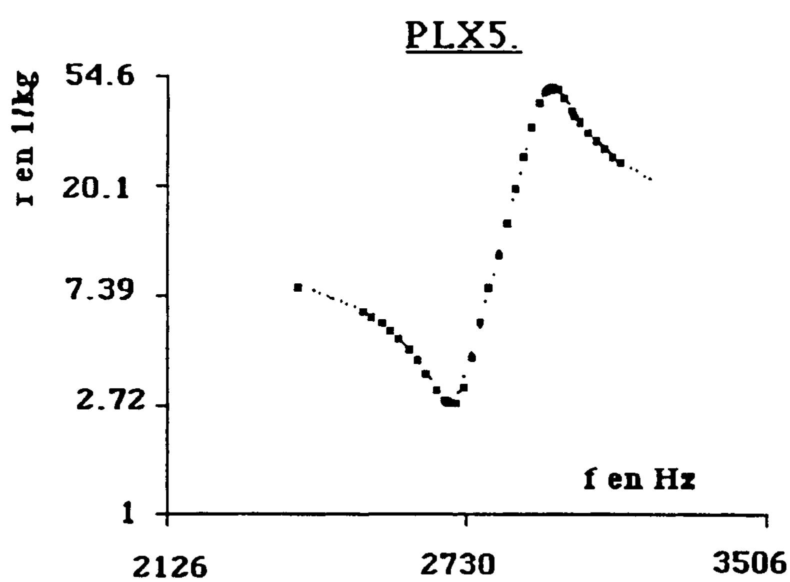

Figure 6 Evolution of the experimental ratio acceleration/force near the second resonance (dots) for a PMMA sample. The model is able to simulate the experimental answer (curve).

Table II Rheological Parameters of PMMA Sample PLX5

E_r (MPa)	ν_1 (%)	ν_2 (%)	E_r/kG_r
5 107	5.14	4.25	3.25

$X(\text{PLX5}) - X(\text{PLX1})/X(\text{PLX5})$, where $X = E_r$, ν_1, ν_2, E_r/kG_r, are written in the Table III.

The reliability of the models is thus established.

Temperature Increase

In order to prove the ability of the experiments to detect the mechanisms of internal losses of an isotropic material such as PMMA, an increase in temperature is realized.

Quasistatic Bending

Changes in internal loss with the temperature were plotted (Fig. 7) for the two frequencies of excitation of 0.847 and 1.20 Hz.

They present a maximum. These maxima are large due to the combined action of two relaxations. The maximum with the greatest value of the internal loss is bound to the β relaxation. The smallest one has to be connected to α' [Part I, Fig. 4(a)]. The measured values are too dispersed to enable us to compute an activation energy value for each mechanism.

Table III Relative Variations of PMMA Rheological Parameters between Two Samples PLX1 and PLX5

$\frac{\delta E_r}{E_r}$	$\frac{\delta \nu_1}{\nu_1}$	$\frac{\delta \nu_2}{\nu_2}$	$\frac{\delta E_r/kG_r}{E_r/kG_r}$
−5%	16%	11%	−8%

The apparent modulus (Fig. 8) shows a small concavity toward the y positive in good agreement with a relaxation temperature of 30°C.

Dynamic Bending

In the experimental area, internal loss ν_1 and ν_2 increase with temperature (Fig. 9). This is the increasing slope bound to the relaxation β. Its activation energy can be computed between 450 and 2600 Hz and has a value of 96 kJ/mol. These results are in good agreement with those published by Bernier.[5]

By comparing the two conservative moduli obtained by the two experiments, we can compute the activation energy value of the β relaxation. We have 75 kJ/mol, computed between 1 and 412 Hz. This value does not take into account a possible influence of the temperature on the relaxed and unrelaxed modulus.

The ability of detecting the mechanisms of internal friction by an increase of temperature is now

