Model Approach to Dielectric-Thermal Analysis of Wood Modified with Polymer

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Synopsis

The modeling of dielectric properties of wood–polymer composite, considered as a multicomponent layered system, was performed. The obtained solutions were used to determine temperature dependences of real and imaginary parts of complex dielectric permittivity characterizing the wood component in the natural and polystyrene-modified wood in the directions parallel and perpendicular to the fibers. The analysis of the calculated dependences proved that the structural changes of wood depended on the applied method of modification. The main effect attributed to the styrene polymerization occurring in wood placed in a hydrophilic heating medium was an increase in the ordering degree of the mesomorphous regions of cellulose. As a consequence, a part of the polar, functional groups distinguished by particularly high activation energies (i.e., low probability of a dipole jump to an adjacent site) was eliminated from participation in the relaxation processes. The application of a hydrophobic heating medium during modification procedure resulted in a permanent swelling effect of the wood component of the composite. Within the applied investigation method it was found that the changes in increment of dielectric permittivity referring to the β-relaxation process in wood substance can be the specific criterion of structural changes in wood modified with polystyrene. The distribution functions of relaxation times for natural and modified wood substance were determined.

INTRODUCTION

In the studies of wood–polymer composites the fundamental problem is the determination of the influence of the applied modificators and of the modification technology on the properties of the material obtained.[1-3] These properties are determined not only by the content and characteristics of the polymer falling into previously empty wood voids but also may be influenced by the possible changes in the wood structure.[4] Dielectric spectroscopy offers a very efficient method, not fully exploited, for studying such problems.[5,6] In particular, the application of the dielectric-thermal analysis (DETA) to investigations of wood modified with polystyrene is justified by essential differences in dielectric properties between the polar wood substance and nonpolar vinyl polymers. The fact that such polymers do not take part in dielectric relaxation in the modified wood makes it possible to estimate selectively the changes in wood substance structure caused by the modification or accompanying it.[7] However, the quantitative and qualitative analysis of these changes requires a model description of the systems studied to enable us to determine and compare dielectric parameters of cell walls of natural and modified wood. In this paper we made an attempt to formulate the dielectric criteria allowing the estimation of the quality of the obtained wood–polystyrene composites

through identification and classification of structural changes occurring in wood substance.

EXPERIMENTAL

Dielectric properties of the natural and polystyrene-modified wood were measured in an experimental setup made of a capacity bridge and a measuring capacitor placed in a variable temperature chamber which was a gas thermostate with liquid nitrogen vapors as a working medium.[8] The required temperature chosen from the range 78 to 373 K was maintained within 0.1 K. The samples of wood and wood–polystyrene composite were prepared in the form of disks of 20 mm in diameter and 1.5 mm in thickness. During the measurements the sample temperature was changed at a rate of 0.5 K/min. Both natural and polystyrene-modified wood samples to be studied were oven-dried in a measuring chamber at a temperature of 376 K. As the criterion of sample dryness we took the stability of its dielectric parameters at 376 K for at least 24 h. The errors in determination of ϵ' and ϵ'' values in the whole range of temperatures considered and for all frequencies of the measuring electric field applied (i.e., 0.4, 2, and 10 kHz) were 2–4% and 3–8%, respectively.

X-ray diffraction studies were performed on a powder diffractometer TUR-M-62. The samples of wood and wood–polystyrene composite were comminuted into the fragments of 0.25 mm in size in order to eliminate the influence of texture of the material. The diffractograms were taken for 2θ angles varying from 6° to 30°.

In this article we present exemplary results obtained for alder wood of the density (540 ± 2) kg/m^3 in the oven-dried state as well as for wood–polystyrene composite obtained by thermally initiated polymerizations.[9] As follows from the procedure of modification described in the previous paper,[7] an important role in styrene polymerization in wood may fall to the kind of material used as a heating medium. Thermal treatment in the first stage is applied to heat the wood saturated with monomers up to the temperature of half-desintegration of the polymerization initiators, which results in starting the exothermic process of polymerization. The liquid applied in thermal processing, during styrene polymerization, had to act a medium removing the heat produced as a result of the reactions taking place in the wood. Thus, the kind of the liquid applied may influence the structural changes in wood. To verify this suggestion, we carried out the structural analysis of wood modified with polystyrene following the procedures differing only in the kind of the heating medium used. We applied a hydrophobic liquid (oil) or hydrophilic liquid (a saturated solution of NaCl). The studied composites contained the same amount of polymer, i.e., (0.80 ± 0.02) kg/kg wood, independently of the technology of production.

