LIGNOCELLULOSE NANOCOMPOSITE CONTAINING COPPER SULFIDE

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Copper sulfide-containing lignocellulose nanocomposites with improved electroconductivity were obtained. Two methods for preparing the copper sulfide lignocellulose nanocomposites were developed. An optimization of the parameters for obtaining of the nanocomposites with respect to obtaining improved electroconductivity, economy, and lower quantities and concentration of copper and sulfur ions in waste waters was conducted. The mechanisms and schemes of delaying and subsequent connection of copper sulfides in the lignocellulosic matrix were investigated. The modification with a system of 2 components: cupric sulfate pentahydrate ($CuSO_4$. $5H_2O$) and sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$) for wood fibers is preferred. Optimal parameters were established for the process: 40 % of the reduction system; hydromodule M=1:6; and ratio of cupric sulfate pentahydrate:sodium thiosulfate pentahydrate = 1:2. The coordinative connection of copper ions with oxygen atoms of cellulose OH groups and aromatic nucleus in lignin macromolecule was observed.

Keywords: Lignocelluloses; Wood fibers; Nanocomposites; Copper sulfide; Electroconductivity

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INTRODUCTION

Metal-containing nanomaterials, and in particular polymer nanocomposites, are of great interest presently because of their unique physical and chemical properties and possibilities for useful applications (Wang 1998).

Composites with improved parameters, including toughness, thermostability, and other specific properties, can be obtained via adding mineral fillers, metals, and fibers to polymers. Recent progress is being marked by the development of nanocomposite materials comprising a low percent of filler that have much larger intrinsic surface area, hence better parameters than the conventional composites (Lio 1995).

Nanocomposites include linear, as well as three-dimentional and amorphous structures of intermixed phase-separated nanocomponents. A considerable advantage of the nanocomposite materials are the uncomplicated and cheap preparative methods and technologies. It has been established that all mentioned types and classes of nanocomposite materials have improved properties in comparison to the similar macrocomposites (Lio 1993). Hence, nanocomposites allow new applications, such as lighter components for reinforcement, nonlinear optical systems, cathode and anode batteries, sensors, etc.

A great variety of inorganic layer materials can be used both as matrix and as additives to polymers, with possibilities for obtaining a wide range of new hybrid nanocomposite materials (Юрков 2002).

An original method for formation of metal-containing polymers via thermal decomposition of precursors (mainly metal carbonyls) in solution or melt has been published. A strong interaction between the nanoparticles and the polymer chain occurs in such nanocomposites on the level of chemical bonding. Electronically dense individual or aggregated metal-containing particles have been observed (Pomagalio 2000; Hershaw 1999).

Recently, special attention has been paid to nanocomposites having a different controllable molecular structure, determined by the polymeric dendrimers. The metal organic derivatives of dendrimers and their numerous macromolecular metalcomplexes of ruthenium, palladium, platinum, etc., are well known (Zend 1997; Floriano 2001; Kim 2001; Grohn 2001; Wang, 2000).

Nanocomposites allow the production of articles possessing superconductivity. It has been noted that the investigations in this field open possibilities of obtaining new materials with unique properties (Wang 2000; Wu 1989a,b).

The method of direct precipitation of colloidal dispersed additive layers and their encapsulation into the polymer matrix has been recommended as one giving a lot of possibilities to the applications of the obtained materials (Bissessur 1993). A new method for in-situ synthesis of precious nanoparticles using cellulose supports has been developed (Sun 2002).

Methods for modification of fabrics with electroconductive pigment on the basis of copper sulfide polymer dispersion have been developed; these include new electro-conductive polyacrylonitrile (PAN) pigments with coordinative connecting of copper sulfide in the nanostate into the PAN matrix for microwave protection (Lekova 1998)

Recently, investigations connected with copper sulfide coating on polyacrylonitrile with a chelating agent of triethanolamine (Chen 2009) and ethylenediaminetetraacetic acid (Chen 2010) by an electroless deposition method and its EMI shielding effectiveness have received great interest. The literature study showed that the obtaining of new metal-containing nanocomposites polymer materials with improved electroconductivity and microwave absorption ability is a question of present interest and it is very useful for articles that can provide electromagnetic wave protection.

In this study, copper sulfide-containing nanolignocelluloses with improved electro-conductivity and microwave absorption ability have been developed, and on this basis polymer composites with special new properties for electromagnetic wave protection may be obtained. Investigations were carried out aimed at the following goals:

- Development of methods for obtaining of copper sulfide lignocellulose nano-composites
- Optimization of the methods for obtaining of copper sulfide lignocellulose nano-composites having improved electroconductivity, economy, and decreased quantities and concentration of copper and sulfur ions in waste waters
- Establishment of probable mechanisms and schemes of delaying and subsequent connection of copper sulfides in the lignocellulose matrix.