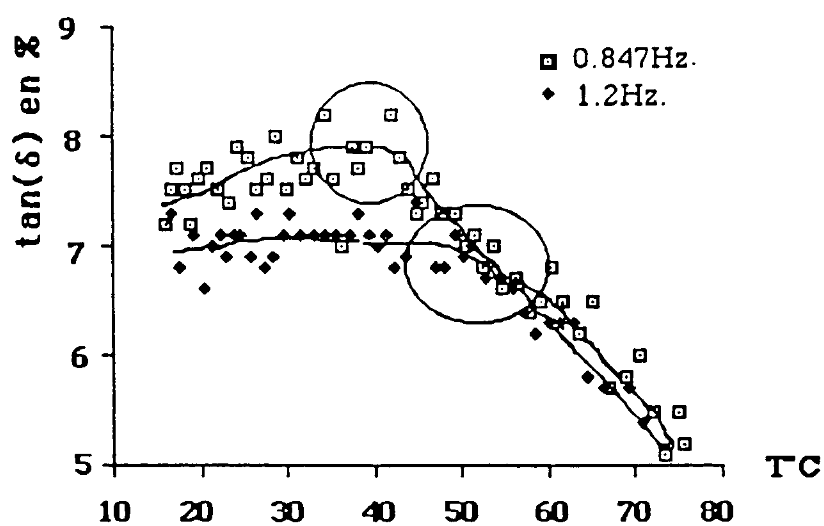

Figure 7 Internal loss of the PMMA for the double pendulum method: two mechanisms are present at these temperatures and frequencies.

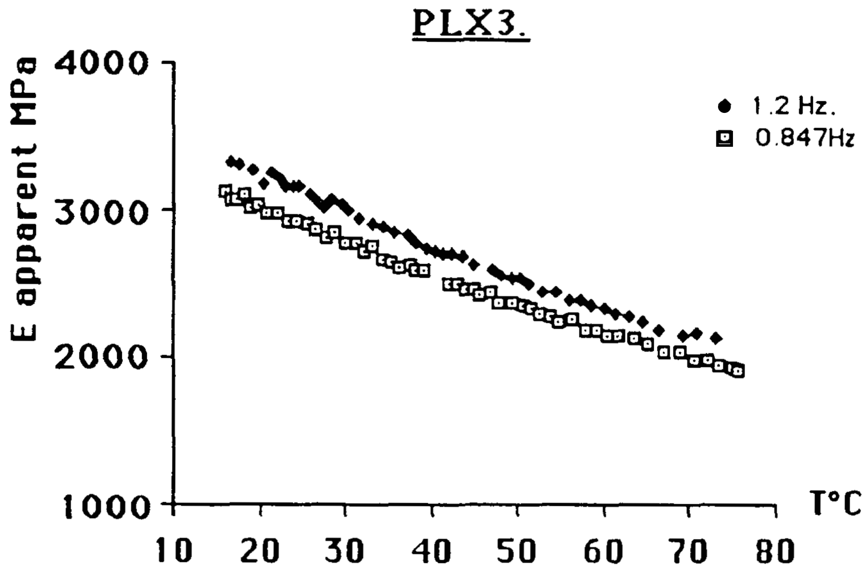

Figure 8 A decrease of the apparent Young modulus is observed during the transition.

established. The method can be used for an anisotropic material.

Anisotropic Material: Wood

The wood material is highly hygroscopic, and the mechanisms are deeply affected by the moisture content. In order to understand the evolutions of the internal loss with the temperature, experiments at several moisture contents have to be made.

Increasing of Temperature

Figures 10 and 11 show the internal loss values for the longitudinal (L), and radial (R) directions for Douglas wood. The sweeping in temperature is not

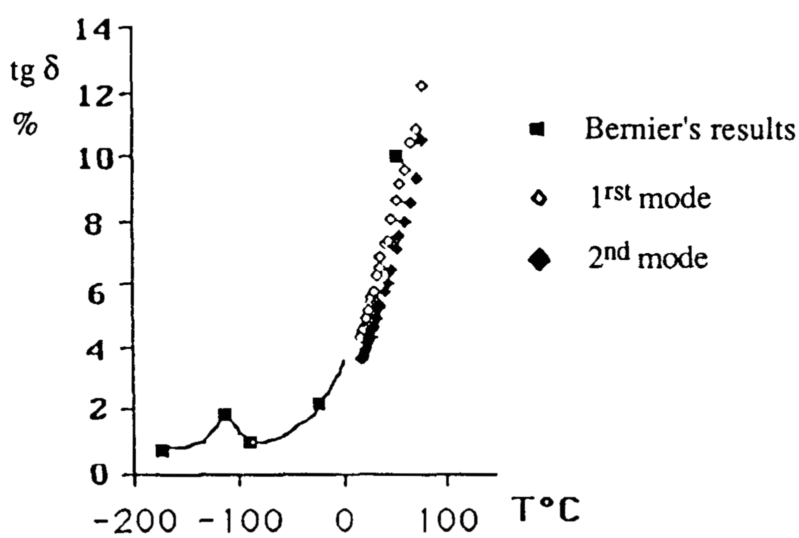

Figure 9 Comparison between the results obtained by Bernier and those obtained by the dynamic bending experiment for the PMMA.

