

Temperature–Frequency Transformation in Dielectric Thermal Analysis (DETA) of Wood Relaxation Properties

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SYNOPSIS

A direct method for the transformation of temperature dependences of dielectric loss factor (ϵ'') obtained at any frequency, into frequency dependences at any temperature was worked out. The method was tested and the accuracy of the analysis was verified for the case of local processes of dielectric relaxation in wood in the directions parallel and perpendicular to the fibers. The obtained solutions proved that a common representative of all considered dielectric absorption spectra is the distribution of dielectric absorption intensity vs. free energy of activation of an adequate individual relaxation process. The origin of the difference in the peak intensity of dielectric relaxation spectra, obtained at various experimental temperatures, was explained as a consequence of simple proportionality between the free energy of activation of relaxation and the energy of activation of rotators generation. A recently developed method of transformation is believed to give a new universal approach to the dielectric and dynamic mechanical thermal analysis of polymer systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Investigations of mechanical and dielectric relaxation phenomena in all kinds of materials, but especially in condensed systems of natural and synthetic polymers, are carried out in laboratories of many universities and industrial centres in the world. The main idea behind this work is to find a relationship between molecular dynamics and the rheological behavior of the materials in the macroscopic scale.^{1–4} At present, the stage of development of experimental techniques adapted to dynamic mechanical and dielectric relaxation spectroscopy is not satisfactory. The “ideal” spectroscopy would require the dielectric or mechanical relaxation spectra to cover a wide range of relaxation times, ranging over a dozen or so logarithmic decades. Unfortunately, in most cases the measuring instruments provide the possibility of carrying out studies in a wide temperature range but only at a few frequencies.⁵

The earlier studies on dynamic mechanical and dielectric properties of cellulose, wood, and wood-

polymer composites^{6–10} have shown that the relaxation spectra have a common feature that can be generalized to give a correct picture of the investigated transitions. However, a comparison of the results obtained by dielectric thermal analysis (DETA) as well as dynamic mechanical thermal analysis (DMTA) requires the application of a procedure that would allow us to eliminate the effect of different frequencies of measuring fields on the localization of dispersion region. It is known that a simple Debye model gives a good description of relaxation processes in simple noninteracting particle systems such as gases. It has also been known, however, that it gives only the first approximation of the response of liquids and solids. A number of modifications, usually empirical, have been made to the Debye approach in order to find the most general formalism describing the cooperative relaxation phenomena in solids. A description of the relaxation process in condensed matter requires determination of the distribution of relaxation time. Because this distribution should cover a wide range of times, the studies have to be carried out over a corresponding, but not available, wide range of experimental frequencies. The search for a unique and valid description of relaxation processes in solids has effected in

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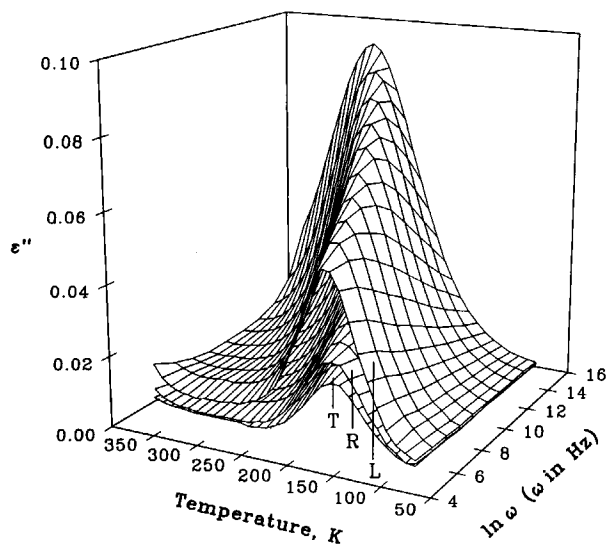


Figure 1 Three-dimensional plots of dielectric absorption as a function of temperature and frequency for absolutely dry wood in the longitudinal (L), radial (R), and tangential (T) direction.

the time-temperature superposition (TTS) principle^{11,12} allowing to a combination of many fragmented relaxation spectra obtained under different experimental conditions (for example, collected at various temperatures) in a single master curve. However, an effective temperature-frequency transformation of relaxation spectra with temperature-dependent intensity of the maximum has not been fully worked out yet. The approach proposed

in this article is aimed at working out the postulated transformation of temperature dependence of dielectric losses at any frequency, into appropriate frequency dependence at any temperature.