The analysis of dielectric properties of the natural and modified wood was carried out for two mutually perpendicular directions. The samples to be studied were cut out so that the force lines of the measuring electric field would be parallel or perpendicular to the axes of wood fibers. In order to
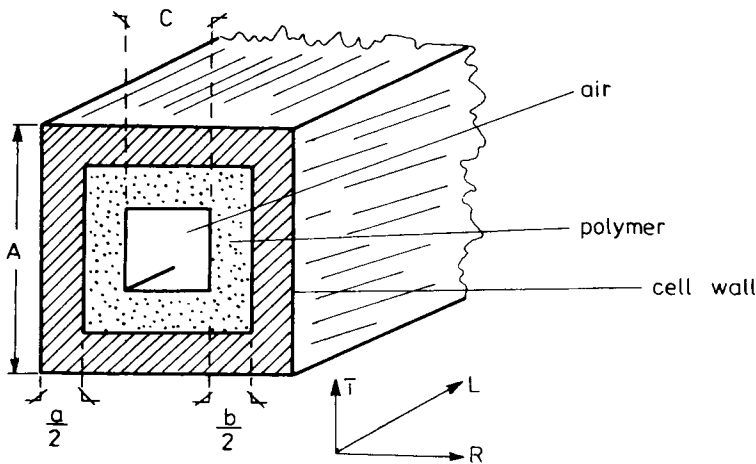
Fig. 1.   A layered model of polystyrene modified wood cell.

determine the influence of wood porosity on its dielectric properties, the measurements were also performed for 19 other wood species of different densities varying from 350 to 1250 kg/m^3.

RESULTS AND DISCUSSION

As far as DETA measurements of wood–polymer composite are concerned, an important methodological problem is to provide a possibility of selective estimation of wood substance formed in cell walls which make the supporting structure for the polymer filling some of the wood voids. The modeling of dielectric properties of wood–polymer composites, considered as a multicomponent system, may lead to recognition of the criteria of changes in structure of wood substance. These dielectric criteria would be independent of such macroscopic parameters as the porosity coefficient of the wood to be modified or the degree of polymer content in the composite. The investigation concerning the estimation of real part of the complex wood permittivity proved that the best agreement with experiment is obtained assuming the layered model.[10–12] The layer model of polymer modified wood cell, which we apply in the following, is presented in Figure 1.

The general assumptions taken in the calculations performed are given below:

a. The complex dielectric permittivity of a system of layers parallel to the force lines of an electric field, $\epsilon_\parallel^*$, is equal to the sum of products of volume fractions, V_i, and complex dielectric permittivities, ϵ_i^*, of individual layers:

$$\epsilon_\parallel^* = \sum_i V_i \epsilon_i^* \tag{1}$$

b. The inverse complex dielectric permittivity of a system of layers perpendicular to the force lines of electric field, $\epsilon_\perp^*$, is equal to the sum of ratios of

volume fractions, V_j, and complex dielectric permittivities, ϵ_j^*, of individual layers:

$$\frac{1}{\epsilon_\perp^*} = \sum_j \frac{V_j}{\epsilon_j^*} \tag{2}$$

According to the assumed model, when the electric field lines are parallel to the wood fibers (L direction) we come to the following formula for the complex permittivity of the composite, ϵ_{cl}^*:

$$\epsilon_{cl}^* = (1 - P)\epsilon_{ccl}^* + S\epsilon_P^* + (P - S)\epsilon_0^* \tag{3}$$

where ϵ_{ccl}^*, ϵ_P^* and ϵ_0^* are the complex permittivities of the modified wood cell walls along the L direction, the bulk polymer, and air, respectively. The volume fraction S of the polymer in the composite studied may be found from the relation: $S = L_P\gamma_w/\gamma_P$, where γ_w is wood density, γ_P the bulk polymer density, and L_P is a degree of wood saturation by polymer, defined as a ratio of the polymer and wood masses in the composite. The volume fraction of cell walls $(1 - P)$ and air $(P - S)$ can be found from the easily accessible wood-porosity coefficient $P = 1 - \gamma_w/\gamma_{cw}$, where γ_{cw} is the wood cell density.

Taking into account the fact that $\epsilon''_0 = 0$, eq. (3) implies the following relations describing the dielectric permittivity and dielectric loss factor of the composite in the longitudinal direction:

$$\epsilon'_{cl} = (1 - P)\epsilon'_{ccl} + S\epsilon'_P + (P - S)\epsilon'_0 \tag{4}$$

and

$$\epsilon''_{cl} = (1 - P)\epsilon''_{ccl} + S\epsilon''_P \tag{5}$$

The calculations of complex permittivity of wood–polystyrene composite when the force lines of the measuring field are perpendicular to the wood fibers requires that eqs. (1) and (2) be taken into account simultaneously. The experimentally found dielectric anisotropy in wood along the R and T directions amounting only to a few percent, allowed us to disregard the differences in the tangential and radial dimensions of wood cell walls, as a first approximation, of course.

The complex permittivities of the composite along the T direction can be found by distinguishing three different groups of layers:

a. the layers composed only of the wood substance parallel to the TL plane
b. the layers composed of the polymer and wood substance parallel to the RL plane
c. the layers composed of the polymer, air, and wood substance parallel to the RL plane

The complex permittivity of a system of such layers can be found from the relation

$$\epsilon_{ct}^* = V_a\epsilon_a^* + V_b\epsilon_b^* + V_c\epsilon_c^* \tag{6}$$

As a result of geometric considerations we come to

$$V_a = a/A = 1 - \sqrt{P}$$

$$V_b = b/A = S/(\sqrt{P} - \sqrt{P - S})$$ (7)

$$V_c = c/A = \sqrt{P - S}$$

where a, b, c, and A are the dimensions indicated in Figure 1.