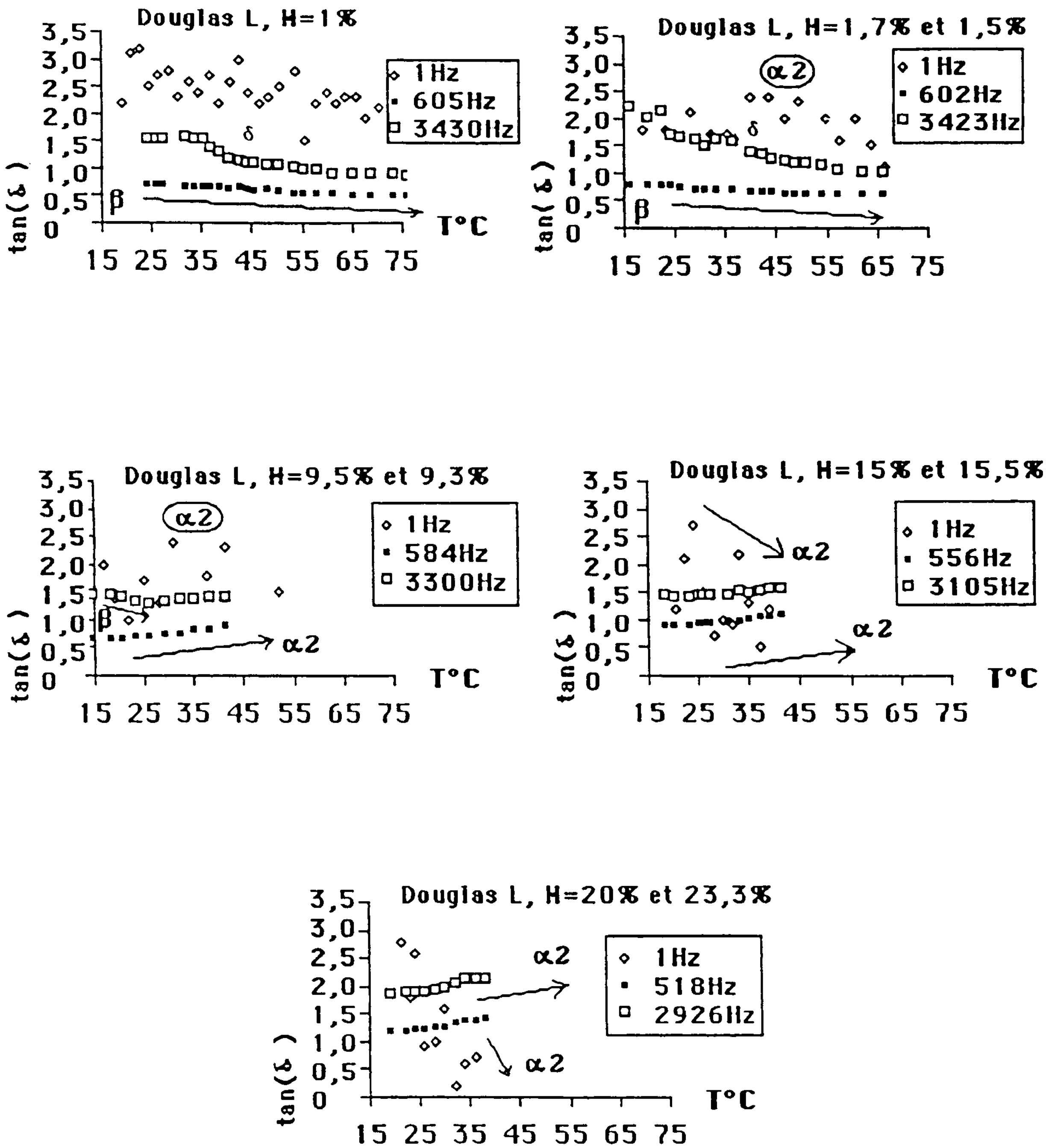

Figure 10 Internal loss of wood in the L direction, versus temperature for three frequencies and five moisture contents.

sufficient to assign properly the different observed mechanisms, but are in good agreement with the following results:

1. Genevaux: the correlation diagrams (first part).
2. Kelley's results (Fig. 12).
3. Bernier's results, after Genevaux's comments.

For example, the following results were used to identify the α_2 and α_1 relaxations in Figure 11 in the radial direction.