EXPERIMENTAL

The samples of wood (*Picea glehnii*, Mast.) of the density 380 kg/m^3 were prepared in the form of disks of 50 mm in diameter and 1.5 mm in thickness. In order to carry out the analysis of dielectric properties for three mutually perpendicular directions of wood, the samples were cut out so that the force lines of the measuring electric field would be parallel (longitudinal direction) or perpendicular (radial and tangential directions) to the axes of wood fibers. The samples were dried in vacuum for about 72 h at 333 K. The dielectric properties were measured in an experimental setup made of a transformer bridge Ando Denki TR-10C and a measuring capacitor was placed in a variable temperature chamber with liquid nitrogen as a working medium. The measurements were performed under dry conditions in the temperatures from 70 K to 373 K and for the frequencies from 30 Hz to 1 MHz, and the sample temperature was changed at the rate of 0.5 K/min.

RESULTS AND CALCULATIONS

Frequency dependences of dielectric loss at given temperatures and its temperature dependences at

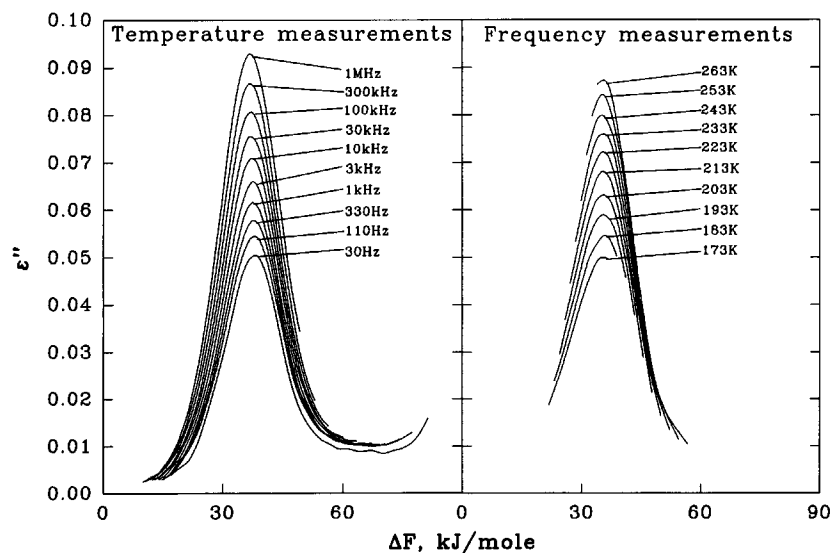


Figure 2 The temperature scans at different frequencies and frequency scans at different temperatures of dielectric losses plotted as a function of free energy of activation for absolutely dry wood in the L direction.

