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Electromagnetic Radiation Shielding by Composites of Conducting Polymers and Wood

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ABSTRACT: Polyaniline or polypyrrole composites with fir or oak wood have been prepared by *in situ* polymerization of the corresponding monomers in an aqueous suspension of wood sawdust. The percolation threshold of compressed coated particles is located below 5 wt % of the conducting component and, above this limit, the conductivity of most composites was higher than 10^{-3} S cm⁻¹. The conductivity of composites containing *ca* 30 wt % of conducting polymer was of the order of 10^{-1} S cm⁻¹, an order of magnitude lower than that of the corresponding homopolymers, polyaniline and polypyrrole. The conductivity stability has been tested at 175°C. The polypyrrole-based composites generally lasted for a longer time than pyrrole homopolymers, also on account of the improved mechanical integrity of the samples provided by the presence of wood.

The reverse order was found with polyaniline composites. The dielectric properties of the composites were determined in the range of 100 MHz–3 GHz, indicating that thick layers of composite material, \sim 100 mm, are needed for the screening of the electromagnetic radiation below –10 dB level in this frequency range. Nevertheless, considering the potential production cost of composites and their low weight, such composite materials could be of practical interest in the shielding of electromagnetic interference. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 807–814, 2005

Key words: polyaniline; polypyrrole; fir; oak; wood; composites; conducting polymers; conductivity ageing; electromagnetic radiation; radiation shielding

INTRODUCTION

Sawdust is a common waste product in the processing of wood. This article addresses a feasible way to convert the wood sawdust into a potentially useful material by the surface modification of wood particles and the fibers constituting them with conducting polymers, like polyaniline (PANI) and polypyrrole (PPy). The surface polymerization of aniline^{1,2} and pyrrole on the wood substrate has been used in the present study.

In relation to wood, conducting polymers have been investigated in combination with its components, lignin or sulfonated lignin, and cellulose.^{3–7} Lignin research served especially in the design of water-soluble complexes comprising PANI that enable the processing of this conducting polymer in a colloidal form. Composites of PANI, PPy, and crosslinked cellulose with a conductivity level of 10^{-4} – 10^{-2} S cm⁻¹ have also been prepared.^{8,9} So far, only a single paper reporting the preparation of PANI–wood composites has appeared in the literature.¹⁰ The present study

extends the studies to the optimization of PANI–wood composite preparation, includes the PPy deposition for comparison, and introduces the assessment of the thermal stability of conductivity.

Conducting polymers can serve as an adhesive for wood sawdust particles, and composites comprising both components could constitute useful construction materials. In most applications, however, PANI and PPy are likely to be regarded as the value-added components, and the wood as a filler that improves the mechanical integrity of a conducting polymer. Conducting composites of this type could be used as antistatic boards, heating elements operating at temperatures slightly above ambient, or shielding materials for various regions of frequencies of electromagnetic radiation.^{11,12} A feasibility test of the shielding efficiency in the MHz–GHz frequency range is reported in this study.

EXPERIMENTAL

Materials

Dry wood from fir (*Picea abies*) and oak (*Quercus robur*) trees grown in the Czech Republic was used as a starting material. The wooden sawdust was produced with a circular saw, 30 cm in diameter and 1.5

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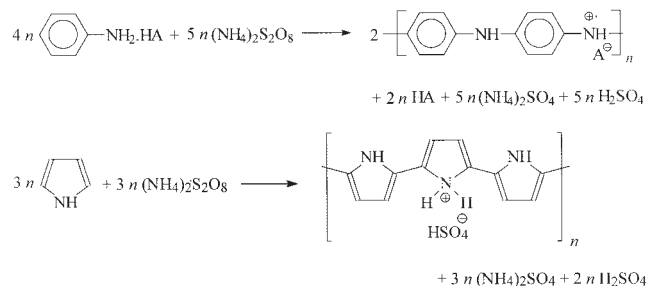


Figure 1 The synthesis of polyaniline (top) and polypyrrole (bottom) by the oxidation of the corresponding monomers with ammonium peroxydisulfate. HA is an arbitrary acid, in the present case a phosphoric acid.

mm thick, having 8 mm cutting edges rotating at 1400 rpm, and sieved with a $1 \times 1 \text{ mm}^2$ mesh.