The parameter ϵ_a^* in eq. (6) is the complex permittivity of polymer-modified wood cell walls, ϵ_{cct}^*, determined along the direction perpendicular to the fiber axes. The parameters ϵ_b^* and ϵ_c^* can be found from eq. (2) and geometric considerations analogous to those presented above.

As a consequence we have

$$\epsilon_a^* = \epsilon_{cct}^*$$

$$\epsilon_b^* = \left[\frac{\sqrt{P}}{\epsilon_P^*} + \frac{1 - \sqrt{P}}{\epsilon_{cct}^*} \right]^{-1}$$ (8)

$$\epsilon_c^* = \left[\frac{\sqrt{P - S}}{\epsilon_0^*} + \frac{S}{\epsilon_P^*(\sqrt{P - S} + \sqrt{P})} + \frac{1 - \sqrt{P}}{\epsilon_{cct}^*} \right]^{-1}$$

It is easy to notice that the above relations found for polymer modified wood for $S = 0$ transform into the appropriate relations for natural wood. Then, the parameters ϵ_{ccl}^* and ϵ_{cct}^* are replaced by the complex permittivities of the unmodified wood cell walls, i.e., with ϵ_{wcl}^* and ϵ_{wct}^*.

For the assumed model and from eqs. (6) and (8) we obtained the following formulae for the real part of complex dielectric permittivity of the composite in the tangential direction, T:

$$\epsilon_{ct}' = V_a \epsilon_a' + V_b \epsilon_b' + V_c \epsilon_c'$$ (9)

where

$$\epsilon_a' = \epsilon_{cct}'$$

$$\epsilon_b' = \left[\frac{\sqrt{P}}{\epsilon_P'} + \frac{1 - \sqrt{P}}{\epsilon_{cct}'} \right]^{-1}$$ (10)

$$\epsilon_c' = \left| \frac{\sqrt{P - S}}{\epsilon_0'} + \frac{S}{\epsilon_P'(\sqrt{P - S} + \sqrt{P})} + \frac{1 - \sqrt{P}}{\epsilon_{cct}'} \right|^{-1}$$

and for the corresponding dielectric loss factor

$$\epsilon_{ct}'' = V_a \epsilon_a'' + V_b \epsilon_b'' + V_c \epsilon_c''$$ (11)

where

$$\epsilon_a'' = \epsilon_{cct}''$$

$$\epsilon_b'' = \left[(\epsilon_{cct}')^2 \left(\frac{\sqrt{P}}{\epsilon_P'} + \frac{1 - \sqrt{P}}{\epsilon_{cct}'} \right)^2 \right]^{-1} \epsilon_{cct}'' \tag{12}$$

$$\epsilon_c'' = \left[\frac{(\epsilon_{cct}')^2}{1 - \sqrt{P}} \left(\frac{\sqrt{P - S}}{\epsilon_0'} + \frac{S}{\epsilon_P'(\sqrt{P - S} + \sqrt{P})} + \frac{1 - \sqrt{P}}{\epsilon_{cct}'} \right)^2 \right]^{-1} \epsilon_{cct}''$$

In deriving the above formulae for wood modified with vinyl polymers we assumed that $\epsilon_P'' \ll \epsilon_{tc}''$ and $\epsilon_0'' = 0$.

The obtained model solutions as well as the experimental results make it possible to determine dielectric parameters characterizing cell walls of the natural and polystyrene modified wood. These parameters are the dielectric permittivity ϵ_{ccl}' and dielectric loss factor ϵ_{ccl}'' along the fibers, calculated from eqs. (4) and (5), respectively, the dielectric permittivity ϵ_{cct}' across the fibers, which is the root of the third degree equation obtained from eqs. (9), (10), and (7), and dielectric loss factor ϵ_{cct}'' across the fibers calculated from eqs. (11), (12), and (7).

Figure 2 presents the dielectric permittivity of oven-dried wood vs. its density, obtained at 373 K, for the parallel and perpendicular (T direction) orientation of force lines of the measuring electric field, with respect to the fibers. The broken lines represent the courses of the above-specified dependences calculated from eqs. (4) and (9) assuming $S = 0$.
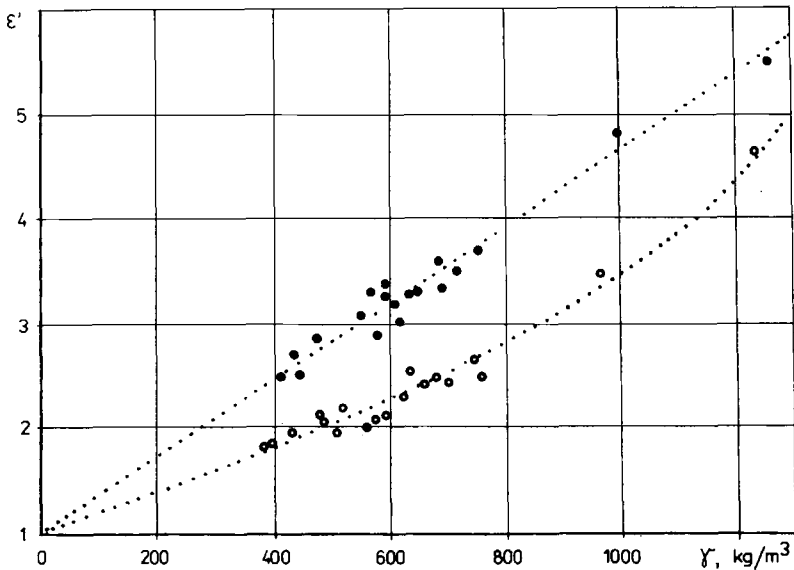