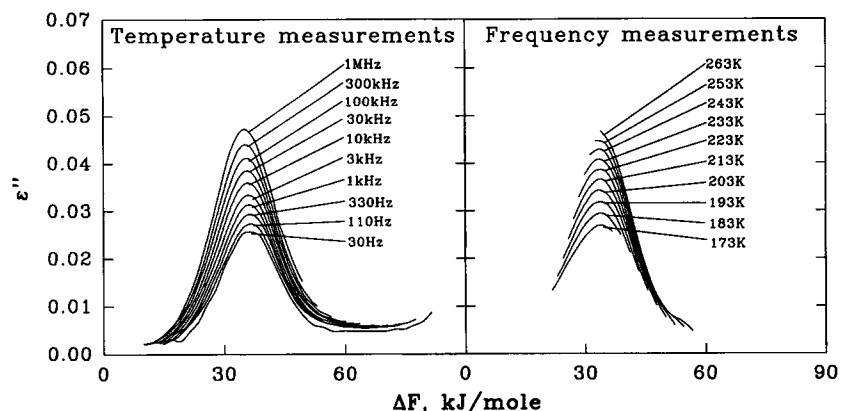


Figure 3 The temperature scans at different frequencies and frequency scans at different temperatures of dielectric losses plotted as a function of free energy of activation for absolutely dry wood in the R direction.

given frequencies for absolutely dry wood in three anatomical directions (L, R, and T) are shown in the form of a three-dimensional plot in Figure 1. The two ways of data presentation, in the (T, ϵ'') or $(\ln \omega, \epsilon'')$ plane, represent the two applied techniques of dielectric absorption measurements. Both dependences $\epsilon''(T)$ and $\epsilon''(\ln \omega)$ reveal maxima that testify to the occurrence of β -relaxation process interpreted as due to reorientations of the polar hydroxymethyl groups CH_2OH in the disordered regions of cellulose.¹³ The detected complex relaxation phenomenon may be considered as a superposition of individual relaxation processes ascribed to different specific values of free energy of activation, ΔF . This suggestion implies a more universal way of presentation of experimental data, covering both the frequency and temperature dependence of dielectric absorption.

As far as the local relaxation processes are concerned, their relaxation times obey the functional form in an equation related to the theory of the absolute reaction rates

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F}{RT}\right) \quad (1)$$

where h , k , and R are the Planck, Boltzmann, and gas constants, respectively.

Because the circular frequency $\omega = 1/\tau$, the free energy of activation of a relaxation process can be expressed by

$$\Delta F = -RT \ln\left(\frac{h\omega}{kT}\right) \quad (2)$$

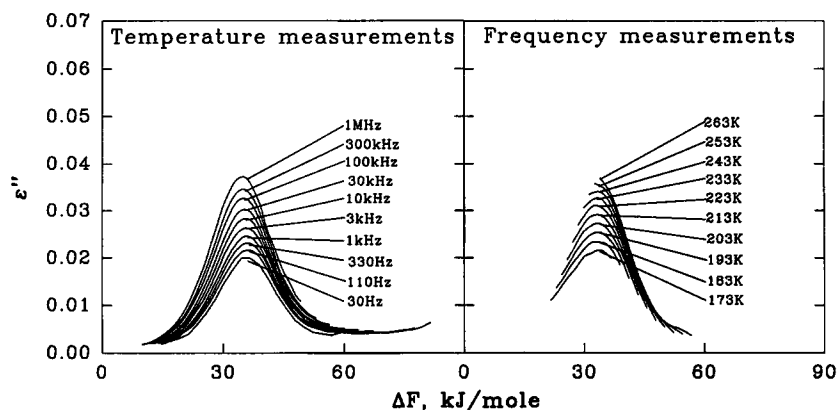


Figure 4 The temperature scans at different frequencies and frequency scans at different temperatures of dielectric losses plotted as a function of free energy of activation for absolutely dry wood in the T direction.

Table I Constant Parameters of the Normalization Factor Calculated for the Relaxation Spectra Obtained for Wood in Longitudinal, Radial, and Tangential Direction

Parameter	Longitudinal Direction	Radial Direction	Tangential Direction
C	0.2464	0.1248	0.0982
n	16	16	16

According to the assumption of the model that treats the observed relaxation transition as a combination of individual relaxation processes, the particular values of the free energy of activation of relaxation corresponding to each individual experimental point have been calculated. Figures 2, 3, and 4 present the traces of temperature scans at different frequencies and frequency scans at different temperatures of dielectric absorption plotted vs. free energy of activation for absolutely dry wood in the L, R, and T direction, respectively.