Aniline was oxidized to PANI in dilute phosphoric acid with ammonium peroxydisulfate. Aniline was dissolved in the phosphoric acid, and wood sawdust was added, followed by the solution of ammonium peroxydisulfate. Typically, 5 g of wood sawdust was dispersed in 100 mL of reaction mixture. The concentration of aniline was 0.2, 0.1, 0.05, or 0.025 M, the phosphoric acid/aniline molar ratio was 1. The ammonium peroxydisulfate/aniline molar ratio was 1.25, corresponding to the expected stoichiometry (Fig. 1). The same reaction conditions have been used for the oxidation of pyrrole to PPy, only the monomer/oxidant ratio was then set to unity (Fig. 1). The reaction mixture was left at rest for 24 h, with occasional brief stirring. The wood sawdust coated with conducting polymer was collected on a filter, rinsed with a copious amount of acetone, and dried. The fraction of conducting polymer in the composite was calculated from the increase in mass.

Characterization

Wood sawdust was compressed in a manual hydraulic press at 700 MPa into pellets, 13 mm in diameter and $\sim 1 \text{ mm}$ thick, and the conductivity was measured by the four-point method using a current source Keithley 238, a scanner Keithley 706 with switching cards, and a Solartron-Schlumberger 7081 Precision Voltmeter. To test the stability of conductivity at an elevated temperature, *viz.* 175°C , the samples were placed in a Heraeus-Vötsch VMT 07/35 chamber operating with a temperature stability of $\pm 1^\circ\text{C}$. The atmosphere in the chamber had a low humidity. The temperature of the pellets, recorded with a thermocouple and a digital multimeter Keithley 195A DMM, was checked before and after each conductivity reading. The densities of the samples were determined by the Archimedes method by weighing the pellets in the air and immersed in decane.

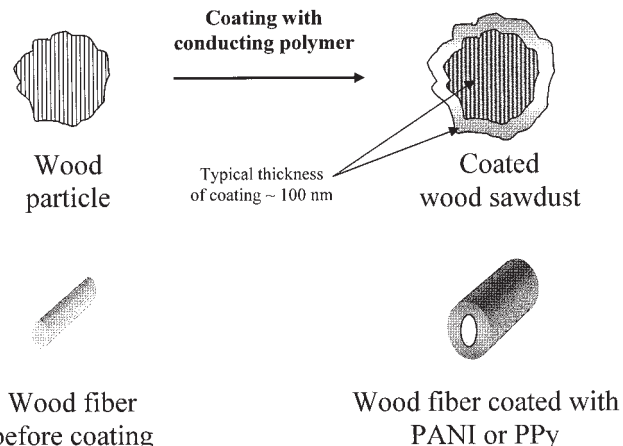


Figure 2 The surface of any substrate, for example, wood sawdust particle (top) or its individual fibers (bottom) which are in contact with the reaction mixture used for the preparation of polyaniline or polypyrrole, becomes coated with a thin film of conducting polymer.

The frequency dependence of the complex permittivity of composites was determined with an RF Impedance/Material Analyser (Agilent E4991A) in the frequency range 10 MHz–3 GHz at room temperature.

RESULTS AND DISCUSSION

Composite preparation

Wood is a complex natural material composed of parts that are easily hydrolyzed in the acidic media and are oxidized in the presence of strong oxidants. We have therefore carried out the polymerization of aniline and pyrrole under mild conditions. For this reason, we have used phosphoric acid rather than sulfuric acid.

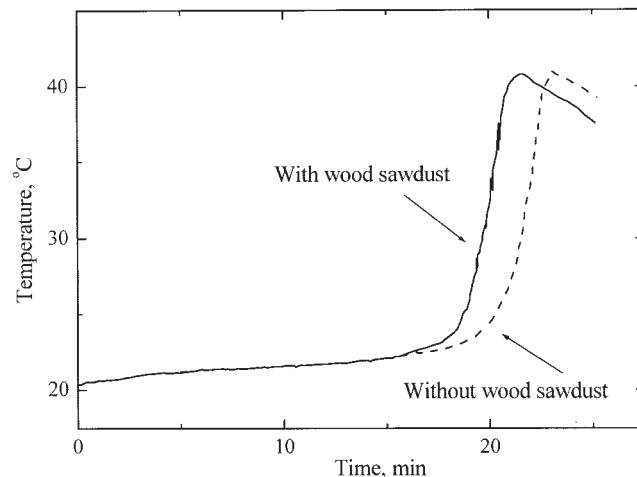


Figure 3 The course of the exothermic aniline polymerization: 0.2 M aniline in 0.2 M phosphoric acid was oxidized with 0.25 M ammonium peroxydisulfate in the absence and presence of 50 g l^{-1} of fir wood sawdust.