In Figure 10, for $H = 1\%$, at 3430 Hz, we notice

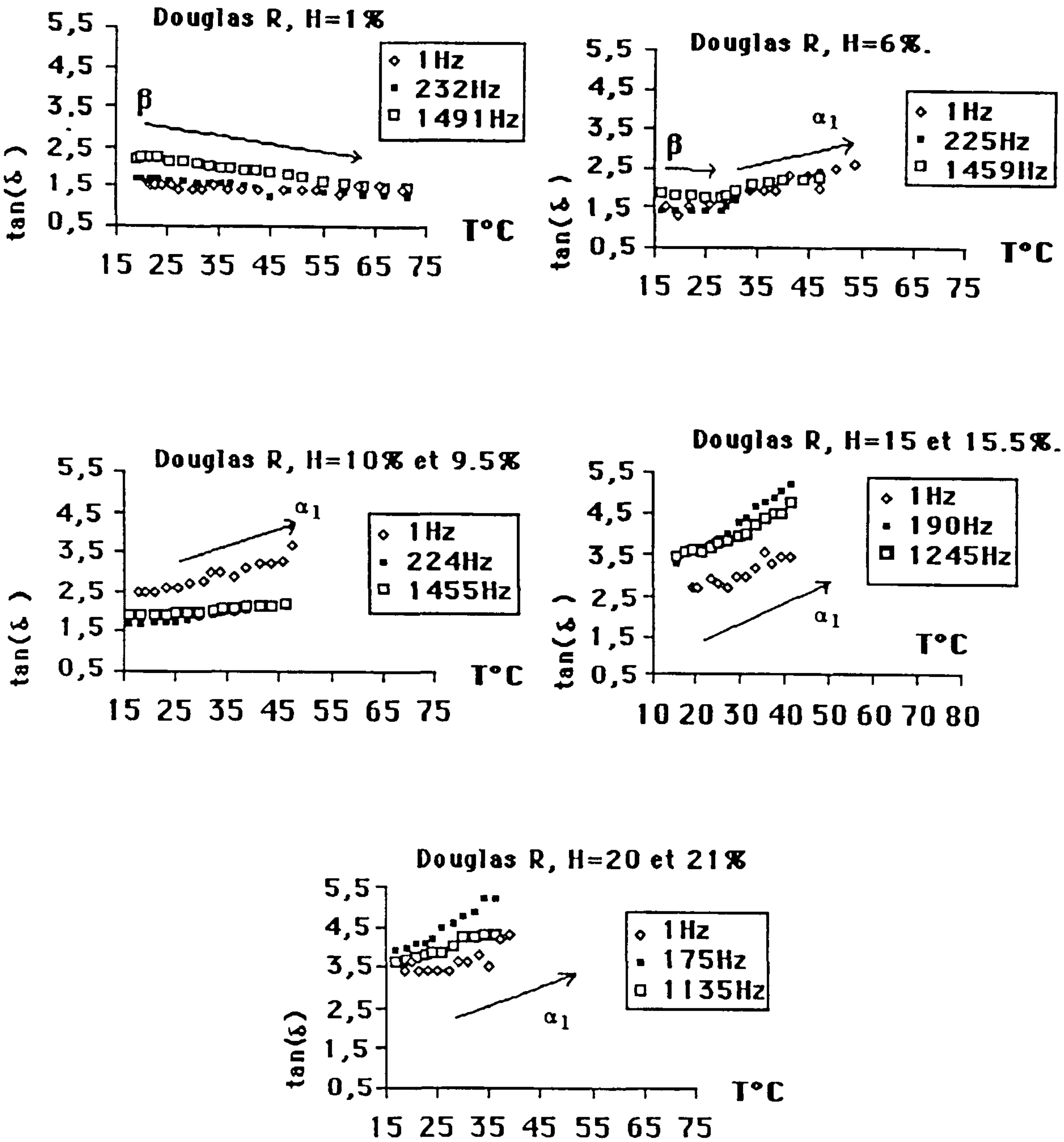

Figure 11 Internal loss of wood in the R direction, versus temperature for three frequencies and five moisture contents.

a small maximum in the graph in the longitudinal direction. According to the first part, this should be δ. The reality of this maximum of internal loss δ in the L direction at 1% moisture content has been confirmed first by a second experiment—increasing the temperature—and by a third test—decreasing the temperature. The accuracy of this maximum is about 5°C on the temperature and 20% on the amplitude between these three experiments.