EXPERIMENTAL

The development of methods for obtaining copper sulfide lignocellulose nano-composites is based on the fact that the copper (Cu^{+1}) sulfide as an additive to polymers gives high electroconductivity. Such electroconductivity as an indirect index for dielectric losses shows that corresponding new materials will posses microwave absorption properties. A higher effect will be achieved with nanocoppersulfide, which is situated as a net in the lignocellulose matrix. In this sense the development of methods is based on the conducting of chemical modification on the different kinds of lignocellulose materials – wood flour (WF), wood fibrous materials (WFM), and waste cellulose fibers WCF) – with water solutions of copper compounds and sulfur-containing reduction systems in suitable quantities and ratios and definite parameters of process, temperature, and conditions. Such conditions will give the possibilities for a reduction process: Cu^{+2} to Cu^{+1} ions and subsequent coordinative precipitation in lignocellulose matrices.

In the present work the following lignocellulose materials were used:

- wood flour (WF);
- wood fibrous material (WFM), produced in Lesoplast AD, Troian (Bulgaria);
- waste cellulose fibers (WCF) by paper production.

Basic Variants for Chemical Modification Process on Lignocelluloses

With previous experiments (varying the kind and composition of components) two variants for experimentation have been established (Nenkova 2010):

- With a system of three components (cupric sulfate pentahydrate ($CuSO_4$. $5H_2O$); sodium thiosulfate pentahydrate ($N_2S_2O_3$.$5H_2O$); glyoxal (OCHCHO)
- With a system only of 2 components (cupic sulfate pentahydrate ($CuSO_4$. $5H_2O$); sodium thiosulfate ($N_2S_2O_3$ .5H $_2O$).

The following indicators for optimization of methods were determined:

- The quantity of wasted water;
- The content of copper and sulfur in waste water;
- The content of copper and sulfur in modified lignocelluloses;

Electroconductivity was determined by measuring the specific electrical resistance. The measurements were made in electrode box for powder materials at constant pressure and quantity of investigated material using the apparatus TERAO II METER (IEC 60093 Ed. 2.0 b 1980).

IR spectrums of non-modified and modified samples were determined with an FTIR – GX apparatus from Perkin Elmer, having a spectral range of 4000 to 350 cm^{-1} and a resolution of 4 cm^{-1}.

Modification with a System of Three Components

The 3-component system comprised cupric sulfate pentahydrate ($CuSO_4.5H_2O$), sodium thiosulfate pentahydrate ($N_2S_2O_3.5H_2O$), and glyoxal (OCHCHO). The modification of three different lignocelluloses was conducted: wood flour (WF), wood fibrous materials (WFM), and waste cellulose fibers (WCF). The three-component system was studied using the previously established ratios between cuprous sulfate ($CuSO_4.5H_2O$):

sodium thiosulfate ($N_2S_2O_3.5H_2O$):glyoxal (OCHCHO) = 1.6:1.4:1.0 in quantity 40% towards lignocelluloses at hydromodule M= 1:12; 90^o C temperature, and duration 30 min.

The characterization data for wastewaters and modified wood samples are given in Table 1.

Table 1. Copper-containing Lignocelluloses, Modified with a System of Three Components

№	Conditions of modification	Copper in sample, %	Sulfur in sample, %	Copper in filtrate, mg/l	Sulfur in filtrate, mg/l	Specific electric volume resistance, Ω.m
1.	Non - modified wood fibers (WF)	0.0006	0.33	-	-	8.25×10^8
2.	Non- modified waste cellulose fibers (WCF)	0.0007	0.25	-	-	5.7×10^7
3.	Non - modified wood flour (WF)	0.0009	>0.05	-	-	8.7×10^8
4.	Modified wood fibers (WF)	3.786	>0.05	362.0	103.0	1.65×10^8
5.	Modified waste cellulose fibers (WCF)	4.319	1.92	5.0	69.0	1.11×10^7
6.	Modified wood flour (WF)	5.058	1.79	1380.0	116.0	1.95×10^8

The data shown in Table 1) can be summarized in various ways. The modification of the three different lignocelluloses (wood flour (WF), wood fibrous materials (WFM), and waste cellulose fibers (WCF) with the system of 3 components: cuprous sulfate ($CuSO_4.5H_2O$); sodium thiosulfate ($N_2S_2O_3.5H_2O$); and glyoxal (OCHCHO) can be characterized as follows:

- The reduction process had a very strong effect on the wood fibrous materials (WFM), and therefore the sulfur content in the modified material was very insignificant.
- On the waste cellulose fibers (WCF) Cu^{+2} ions are reduced to Cu^{+1}.
- The modified wood flour (WF) contained not only Cu_2S but also copper particles; therefore the reduction process was strongest in that case.

As regards to the copper and sulfur contents in waste waters, the waste cellulose fibers (WCF) showed an advantage over wood flour (WF) and wood fibrous materials (WFM). Probably, these results indicate that the lowest cupper and sulfur contents were due to the specific composition of used waste cellulose material.

Lower copper and sulfur contents in waste waters were observed after the modification of the wood fibrous materials (WFM) in comparison with those after the modification at wood flour (WF).

The specific electric resistance decreased in the order 0.5 to 1.0 after the modification of the three different lignocelluloses.