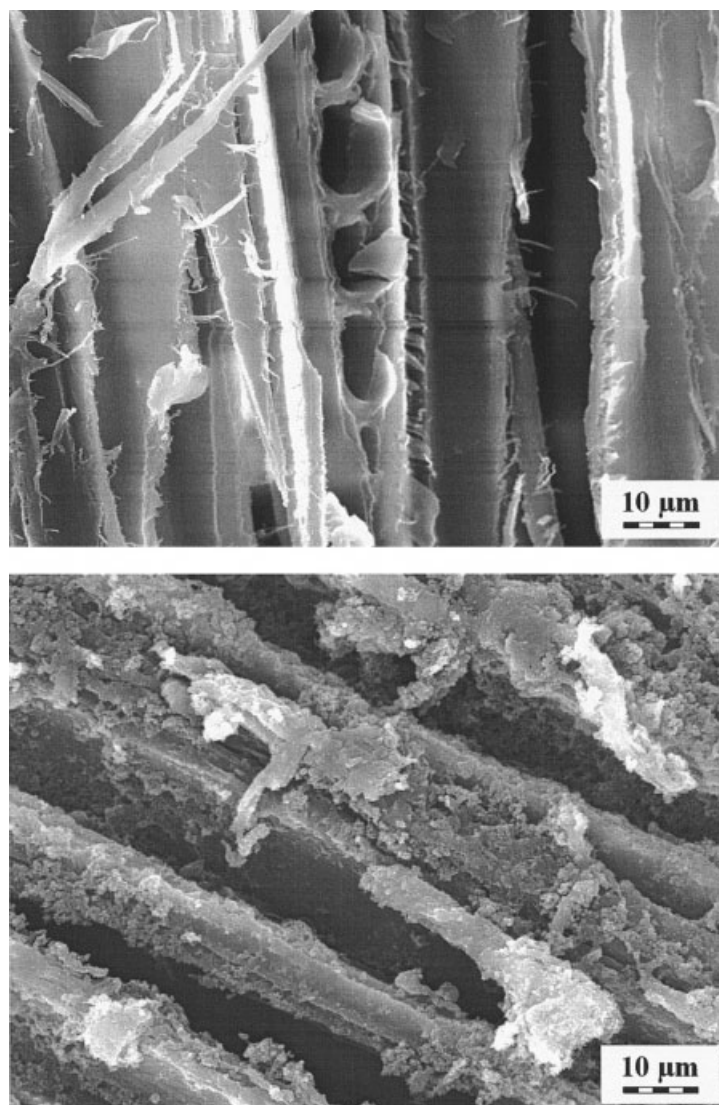


Figure 4 SEM micrographs of uncoated (top) and PANI-coated (bottom) fir sawdust.

The degree of hydrolysis of cellulose and related compounds in this strong mineral acid is minimal.¹³

Wood particles become yellow after dispersion in the solution of aniline. The coloration reflects the formation of Schiff base by the reaction of aniline with conjugated aldehyde groups present in the lignin that constitutes, along with cellulose, the bulk of the wood mass. The fraction of aniline consumed in this reaction, however, is extremely low and most of the aniline is available for the subsequent polymerization.¹⁰ The reaction mixture soon becomes blue, and then green, as PANI is produced. In the case of pyrrole, no distinct coloration appears after mixing the reactants, and the mixture gradually becomes dark brown as the polymerization proceeds. The conversion of both monomers to polymer is practically quantitative.¹⁴

The preparation of composites comprising wood and conducting polymer is based on the concept of the *surface polymerization* of aniline^{1,2,15,16} and pyrrole¹⁷ on various substrates. Virtually any surface in contact

with the aqueous mixture used for the oxidation of these monomers becomes coated with a thin film of conducting polymer (Fig. 2). This process can be regarded as a template polymerization at the solid-liquid interface.¹⁵ The thickness of the coating is typically 50–400 nm, depending on reaction conditions.^{10,18} It should be stressed that, during this process, the film of conducting polymer *grows* at the surface as the polymerization proceeds.¹⁹ It is thus not formed as a result of a mere adsorption of the polymer produced in the surrounding liquid medium at the immersed surfaces.