Fig. 2. Wood dielectric permittivity vs. its density, for the measuring electric field applied in the directions parallel (●) and perpendicular (○) to the fibers.
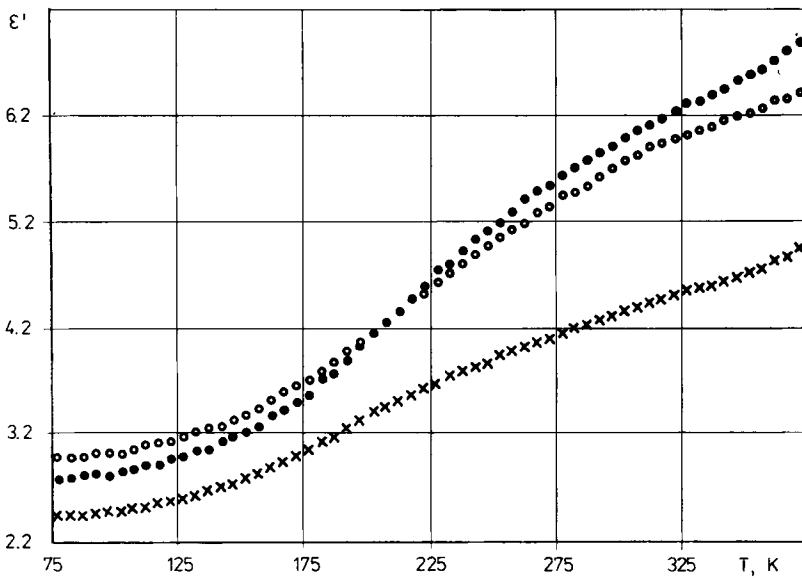
Fig. 3. Temperature dependences of dielectric permittivity of the wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, calculated for the longitudinal direction.

Model calculations of wood permittivity demand both wood density and dielectric permittivity of wood cell walls to be known. In order to estimate the parameters of wood cell walls, we subjected the functions (4) and (9) to the fitting procedure on the grounds of experimental data, assuming that these parameters are constant for different species of wood characterized by different macroscopic density. The best agreement between the experimental data and the assumed model was obtained for the wood cell wall density of $\gamma_{cw} = (1300 \pm 20)$ kg/m^3. The "equivalent" wood cell wall density found in this way was applied in further calculations. The mean values of dielectric permittivity of cell walls of all kinds of wood considered were $\epsilon'_{cwl} = 5.82 \pm 0.25$ and $\epsilon'_{cwt} = 5.15 \pm 0.33$ in the directions parallel and perpendicular to the wood fibers, respectively. The calculated values are fully consistent with the results obtained by other authors.[11]

Figures 3 and 4 present the dependences $\epsilon'_{ccl}(T)$ and $\epsilon''_{ccl}(T)$ for polystyrene-modified wood substance in hydrophobic and hydrophilic heating medium, calculated along the fibers and at the electric field frequency of 400 Hz. For the sake of comparison both figures also include the dependences $\epsilon'_{wcl}(T)$ and $\epsilon''_{wcl}(T)$ calculated for the wood substance of natural wood. Temperature dependences $\epsilon'_{cct}(T)$ and $\epsilon''_{cct}(T)$ calculated for the tangential direction at the same electric field frequency are shown in Figures 5 and 6, which also present the appropriate dependences $\epsilon'_{wct}(T)$ and $\epsilon''_{wct}(T)$ obtained for the unmodified wood.

