Dielectric Behavior of Wood–Polystyrene Composite

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Synopsis

The dielectric phenomena for alder wood natural and modified with polystyrene were studied. Temperature dependences of the complex permittivity components of these materials were obtained for the temperature interval from 100 to 450 K at the frequencies of measuring electric field of 420 Hz, 2 kHz, and 10 kHz. The changes in structure of wood cell walls were found, detected as an increase in number of polar functional groups taking part in the relaxation processes and as a partial freezing of conformational degrees of freedom of macromolecule fragments carrying these groups. The origin of the structural changes can be the efect of wood substance swelling caused by polystyrene, which penetrates the composite cell walls.

INTRODUCTION

In the studies of wood modification with polymers the important problem, especially with regard to dimensional stabilization, is the penetration of the cell walls by a monomer introduced. This problem is not yet fully elucidated. It has been assumed that unpolar vinyl monomers applied presently in modification of wood on industrial scale[1,2] do not penetrate dry wood and, only provided that the water swelling the wood is gradually replaced with unpolar monomer, it can be localized in cell walls.[3]

As follows from the results of solvent extraction analyses and from the data indicating a 10–15% decrease in contractility of wood modified with vinyl polymers, the water is at least partly replaced by monomer also under the classical conditions of modification of wood with different from zero initial moisture.[4] The investigation methods applied so far did not allow the unequivocal verification of this thesis. In the work presented attempts were undertaken to verify this question with dielectric spectroscopy method, which is of particular use in the studies of multicomponent systems.[5]

EXPERIMENTAL

Dielectric spectroscopy method offers itself for determination of dependences of components of complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) on temperature and frequencies of measuring electric field in a wide range of their variability. The measurements of $\epsilon'(\omega,T)$ and $\epsilon''(\omega,T)$ of the natural and polymer-modified wood were performed with a dielectric spectrometer built on the basis of RLC bridge adapted for measurements of capacity and tangent of dielectric loss angle within the frequency range from 20 Hz to 20 kHz. The spectrometer was equipped with a chamber allowing measurements in nitrogen atmosphere for temperatures varying from 100 to 450 K.[6] A standard capacitor placed in the working space of the chamber was adjusted for the

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measurements of the samples shaped as circular disks of a diameter 20 mm and a thickness of 1.5 mm.

The studies were performed on natural wood of alder with a density of 540 kg/m^3 and the same wood modified with polystyrene.

In order to realize the aim of the work, a composite obtained by thermal-catalytic polymerization applied in industrial production of wood–plastic composite[7] was used during investigations as test material. The samples to be modified in the form of beams of 50 × 50 × 200 mm dimensions and moisture of 11% were placed in an autoclave and kept there for 1 h under pressure of 0.09 MPa. Then the solution of the monomer with initiators of polymerization of the following content: styrene (98.5%), benzoyl peroxide (0.5%), cumene hydroperoxide (0.5%), and menthapinene hydroperoxide (0.5%) were introduced into the chamber of the autoclave. Next, having introduced the solution, the pressure was increased to its atmospheric value, and the wood was saturated for 24 h. Before carrying out the polymerization, the excess of monomer–initiator solution was removed from the autoclave. Polymerization ran in an oil bath at a temperature of 363 K for 2 h and then at a temperature of 383 K for 4 h. Afterwards the oil bath the obtained composite was seasoned for 2 months in a laboratory. Test samples were prepared to ensure the accordance between the direction of the measuring electric field and the wood fibers.

RESULTS AND DISCUSSION

In this work the dielectric constant ϵ' and the loss factor ϵ'' of oven-dried natural and polymer-modified wood were measured for temperatures ranging from 100 to 450 K at the frequencies of measuring electric field of 420 Hz, 2 kHz, and 10 kHz. The results of measurements for oven-dried alder wood are presented in Figures 1 and 2.

In the low-temperature dependences of $\epsilon''(T)$ the maxima are observed which reflect the occurrence of relaxation phenomena ascribed to reorientations of the polar functional groups localized in disordered regions of cell walls.[8,9] The maxima in $\epsilon''(T)$ are accompanied by a dispersion of ϵ'(T), which is typical for relaxation phenomena.