The exothermic oxidative polymerization of aniline can conveniently be followed by monitoring the temperature (Fig. 3). After an induction period, the temperature increases as the polymerization proceeds. It is a typical feature of the surface polymerization that the induction period becomes shorter when a substrate with a large surface is present in the reaction mixture. This is also the case with wood sawdust

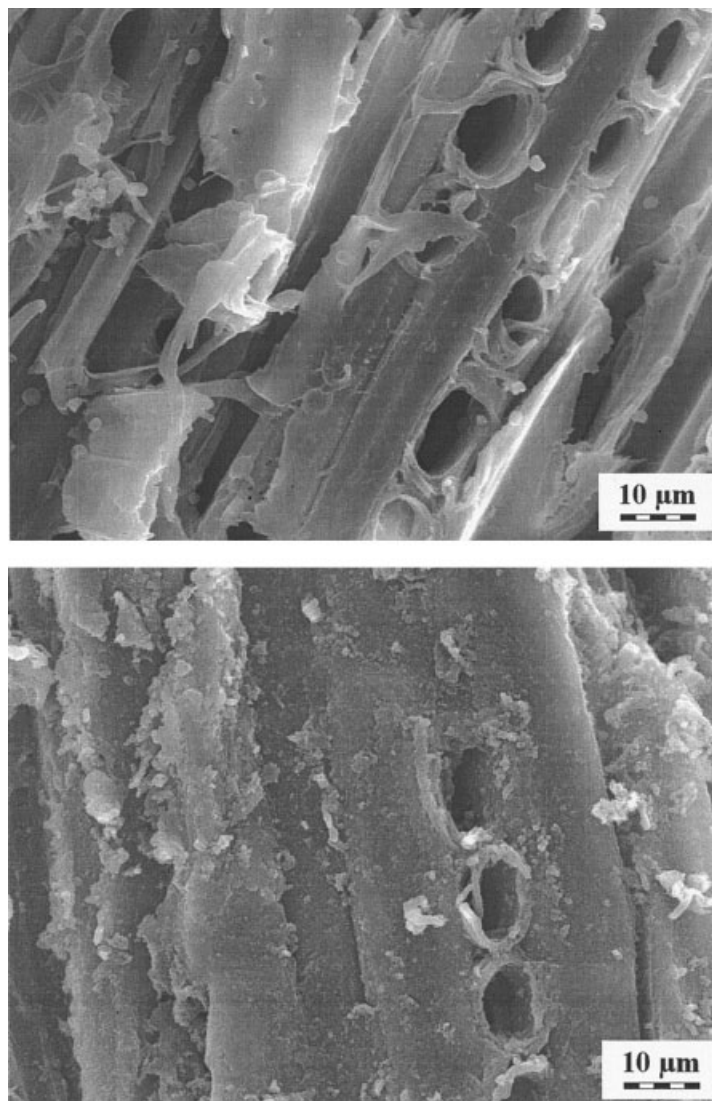


Figure 5 SEM micrographs of uncoated (top) and PANI-coated (bottom) oak sawdust.

(Fig. 3). At 0.2 M aniline, the polymerization was completed in *ca* 20 min; at lower monomer concentrations the reaction time extended to several hours.

The morphology of sawdust before and after coating with PANI is illustrated in Figures 4 and 5. The uniform coating with conducting polymer film produced by surface polymerization is very visible. The coating of fir wood has always been found to be uniform by visual inspection, while coating defects have been suspected in the case of oak wood at low PANI or PPy contents. Some PANI precipitate produced by the precipitation polymerization of aniline in the liquid phase adhered to the PANI-coated fibers (Figs. 4 and 5) when the polymerization proceeded at a high (0.2 M) concentration of aniline. The macroscopic particles of sawdust are not coated only at the surface but the fibers that constitute their body have also been coated (Fig. 2). This was proved by the following experiment: when a block of wood was immersed into the reaction mixture, a green 2 mm

deep layer of PANI-coated wood was clearly visible at the cross section of the cut block. The wood sawdust particles are all smaller than 1 mm. This means that the reaction mixture diffuses into particles and all fibers inside the particles become coated with conducting polymer.