Even rough estimation of the results reveals the opposite influence of the two applied technologies of wood modification on dielectric properties of wood substance. The differentiation between the dielectric permittivities of the composite and natural wood substance increases with increasing temperature.
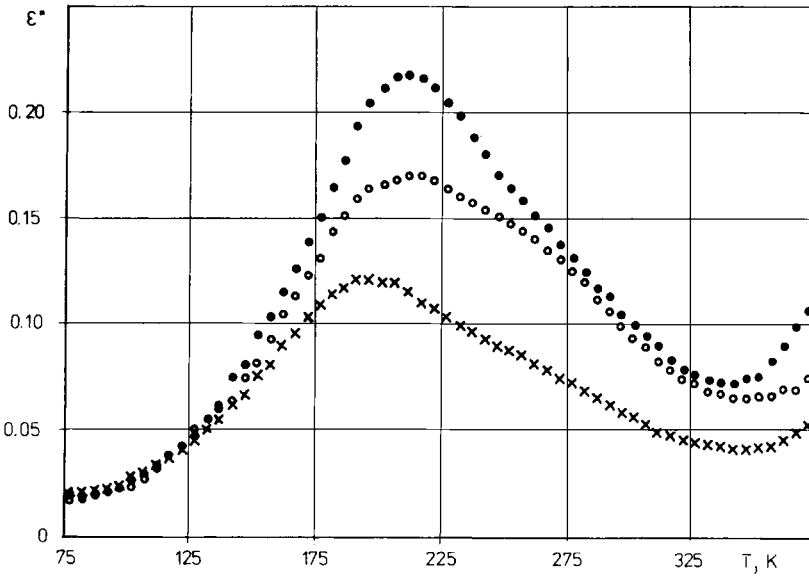
Fig. 4. Temperature dependences of dielectric loss in wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, calculated for the longitudinal direction.
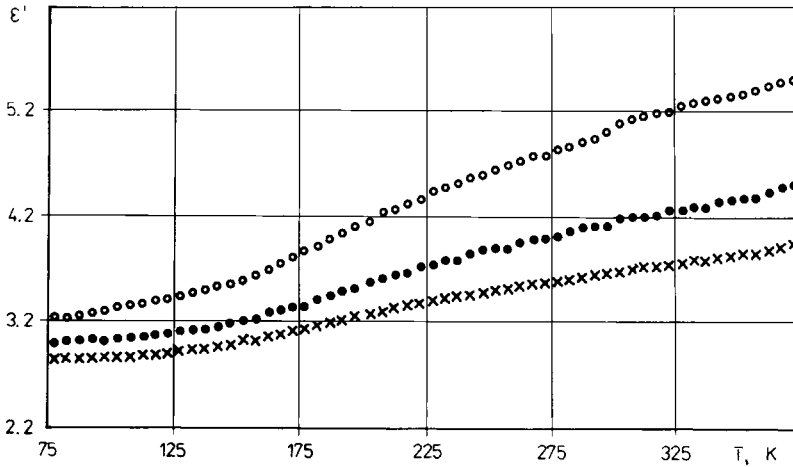

Fig. 5. Temperature dependences of dielectric permittivity of the wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, calculated for the tangential direction.

This differentiation is, for both directions considered, described by the changes in the dispersion degree of the dielectric permittivity, $\Delta\epsilon'$, defined, in the temperature range applied, as the difference in ϵ' values measured at 78 and 373 K. As follows from Figure 3 the dispersion degree of permittivity of wood substance along the fibers increases or decreases, depending on whether the wood has been modified in hydrophobic or hydrophilic conditions. These changes are accompanied by an increase or decrease in dielectric loss intensity.
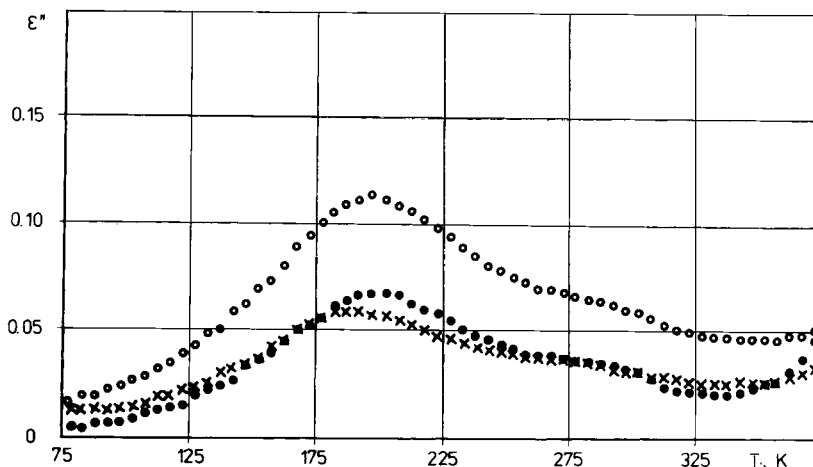
Fig. 6. Temperature dependences of dielectric loss in wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, calculated for the tangential direction.

The data presented suggest that the modification involves the changes in structure of amorphous or mesomorphous regions in wood, since the reorientation of polar functional groups in these regions are believed to be responsible for the β-relaxations appearing in wood.[11] The observed structural changes in polystyrene-modified wood with a hydrophobic or hydrophilic liquid applied result in a 30% increase or decrease in the number of polar groups per unit volume which are effectively involved in electric energy dissipation in longitudinal direction. The increase in dielectric absorption can be explained by the fact that the wood substance of the composite is transformed into a swollen state. Hypothetically this state results from localization of grafted or mechanically bound polystyrene in the amorphous regions in wood cell walls.[7] The postulated effect has been confirmed by a decrease in the activation energy of β-relaxation process in the composite $\Delta E = (36.5 \pm 1.0)$ kJ/mol, when compared to that for natural wood: $\Delta E = (39.8 \pm 1.2)$ kJ/mol. A reduction in dielectric loss in wood substance observed in the L direction of the composite obtained with the hydrophilic liquid may result from an increase in the degree of crystallinity of cellulose. The activation energy in this case $\Delta E = (34.0 \pm 1.3)$ kJ/mol, is lower than the activation energy of the corresponding processes in natural wood or polystyrene-modified wood with a hydrophobic heating medium. This result may be also explained on the basis of the structural changes on the submolecular level. An increase in the degree of ordering in mesomorphous cellulose regions eliminates the functional groups characterized by activation energies higher than those in amorphous regions, from the participation in β-relaxation phenomena.