The way of presentation of the experimental data obtained both from the temperature and frequency measurements of dielectric absorption reveals that there is one and the same value of the free energy of activation corresponding to the position of dielectric loss peak. However, the curves considered reflect the expected but undesired effect of different intensity of dielectric loss maxima. In order to solve this problem, we proposed a unique normalization procedure.

When the rotators are thermally activated, the temperature dependence of the rotator concentration as well as the intensity of the dielectric loss peak can be expressed on the basis of the Boltzmann's law as follows

$$\epsilon''_{\max} = C \exp\left(\frac{-\Delta F^*}{RT}\right) \quad (3)$$

where ϵ''_{\max} , F^* , T , and R are the height of dielectric loss peak, the energy of activation of rotators generation, temperature, and Boltzmann constant, respectively.

We assumed a simple proportionality between the free energy of activation of relaxations, ΔF , and the energy of activation of rotators generation, ΔF^* , i.e., $\Delta F = n\Delta F^*$. Taking this as well as relations (2) and (3) into account, we obtained the following formulae for the dielectric loss peak intensity

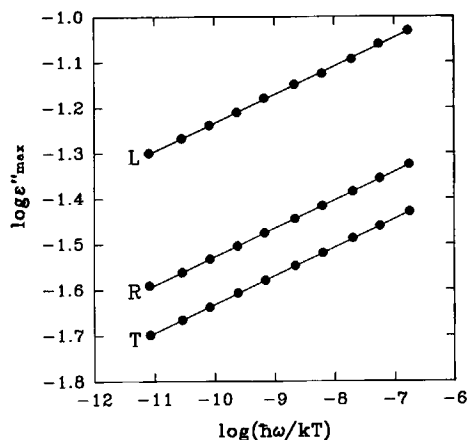


Figure 5 Dependences of $\log \epsilon''_{\max}$ vs. $\log (\hbar\omega/kT)$ for absolutely dry wood in the longitudinal (L), radial (R), and tangential (T) direction.

$$\epsilon''_{\max} = C \left(\frac{\hbar\omega}{kT}\right)^{1/n} \quad (4)$$

The obtained solution as well as the experimental results enable determination of the constant parameters C and n . The postulated calculations have

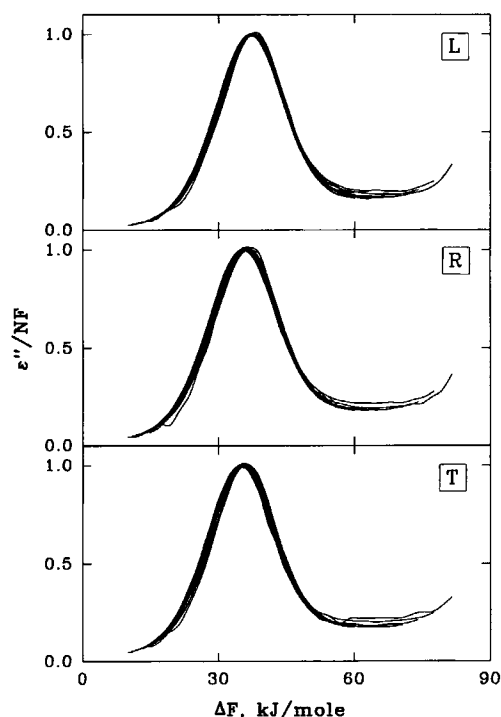


Figure 6 The normalized temperature scans at different frequencies and frequency scans at different temperatures of dielectric losses plotted as a function of free energy of activation for absolutely dry wood in the longitudinal (L), radial (R), and tangential (T) direction.