Effects of Frequency and Temperature at a Given Moisture Content

Longitudinal Direction

An activation energy of 80–100 kJ/mol was computed for the mechanism δ. This value is higher than the value proposed by Genevaux, and the value computed by Tsutsumi, at 15% moisture content, respectively, 40 and 54 kJ/mol.

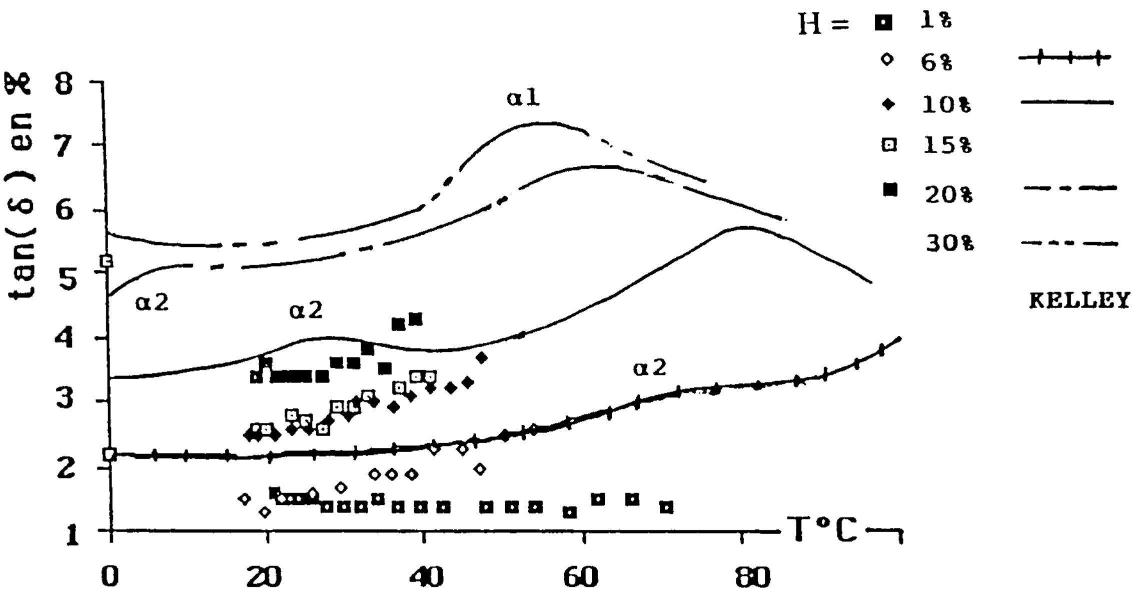

Figure 12 Comparison of the measured internal loss (points) with Kelley's results[6] at 1 Hz (lines). The % indicate the fixed value of the moisture content.

The internal loss at 1% moisture content shows clearly (Fig. 13) the effects of the activation energy of relaxation β between the two dynamic frequencies 605 and 3430 Hz. The small influence of the δ relaxation can be seen here.

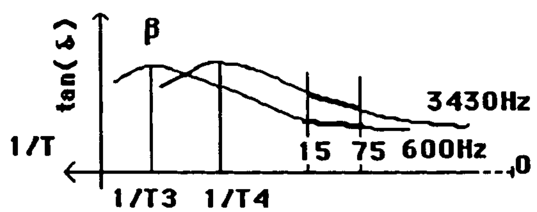

Figure 13 Interpretation of the effects of the frequency in the L direction, at 1% moisture content.

At elevated frequencies, the activation energy of the β relaxation is lower than the α_2 one (correlation diagram). The shift in temperature, for two given frequencies, is then greater for the β relaxation than for α_2. This explains a higher value of the internal loss at 2926 Hz than at 518 Hz (Fig. 14), for a moisture content of 20% (Fig. 10). That could not be explained if the α_2 relaxation existed on its own (Fig. 15).

Figure 18(a, b, c) present the evolutions of the internal loss, for three moisture contents.

The knowledge of the microstructural elements of wood (ray-cells, fibers, etc.), and the importances of the basic polymers in each of them (Fig. 2 of the Part I), will permit localizing the mechanisms by testing the wood sample in the other direction.

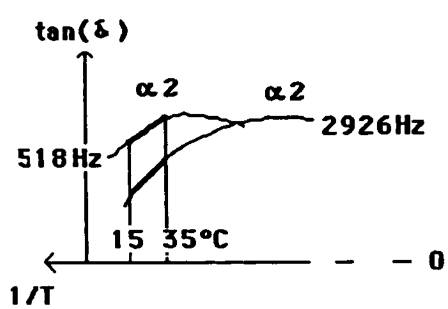

Figure 14 If $\alpha 2$ has existed alone, the internal loss at 2926 Hz should be lower than at 518 Hz, at a moisture content of 20%.