Different behavior has been observed for the temperature dependences of wood substance dielectric permittivity calculated in the tangential direction. The degree of dispersion of permittivity as a consequence of wood modification in this case decreases independently of the kind of the heating medium used. For both composites in the T direction we noticed a reduced intensity of dielectric dissipative processes in wood substance. The activation energy of

β-relaxation processes forced by the electric field applied perpendicularly to the fibers is $\Delta E = (34.4 \pm 0.9)$ and (31.3 ± 0.7) kJ/mol for the composite obtained with the hydrophobic and hydrophilic liquid, respectively. These values are comparable with the corresponding value $\Delta E = (33.7 \pm 0.6)$ kJ/mol, calculated for natural wood.

To verify the above suggested structural changes in wood, a comparative analysis of IR spectra of both type composites as well as natural wood was performed with the use of standard apparatus. The lack of essential differences in IR spectra of the composites obtained with different methods proves that an increased or decreased participation of polar groups in dielectric relaxation phenomena is not a consequence of the changes in their number in wood but of the change in the conditions of reorientation. The structural changes may either release or freeze the part of degrees of freedom of the relaxing groups. This is fully consistent with the justification of the differences in dielectric properties of the composite and natural wood cell walls. The proposed changes in wood structure which are claimed to be the durable swelling of wood component in the case of modification in the hydrophobic bath, and an increase in crystallinity of cellulose of the wood modified in the hydrophilic bath, have been confirmed by X-ray diffraction patterns of the composite and unmodified wood (Fig. 7). The experimental method of determination of the degree of crystallinity of wood cellulose[13,14] is based on the relation between the intensity of main interference peak and the minimum
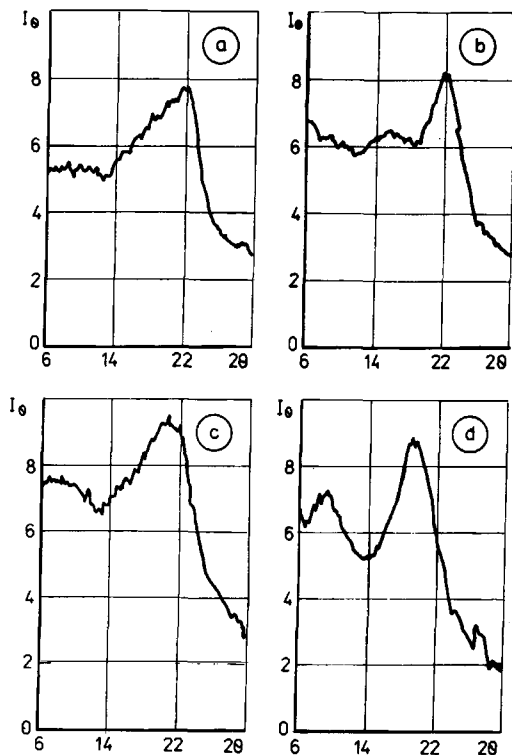

Fig. 7. X-ray diffraction patterns of polystyrene (d), natural wood (b), and polystyrene-modified wood in hydrophobic (a) and hydrophilic (c) heating medium.

intensity of diffraction pattern observed at an angle $2\theta = 18°$. However, the X-ray diffraction patterns of the composites studied are complex because they are the result of the overlapping of the individual patterns of wood and polystyrene. It is thus impossible to determine the degree of crystallinity of the wood component, because there is no procedure to eliminate the background so far. As a consequence, the diffraction patterns can be only analyzed by comparing the relative intensities of the main maxima obtained at an angle corresponding to that of natural wood main peak. This comparison has not only confirmed the postulated increase in the crystallinity of cellulose in the wood modified in hydrophilic bath, but also revealed a partial decrease in the crystallinity of cellulose in the wood modified in hydrophobic bath.

To explain the reasons for the submolecular level changes in wood structure, one should scrutinize technological conditions of the composite production. In our investigations, we subjected to modification, by both methods, wood of initial humidity different from zero (10%). We may assume that when thermal processing with the hydrophilic heating medium is applied, the escape of H_2O molecules from wood is an ineffective process because the chemical potentials of the water bound in the wood and that in the NaCl solution are equal. On the other hand, thermal processing of the humid wood at 385 K could hypothetically lead to the partial crystallization of the mesomorphous or amorphous cellulose. Both these processes could not accompany the modification of wood by polystyrene in an oil bath. In this case, the hydrophobic medium and high temperature favored desorption of the water bound in the wood. An accompanying decrease in degree of wood crystallinity may occur due to a decrease in the ordering degree in the mesomorphous cellulose regions as a result of that postulated, on the basis of dielectric measurements, permanent swelling of wood component.