Conductivity and its thermal stability

The conductivity of PANI-wood composites increases with increasing content of conducting polymer (Fig. 6, Table I). Typical percolation behavior is observed with all composites. The conductivity suddenly increases when the percolation threshold at a certain fraction of the conducting component has been reached and continuous conducting pathways have been produced in the material. A system composed of a mixture of conducting and non-conducting spheres, uniform in size, is predicted to have a percolation limit at 16–17 vol % of conducting spheres.²⁰ For non-spherical particles

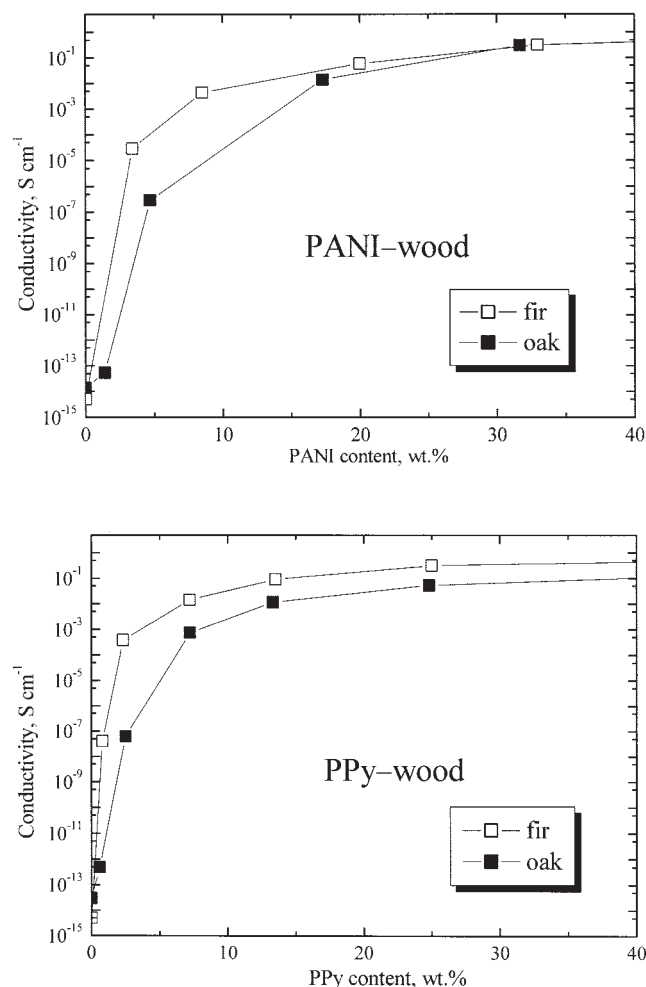


Figure 6 Conductivity of polyaniline (top) and polypyrrole (bottom) composites with wood sawdust.

coated on the surface with a conducting polymer, the percolation threshold is expected to be located at a lower volume fraction of the conducting component. For composites containing conducting particles with a high aspect ratio, the percolation limit drops below

TABLE I
Conductivity and Density of Wood Sawdust, Conducting Polymers, and their Composites^a at 20 °C

	Conductivity (S cm ⁻¹)	Density (g cm ⁻³)
Fir wood	5.8×10^{-15}	1.28
Oak wood	1.4×10^{-14}	1.30
Polyaniline (33 wt %) fir wood	0.32	1.34
Polyaniline (33 wt %) oak wood	0.31	1.32
Polypyrrole (25 wt %) fir wood	0.32	1.31
Polypyrrole (25 wt %) oak wood	0.054	1.35
Polyaniline phosphate	3.4	1.40
Pyrrole phosphate	1.4	1.44

^a Composites prepared at 0.2 M aniline concentration, *i.e.*, with a maximum content of conducting polymer in the series of investigated samples.