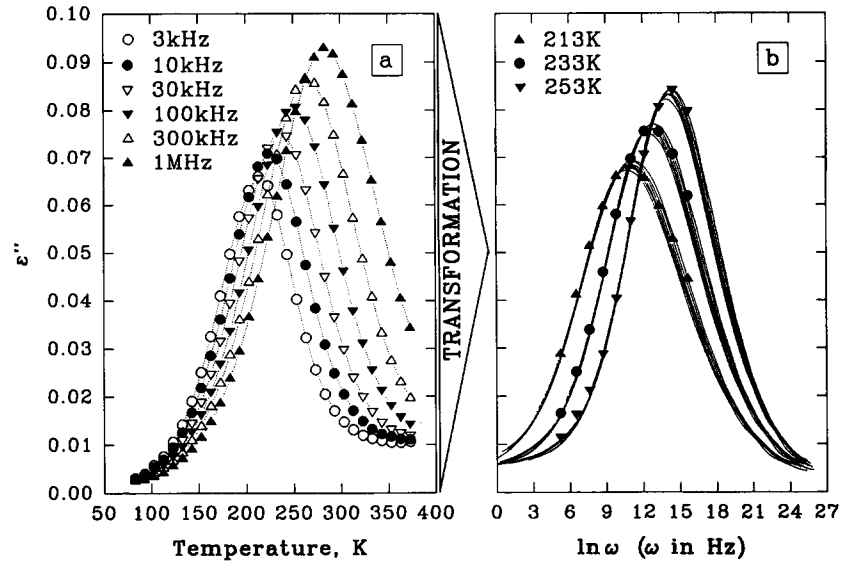


Figure 7 The frequency scans of dielectric losses at various temperatures (b) measured experimentally (points) and calculated (solid lines) on the basis of each of the temperature scans (a) of dielectric losses detected at various frequencies for absolutely dry wood in the longitudinal direction.

been performed for the relaxations detected during temperature measurements at $T = T_{\max}$ under various experimental frequencies and observed in three anatomical directions of wood. Figure 5 presents the course of the above-specified dependence in the log-log scale while the estimated parameters C and n are given in the Table I.

In the case of the distribution of absorption intensity vs. free energy of activation, the relation (4) has a meaning of the normalization factor, NF, to be applied for each experimental point separately. Figure 6 presents traces of the normalized temper-

ature and frequency scans normalized in the above-described way for absolutely dry wood in the L, R, and T direction, respectively.

Eventually, a single curve was found, characteristic of the detected local type of dielectric transition, which can be used instead of 20 different temperature scans at various frequencies and frequency scans at various temperatures obtained for the analyzed-relaxation phenomenon in wood. Because the presented master curve is constructed on the basis of the individual points with each of them ascribed to a single and specific value of a free energy of ac-

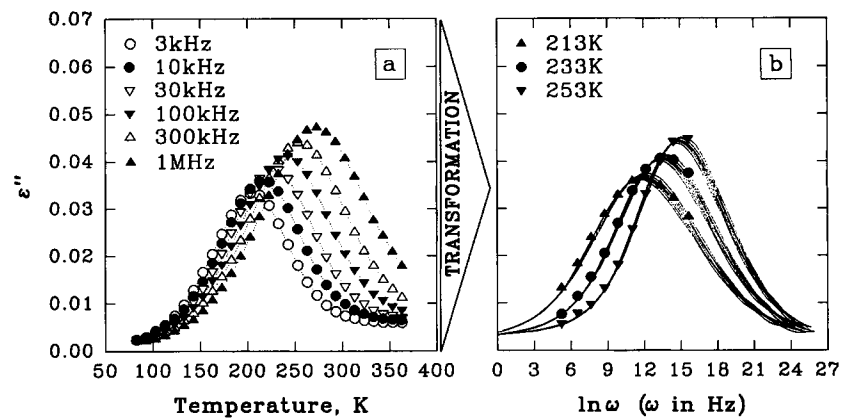


Figure 8 The frequency scans of dielectric losses at various temperatures (b) measured experimentally (points) and calculated (solid lines) on the basis of each of the temperature scans (a) of dielectric losses detected at various frequencies for absolutely dry wood in radial direction.