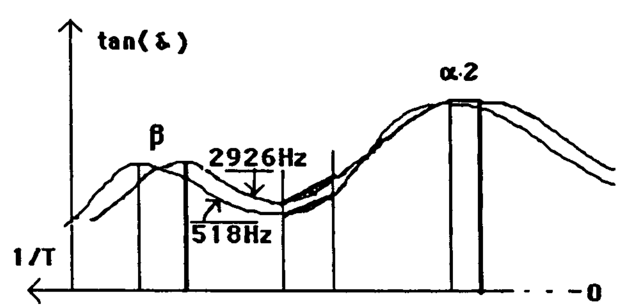

Figure 15 If $\alpha 2$ and β are existing together, the opposite is possible to be observed.

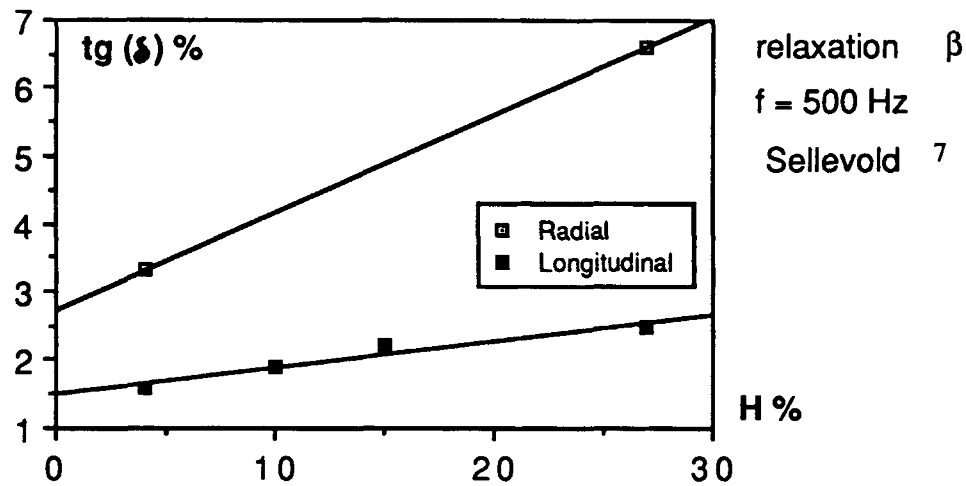

Figure 16 Increasing of the internal loss of β with the moisture content, in a range of about 300 to 500 Hz, −95°C to −50°C.

Radial Direction

In the R direction, the middle lamella of the fibers is more solicited than in the longitudinal direction. The middle lamella is composed for the most important part by the lignin. Its relaxation (α_1) has a higher amplitude than α_2's (Fig. 12).[6] Thus it dissimulates the relaxation α_2 in our results (Fig. 11).

The slopes of the curves (Fig. 11) agree with the existence of two internal sources β and α_1. The α_2 relaxation, which is not observed, is located in the correlation diagram (Fig. 19) at the same place as in the longitudinal direction.

Internal loss levels can be also analyzed. For example, the apparent inversion of the level of the internal loss of Figure 11, for H = 20%, can be explained in two ways:

1. Relaxation β gets closer to the experimental zone, and it induces a complementary internal loss, which is greater when the frequency is higher. The effect of increasing the level of tan(δ) of the source β with the moisture content (Fig. 16),[7] is useful to understand the internal loss levels found for H = 15% versus H = 10% [Figs. 17 and 19(c)].
2. The second explanation is that the level of the highest point of internal loss for a relaxation depends on the tested domain (frequency-temperature)[4] [Fig. 19(c)].

Effects of Moisture Content

The higher the moisture content, the lower the temperature of the maximum of internal loss α_2.