Apart from the low-temperature maxima an increase in the dielectric loss factor is observed in high temperatures. The shifts of the high-temperature branches of $\epsilon''(T)$ curves appearing with the change in frequency

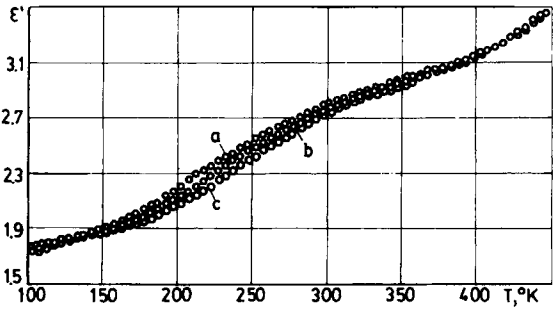

Fig. 1. Temperature dependence of ϵ' at various frequencies for oven-dried wood in longitudinal direction: (a) 420 Hz; (b) 2 kHz; (c) 10 kHz.

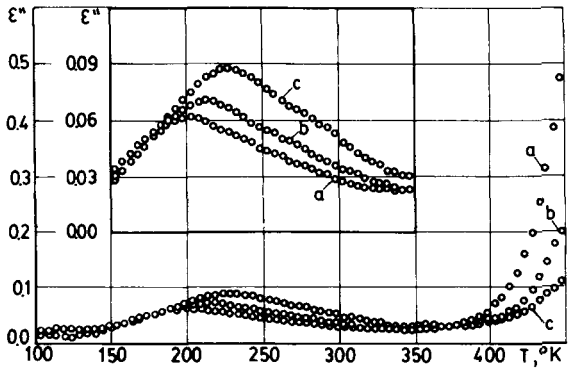

Fig. 2. Temperature dependence of ϵ'' at various frequencies for oven-dried wood in longitudinal direction: (a) 420 Hz; (b) 2 kHz; (c) 10 kHz.

of the electric field may indicate the occurrence of high-temperature dielectric relaxation processes corresponding to the earlier observed processes of mechanical relaxation.[10] To analyze the origin of these processes, we should take into account the fact that at a temperature $T_g \simeq 400$ K the glass transition of the amorphous phase of high-molecular components of wood begins. It is detectable by the quasistatic DTA method.[11]

According to the WLF equation[12] we assume the high-temperature relaxation time to be determined by the formula[13]:

$$\tau = \tau_0 \exp\left[\frac{U^*}{R(T - T_g + T_0)}\right]$$

where $U^* = 17.24$ kJ/mol and $T_0 = 51.6$ K are the empirical values approximately the same for all amorphous polymers. From the condition for the maximum $\omega\tau(T_{max}) = 1$ and from the known frequency shift of $\epsilon''(T)$ curves the temperature of the high-temperature peak in dielectric loss factor in alder wood was found to be at the frequency 420 Hz at 500 K. This result is consistent with the data from mechanical studies.[10]

Figures 3 and 4 present the measured dependences $\epsilon'(T)$ and $\epsilon''(T)$ obtained for oven-dried wood–polystyrene composite. A comparison between the results obtained for the natural wood and the composite allows us to analyze the possible changes in structure of wood due to its modification with polystyrene. Hypothetically such modification can lead to localization of polystyrene in empty spaces of wood or to bond styrene with the components of wood cell walls causing the formation of copolymer.

According to the additivity principle,[14] dielectric properties of homopolymers should be the resultant of the properties of individual components of the mixture and should be determined by their relative contributions in a unit of volume of the composite. As follows from the literature on dielectric properties of pure polystyrene[15] its value of ϵ'_p is approximately constant at low temperatures and equal to 2.52, and the values of dielectric loss factor are very small (ca. 10^{-4}) by about 1000 lower than for the natural wood (ca. 10^{-1}). As a consequence for a homopolymer wood–polystyrene composite,

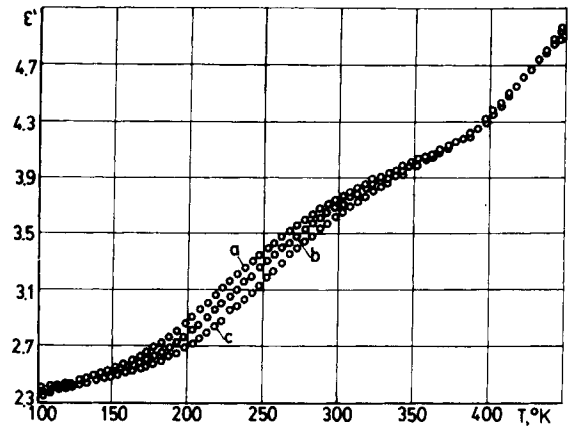

Fig. 3. Temperature dependence of ϵ' at various frequencies for oven-dried wood–polystyrene composite in longitudinal direction: (a) 420 Hz; (b) 2 kHz; (c) 10 kHz.