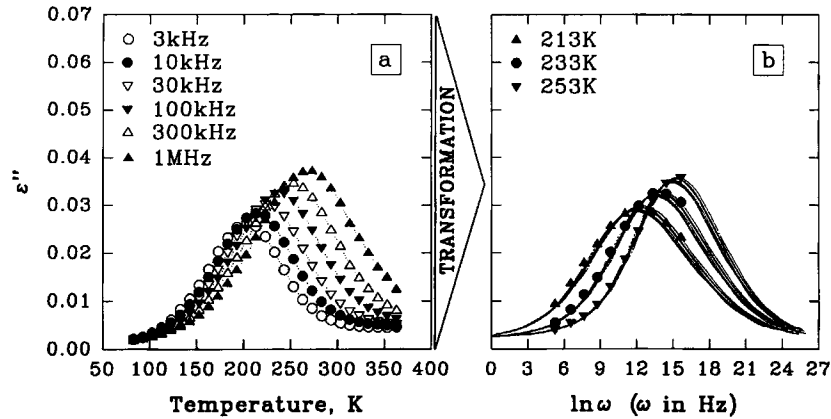


Figure 9 The frequency scans of dielectric losses at various temperatures (b) measured experimentally (points) and calculated (solid lines) on the basis of each of the temperature scans (a) of dielectric losses detected at various frequencies for absolutely dry wood in tangential direction.

tivation, it may be concluded that the curve forms a “transformation junction” that permits determination of each curve presented in plane $(\ln \omega, \epsilon'')$ on the basis of each curve presented in plane (T, ϵ'') and inversely. In order to test the proposed procedure of transformation, a conversion of temperature dependences of $\epsilon''(T_i)$ at any frequency ω_o into frequency dependences $\epsilon''(\ln \omega_x)$ at any temperature T_o , was performed. According to eq. (1), and taking into account that $\Delta F(\omega_o, T_i) = \Delta F(\omega_x, T_o)$ for the same type of an individual relaxation process, the corresponding frequency coordinates $(\ln \omega_x)$ may be calculated from the temperature coordinates (T_i) related to the experimental points as follows

$$\ln \omega_x = \frac{T_i}{T_o} \ln \left(\frac{\hbar \omega_o}{k T_i} \right) - \ln \left(\frac{\hbar}{k T_o} \right) \quad (5)$$

Figures 7, 8, and 9 present the frequency dependences of dielectric loss factor ϵ'' at various temperatures [Figs. 7(b), 8(b), and 9(b)] calculated in the above-described way on the basis of the temperature measurements performed at a given experimental frequency [Figs. 7(a), 8(a), and 9(a)] for absolutely dry wood in the L, R, and T direction, respectively. Each of these dependences is built of many traces obtained from each of the temperature scans recorded at different frequencies. To verify the accuracy of the applied method of transformation, the real experimental points, representing adequate frequency measurements, have been attached to the proper, calculated courses. The intensities of the calculated absorption spectra were found according to the above described normalization procedure, however applied in the opposite sequence.

Even a rough estimation of the obtained results reveals a satisfactory agreement between the calculated and empirically measured courses of the $\epsilon''(\ln \omega)$ dependence. However, a slight effect of the growing width of the estimated traces of dielectric spectra towards higher frequencies could require further studies to increase the accuracy of the proposed approach. The obtained results have confirmed that the postulated transformation of temperature dependence of dielectric absorption into the appropriate frequency dependence is possible.

CONCLUSIONS

Each of the observed temperature or frequency dependences of dielectric loss factor in the β -relaxation region is only another reflection of the same phenomena observed in the studied material.

The common representative of all considered dielectric absorption spectra is the distribution of absorption intensity vs. free energy of activation of adequate relaxation process.

The difference in the peak intensity of dielectric β -relaxation spectra, obtained at various experimental temperatures, reflects the simple proportionality between the free energy of activation of relaxation and the energy of activation of rotators generation.

A direct method for the transformation of temperature dependences of dielectric loss factor, obtained at any frequency, into frequency dependences at any temperature is possible.

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