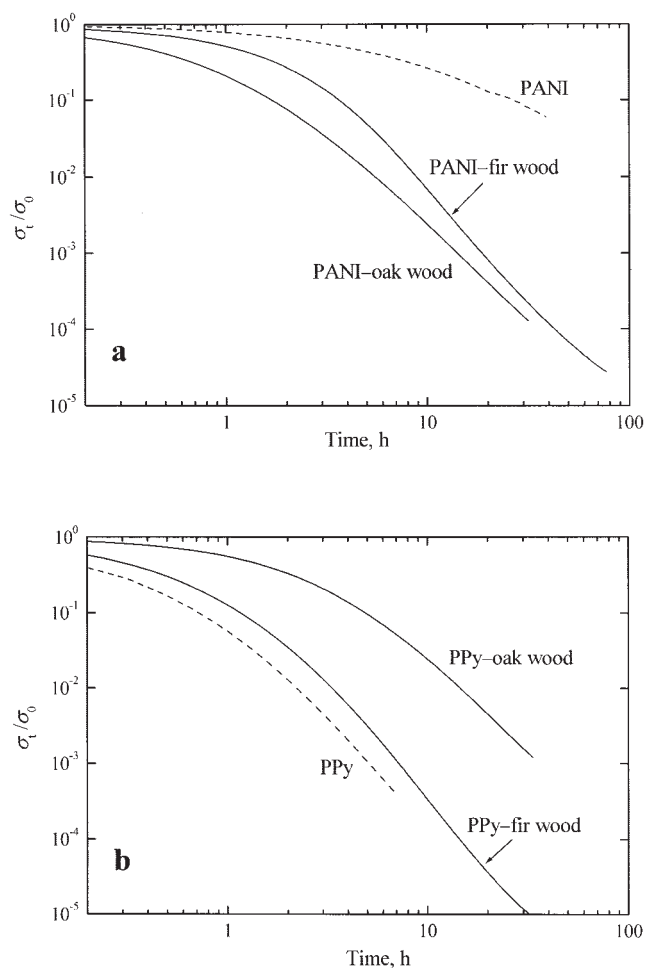


Figure 7 Conductivity ageing of (a) polyaniline-wood and (b) polypyrrole-wood composites at 175°C and the comparison with the parent homopolymers. Composites were prepared at 0.2 M aniline concentration.

5 vol % of the conducting component.^{21,22} The non-conducting particles coated with conducting polymers also have a lower percolation limit²³⁻²⁵ compared with composites in which compact conducting particles are dispersed in the non-conducting matrix, where the formation of conducting pathways is much more difficult. In the case of coated sawdust, both of these effects are combined, and the observation of a percolation threshold below 5 wt % of conducting polymer is thus not surprising.

The volume and weight fractions of the conducting polymer in the composites are close to each other, because of the similar densities of the components (Table I). This means that the conductivity of composites containing more than 5 wt % of conducting polymer is usually of the order of at least 10^{-3} S cm⁻¹ and approaches the conductivity of the constituent homopolymer, 10^0 S cm⁻¹, as the content of the conducting polymer increases (Fig. 6, Table I).

The conductivity of PANI-fir wood composites is always higher and the percolation threshold lower