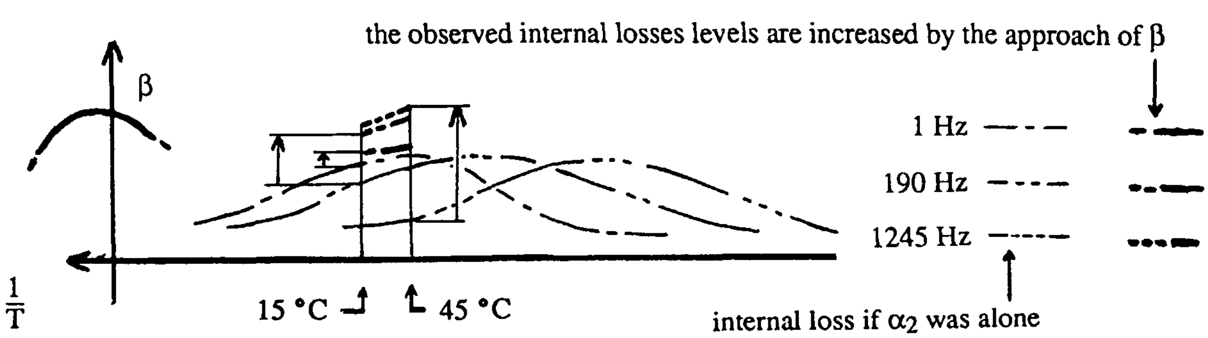

Figure 17 The proximity of two relaxations may induce an inversion of the internal loss levels.

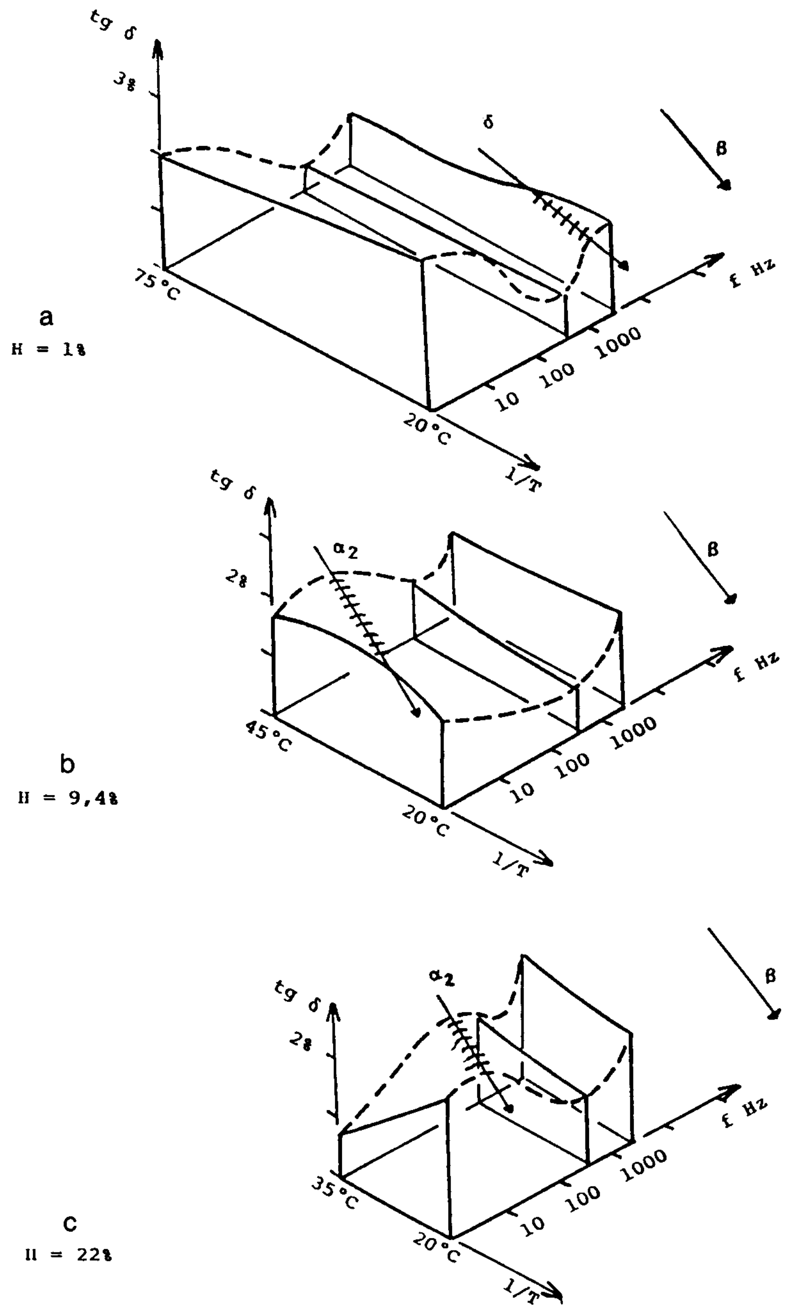

Figure 18 Evolution of the internal loss in the longitudinal direction of wood, for three moisture contents.

CONCLUSION

This part has been proved to be useful in measuring the internal loss of solids with similar properties such as PMMA and wood (composed of several polymers). It provides convincing information on the existence of several sources of internal loss.