Having considered all the results, we can say that a comparison of the appropriate dielectric parameters of the natural and polystyrene-modified wood cell walls may be a useful and sensitive indicator of qualitative and quantitative changes of wood substance structure. The parameters to be compared may be: the intensity levels of the maxima of dielectric loss in the β-relaxation region or the corresponding ranges of dielectric permittivity variation in the temperature range covering the β-relaxation region. There is, however, some difficulty in determination of the limits of the above-mentioned temperature range caused by partial overlapping of the energy absorption bonds corresponding to β- and α-relaxation in wood.[8,15]

Much more reliable criteria of the structural changes in wood substance would be obtained if we related them to the increment of the cell walls dielectric permittivity: $\delta\epsilon = \epsilon_0 - \epsilon_\infty$, where the limiting values ϵ_0 and ϵ_∞ are the permittivities at $\omega \to 0$ and $\omega \to \infty$, respectively. According to literature data on wood dielectric properties obtained from frequency measurements, the observed β-relaxation process is characterized by a symmetric distribution of relaxation times within a wide range of temperatures,[16,17] and by an insignificant temperature dependence of $\delta\epsilon$.[11] In this situation the approximate determination of the permittivity increment is also possible from temperature measurements of dielectric dispersion and absorption,[18] taking $\epsilon_0 \simeq \epsilon'$ $(T \to \infty)$ and $\epsilon_\infty \simeq \epsilon'(T \to 0)$.[5] Figures 8 and 9 present the so-called pseudo Cole–Cole plots, i.e., the dependences of dielectric loss factor $\epsilon''(T)$ as a

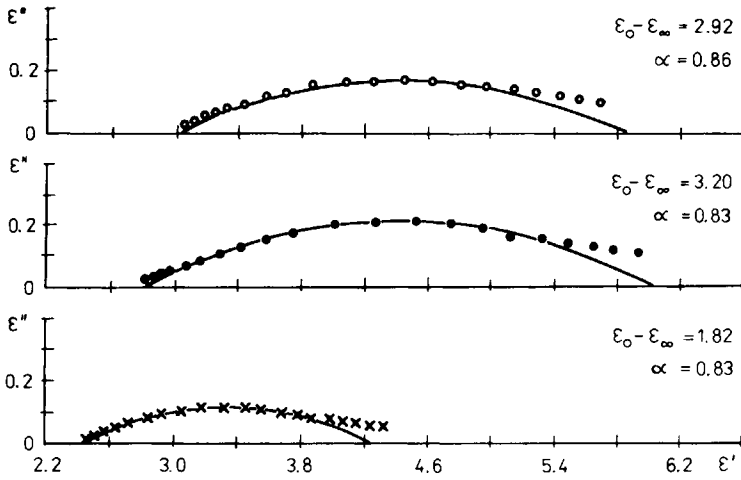Fig. 8. Pseudo Cole–Cole plots for wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, obtained for the longitudinal direction.

function of permittivity $\epsilon'(T)$, obtained for wood substance of natural and polystyrene-modified wood for the electric field frequency 400 Hz and orientation along the L and T directions, respectively. In order to enhance the characteristic features of these plots we applied a different scale for the ϵ''-axis. The relaxation time distribution parameters $\delta\epsilon$ and α were obtained graphically from the appropriate curves drawn in the proper scale of both coordinates.

The interrelations between the permittivity increments, $\delta\epsilon$, of wood substance of the natural and modified wood both in hydrophobic and hydrophilic baths confirm our above conclusions based on the analysis of dielectric
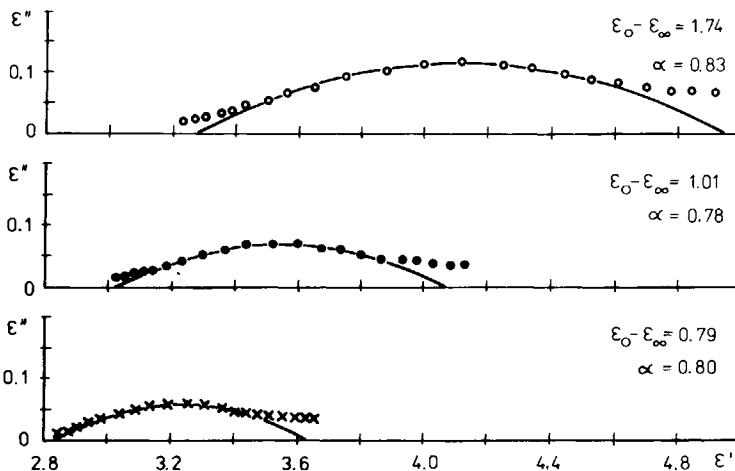