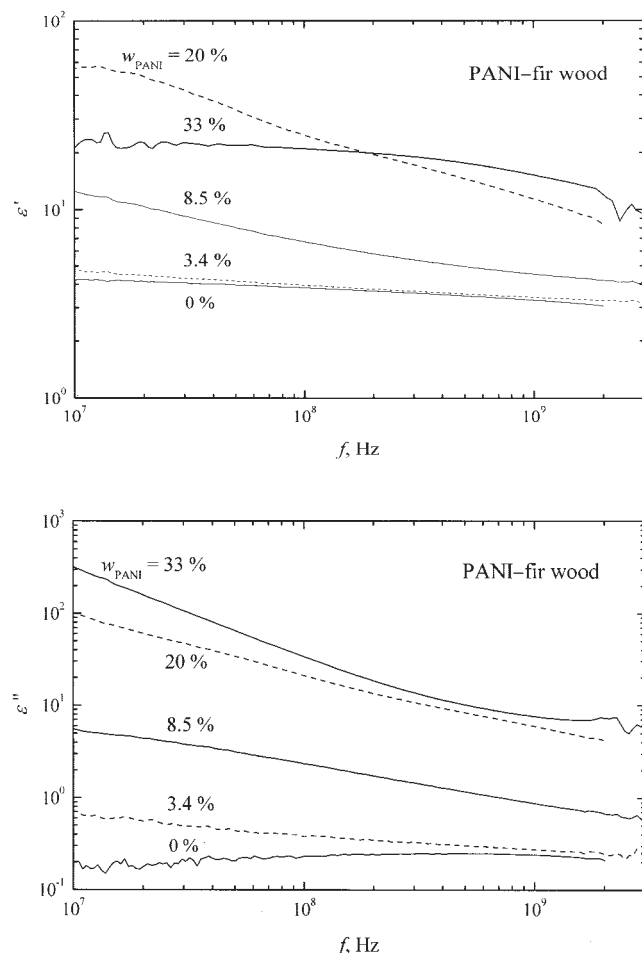


Figure 8 Frequency dependences of the real (top) and imaginary (bottom) parts of the dielectric permittivity, ϵ' and ϵ'' , of polyaniline-wood composites containing various fractions of the conducting polymer, w_{PANI} .

than in the case of PANI-coated oak wood. This is a result of the higher porosity of fir wood and the more uniform distribution of conducting polymer within the composite.

The thermal stability of conductivity has been tested at 175°C. At this temperature, the ageing was fast enough to be conveniently followed, and the pyrolysis of wood mass, which takes place above 200°C, was prevented. In potential applications, however, the working temperature is expected to be much lower. The conductivity stability of PANI is generally better than that of PPy,²⁶ as is observed also in the present study (Fig. 7). In the case of surface-modified wood sawdust, the stability is also affected by the nature of the wood component. For PANI, the stability of the conductive polymer alone is superior to PANI-wood composites, both types of composite being in this respect comparable in their performance (Fig. 7a). With PPy, on the contrary, the composites have better electrical stability than the parent homopolymer (Fig. 7b).

The ageing experiment was terminated after reliable electrical contact with the pellets could not be main-

tained any longer, for example, due to the appearance of cracks, deformation, or shrinkage, rather than because of complete loss of the material conductivity. In this respect, the PPy-based composites lasted in repeated experiments for a much longer time, their mechanical integrity and material properties obviously being improved by the presence of wood in comparison with the PPy homopolymer alone.

Electromagnetic radiation shielding

The dielectric properties of composites are determined mainly by the presence of conducting polymer at the surface of wood fibers and in that way by the structure of particles. The permittivity of uncoated wood is low (Fig. 8). Both the real and imaginary parts of the complex permittivity ϵ^* , ϵ' , and ϵ'' increase as the content of PANI or PPy increases (Fig. 8). The composites based on fir wood have generally a higher