the observed dependence $\epsilon''(T)$ should not differ from that of unmodified wood while the course of $\epsilon'(T)$ dependence for a homopolymer should be a parallel shift of the curve for the natural wood. However, the experimental results prove that the expected course of $\epsilon'(T)$ is limited to temperatures not exceeding 200 K and differs from the expected one for the temperatures above 200 K. Also in the latter range the dielectric loss factor for the composite is increased by 50% when compared to that for unmodified wood. The data obtained indicate that during the modification process the structure of the amorphous regions in wood cell walls changes. The character of these changes including, among others, an increase by about 50% in the number of polar groups per unit volume, which take part in the relaxation process, can be explained by the fact that the wood substance of the composite is transformed into a swollen state. This state results from localization of grafted or mechanically bound polystyrene in the amorphous regions in wood cell walls.

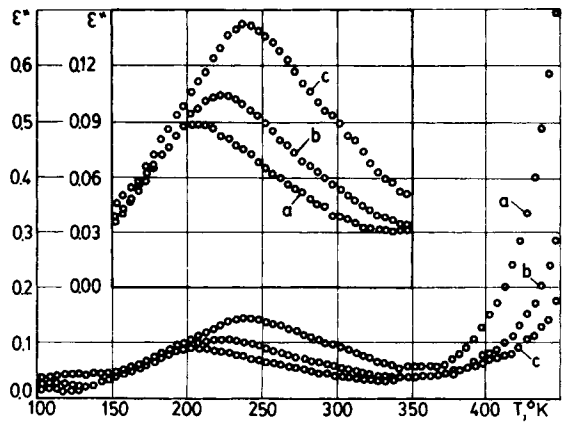

Fig. 4. Temperature dependence of ϵ'' at various frequencies for oven-dried wood–polystyrene composite in longitudinal direction: (a) 420 Hz; (b) 2 kHz; (c) 10 kHz.

Additional observation supporting the possibility of penetration of cell walls by styrene are the differences appearing in the position of low-temperature maximum in dielectric loss factor for the natural and modified wood. In the case of the symmetric distribution function of relaxation times characteristic of wood,[9] the condition for the maximum in $\epsilon''(T)$ determined at a constant frequency becomes

$$\frac{h\omega}{kT_m} \exp\left(\frac{\Delta H - T_m \Delta S}{RT_m}\right) = 1$$

where h, k, and R are the Planck, Boltzmann, and gas constants, respectively, ω is the angular frequency of the applied electric field, T_m is the absolute temperature of the low-temperature loss peak, and ΔH and ΔS are the enthalpy and entropy of activation of relaxation process.

The values of enthalpy and entropy of activation for the natural and modified wood, which have been calculated on the grounds of experimental results, are $\Delta H_w = 44$ kJ/mol, $\Delta S_w = 44$ J/K mol and $\Delta H_c = 41$ kJ/mol, $\Delta S_c = 20$ J/K mol. A decrease in enthalpy of activation for the wood–polystyrene composite indicates that the structure becomes loose, and confirms the postulated effect of swelling of wood substance due to styrene penetrating it. A considerably greater decrease in entropy of activation proves that in modified wood the degree of dipole ordering by external electric field is significantly lowered. This effect may be originate from freezing a part of conformational degrees of freedom of fragments of macromolecules carrying polar functional groups, caused by the presence of network or filling.

Quantitative analysis of the content of styrene grafted in cell walls can be performed only within a limited range as the numerical data on the influence of swelling alone on the dielectric relaxation processes in wood are still lacking. Comparing the changes in the curves of $\epsilon'(T)$ and $\epsilon''(T)$ due to wood modification with polystyrene with those due to wood swelling with water,[16] we found that the amount of styrene penetrating cell walls of the composite was not greater than 0.06 kg/kg wood.

Detailed analysis of the changes in the high-temperature range in the dependences $\epsilon'(T)$ and $\epsilon''(T)$ for wood–polystyrene composite requires additional experimental studies to be performed.

CONCLUSIONS

On the grounds of a comparison between the temperature dependences of the complex permittivity components obtained for the natural and polystyrene-modified wood, the possibility was confirmed that the cell walls of the composite are penetrated by polystyrene.

The observed increase in number of polar groups taking part in the relaxation processes can be explained by the possibility of durable swelling of wood substance.

The changes in entropy of activation of the low-temperature relaxation process indicate the occurrence of freezing of a part of conformational de-

grees of freedom of macromolecule fragments in result of the presence of grafted or mechanically bound polystyrene in their environment.

The weight content of the modificator in the cell walls is estimated to be about 6%.

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