A temperature increase in a range from 20 to 60°C, and 1 to 20% moisture content, shows the influence of the four mechanisms of internal loss β, δ, α_2, and α_1, but the too short sweep in temperature has not permitted us to assign these mechanisms. These are in good agreement with the results of the literature. The higher the moisture content, the

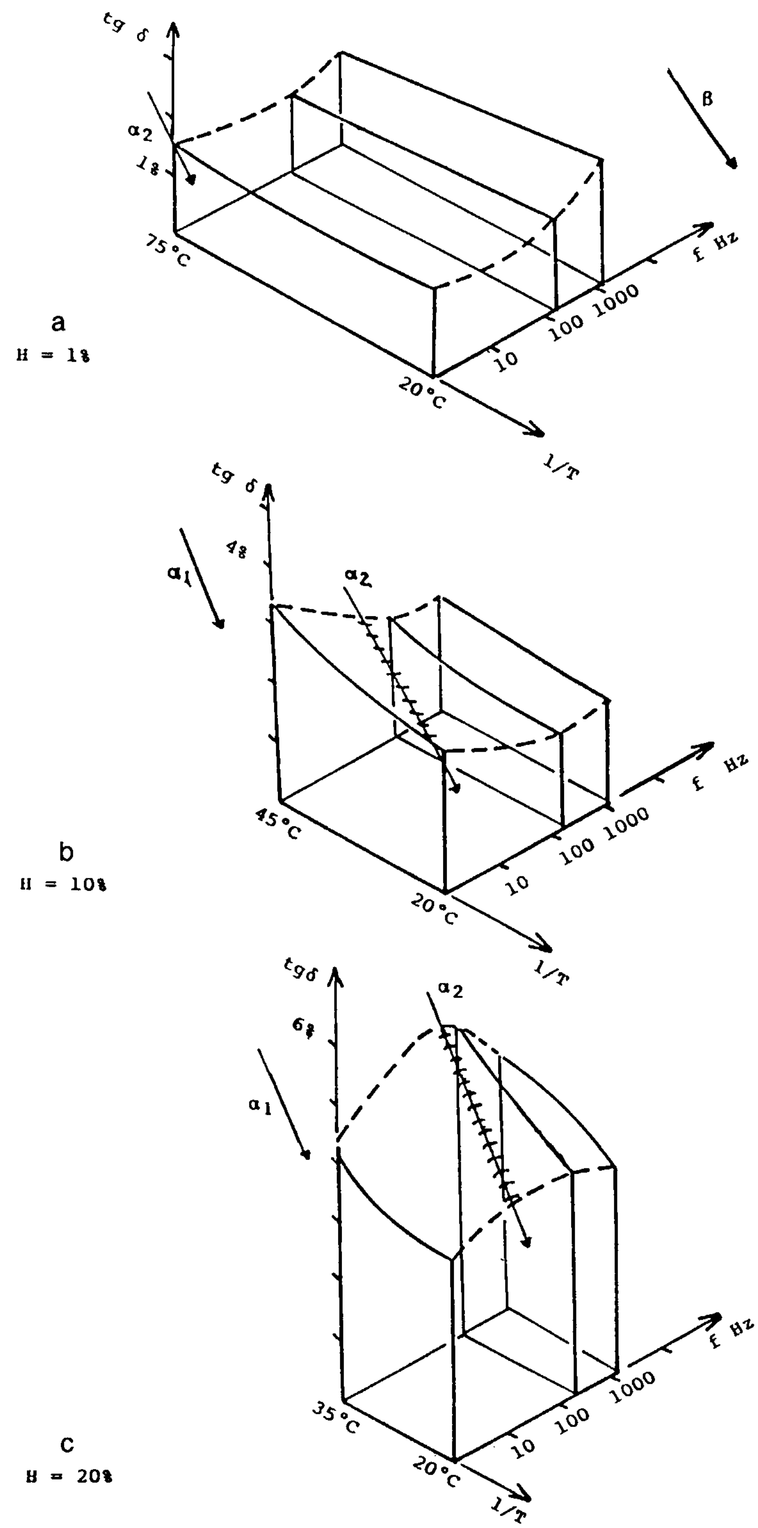

Figure 19 Evolution of the internal loss in the radial direction of wood, for three moisture contents.

lower the temperature of the maximum of internal loss.

The relaxation δ, which was never pointed out clearly before, but suggested by Genevaux, is confirmed here. Its activation energy is evaluated at around 90 kJ/mol.

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