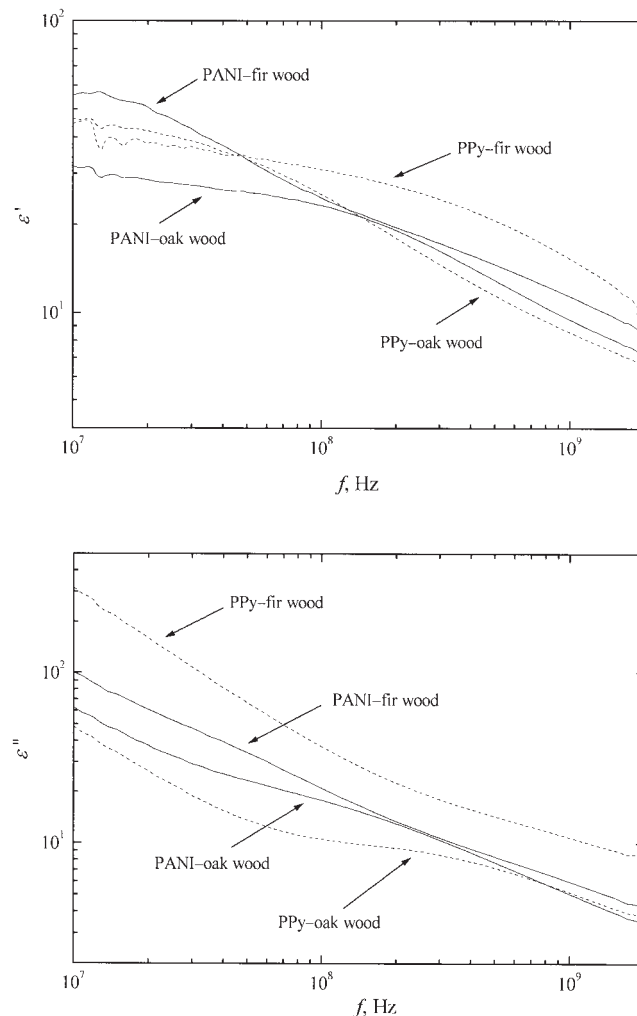


Figure 9 Frequency dependences of the real and imaginary parts of the dielectric permittivity, ϵ' and ϵ'' , of different wood composites containing 20 wt % of conducting polymers.

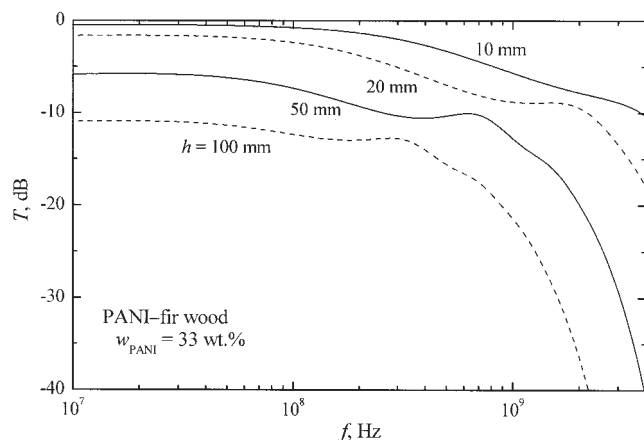


Figure 10 Calculated frequency dependences of the transmittance T for layers of a composite of polyaniline (33 wt %)-fir sawdust having the thickness h .

permittivity; the frequency dispersion depends on the type of composite (Fig. 9).

The shielding efficiency can be improved by control of the frequency dispersion of complex permittivity ϵ^* . Based on the experimental frequency dependence of permittivity, the transmittance coefficient T of the material can be calculated by using the Fresnel formulae for the reflection and transmittance of electromagnetic radiation on the border of two dielectric media of different thicknesses located in free space.²⁷

Let us take the composite of PANI (33 wt %)-fir sawdust as an example. Results of the calculation of transmittance for this composite, using the experimental values of ϵ^* , are given in Figure 10. The practically useful shielding performance, $T < -10$ dB in MHz frequency range and $T < -40$ dB for GHz frequency, can be achieved only for a composite material with a thickness of $h = 100$ mm (Fig. 10). Considering the low cost and low weight of the composite material, the application of such composites is thus feasible, for example, for the shielding of rooms or buildings. Better results are expected to be achieved: (a) by increasing the content of conducting polymer in the composite and (b) by increasing the conductivity of the polymer, for example, by suitable protonation, or (c) by changing the type of conducting polymer, for example, to PPy. It can be estimated that, if the real part of permittivity were increased 5 times and the imaginary part 10 times, similar shielding properties would be achieved at a thickness of 10 mm. Such approaches to increase the performance of composites are under investigation.

CONCLUSION

Sawdust particles made from fir or oak wood have been coated with a polyaniline or polypyrrole overlayer during the *in situ* polymerization of the corre-

sponding monomer. The fibers constituting the particles were coated with conducting polymer at the same time. The conductivity of coated fir wood is always higher compared with oak wood. The deposition of polyaniline leads to a higher conductivity than that of polypyrrole. The percolation limit is located below 5 wt % of conducting component in the composite. The thermal stability of conductivity tested at 175°C is better for polyaniline than for its composites with wood. On the other hand, composites based on polypyrrole perform better than polypyrrole alone, partly on account of the better mechanical integrity of composite samples provided by the incorporated wood fibers. Both the real and imaginary components of the permittivity increase with increasing weight fraction of polyaniline or polypyrrole in the composite. The dielectric constants are generally higher for composites based on fir wood, due to better distribution of the conducting component in a more porous substrate. Relatively thick layers of composite materials, ~ 100 mm, are needed for practically interesting shielding of electromagnetic radiation in the MHz-GHz frequency region.

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