Fig. 9. Pseudo Cole–Cole plots for wood substance of the natural (○) and polystyrene-modified wood in hydrophobic (●) and hydrophilic (×) heating medium, obtained for the tangential direction.
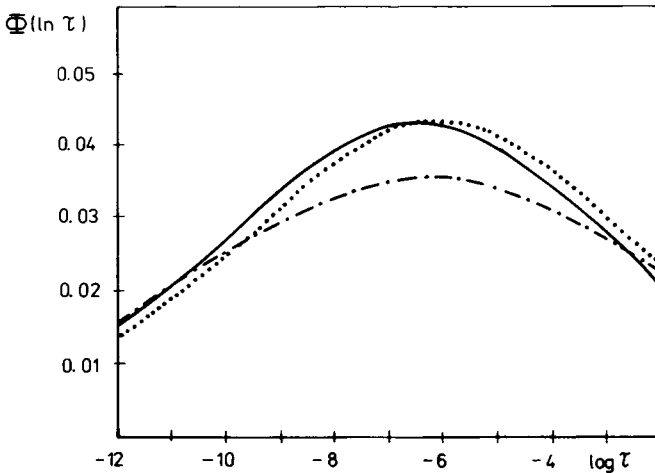
Fig. 10. The distribution function of relaxation times for wood substance of the natural (— · —) and modified wood in hydrophobic (· · ·) and hydrophilic (— — —) heating medium, taken for the electric force lines parallel to the fibers.

permittivity changes in the whole temperature range considered. They imply that in the temperature ranges of β-relaxation both methods of modification exert an opposite or a similar influence on dielectric properties of wood substance in the directions L and T, respectively. Thus, we may conclude that the correlation between the postulated structural changes in wood and the changes in the increment of permittivity of cell walls may provide the basis for the determination of the criteria of estimation of wood–polystyrene composites by the DETA method.

The obtained results provide additional data permitting the determination of the relaxation time distribution $\Phi(\ln \tau)$ described by the following function[18]:

$$\Phi(\ln \tau) = \frac{1}{2\pi} \frac{\sin \alpha \pi}{\cosh\left[(1 - \alpha) \ln(\tau/\tau_0)\right] - \cos \alpha \pi} \tag{13}$$

where τ_0 and α $(0 \leq \alpha \leq 1)$ are the generalized relaxation time and the parameter related to the width of that spectrum.

Figures 10 and 11 present the courses of relaxation time distribution functions for natural and modified wood substances obtained from relation (13) for temperature 293 K in the directions parallel and perpendicular to the fiber axes, respectively.

The lack of literature data on the shape of the relaxation time spectra for cell walls of natural wood prevents direct verification of the accuracy of the results. A comparison of the distribution curves with the appropriate curves obtained for bulk wood from the temperature measurements of mechanical[19] and frequency measurements of dielectric relaxations,[17] points to the same 10^{-7} s value of the most probable β-relaxation time at 293 K. For wood substances of polystyrene-modified wood in hydrophobic and hydrophilic heating medium, we observed a slight shift in the τ_0 parameter towards longer and shorter relaxation times, respectively. However, the analysis of the ob-
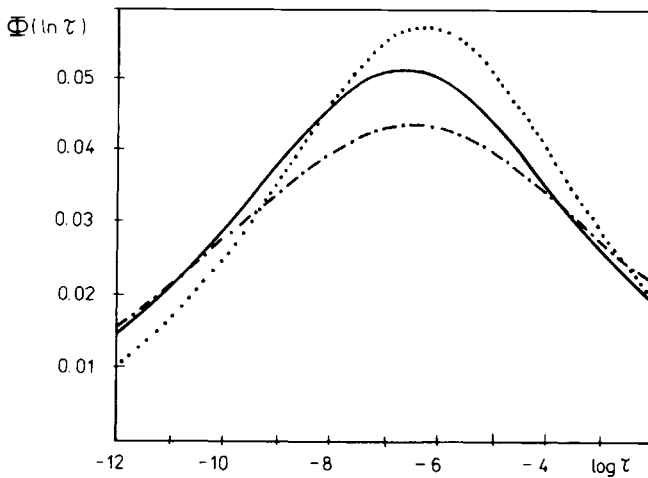
Fig. 11. The distribution function of relaxation times for wood substance of the natural (——·——) and modified wood in hydrophobic (· · ·) and hydrophilic (————) heating medium, taken for the electric force lines perpendicular to the fibers.

served effect requires further studies to identify the functional groups in the wood component, which could be responsible for the energy loss in the analyzed range of relaxation times spectrum.[20]

CONCLUSIONS

On the basis of a layered model the temperature dependences of the dielectric permittivity and loss factor in longitudinal and tangential directions were calculated and compared for the cell walls of natural and polystyrene-modified wood both in hydrophilic and hydrophobic heating medium.

The observed changes in wood substance structure can be explained by the increase in degree of crystallinity of cellulose of the wood modified in the hydrophilic bath and by the permanent swelling of wood amorphous components accompanying the modification in the hydrophobic bath.

The localization of the detected structure effects in disordered regions of cell walls was confirmed by the changes in activation energies and in dielectric absorption intensities relating to the β-relaxation processes.

The correlation between the permittivity increments $\delta\epsilon$ and structural changes of wood cell walls was observed.

The distribution functions of relaxation times for natural and modified wood substances were determined.

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