The accomplished investigations and the results that were obtained with the system of the 3 components cuprous sulfate ($CuSO_4.5H_2O$), sodium thiosulfate ($N_2S_2O_3.5H_2O$), and glyoxal (OCHCHO) unambiguously showed that it is possible to obtain Cu-containing lignocelluloses by using only a sulfur-containing reducing agent (for example $N_2S_2O_3.5H_2O$) on the basis of wood fibrous materials. In this way the use of an additional reducer (in example OCHCHO) is not needed, which can be considered as an advantage in view of economics and the environment.

The findings given above motivated the trend of the next set of investigations: the development and the optimization of a method for modification with a reduction system of two components containing Cu and S, respectively.

Modification with a System of 2 Components

The two-component system investigated comprised cupric sulfate pentahydrate ($CuSO_4.5H_2O$) and sodium thiosulfate pentahydrate ($N_2S_2O_3.5H_2O$). This section describes the development and optimization of the method. The idea for a modification in condition of saturated water vapor was very successful.

At first, the modification of wood fibres (WF) was carried out in a temperature-controlled chamber with saturated water vapor at 110^o C for 30 minutes with a 2-component reduction system, containing copper and sulphur (ratio of cupric sulfate : sodium thiosulfate = 1:1 and 1:2, quantity 20% and 40% based on the mass of lignocellulose material at a weight ratio (*M*) equal to 1:12.

The data for specific electric resistance showed a decrease by a factor of about two after the modification, but the required copper and sulfur quantities were considerable. For this reason that the modification process was conducted again at lower weight ratio: *M* = 1:6; ratio of cupric sulfate : sodium thiosulfate = 1:2, and with variation of component content from 20% to 40% toward lignocellulose material. The modification at low module was very suitable, because the quantity of waste waters was low and the modification process was accomplished normally. The investigation results for waste waters and the samples are given in Table 2.

Table 2. Copper-containing Lignocelluloses, Modified with Two Components

№	Conditions of modification	Copper in sample, %	Sulfur in sample, %	Copper in filtrate, mg/l	Sulfur in filtrate, mg/l	Specific electric volume resistance, Ω.m
1.	Non-modified wood fibers (WF)	0,0006	-	-	-	$8,25.10^8$
2	Modified wood fibers (WF): module = 1:6, ratio 1:2, 20 %	1,383	2,06	21,5	98,0	3.10^7
3	Modified wood fibers (WF): module = 1:6, ratio 1:2, 30 %	1,945	3,82	35,5	67,0	$1,28.10^7$
4	Modified wood fibers (WF): module = 1:6, ratio 1:2, 40 %	2,783	2,88	20,7	80,0	$1,65.10^7$

On the basis of the data (Table 2) the following findings and conclusions can be stated:

1. Specific electric resistance data showed an increase in electroconductivity of wood material due to the treatment: the decreasing of resistance was of the order of 2.0 for samples modified at the 20%, 30%, and 40% levels.

2. An optimal ratio of modifying components (copper:sulfur) was achieved with a 40% reduction system.

The scheme of the reduction process is as follows:

$$Cu^{+2} + 1e^{-} \rightarrow Cu^{+1} \quad (1)$$

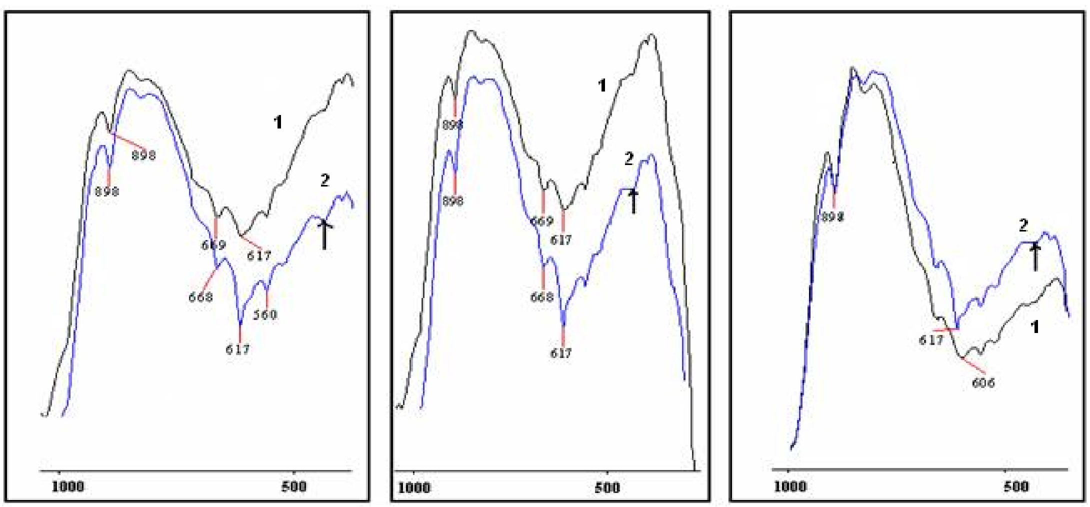
$$2S^{+2} – 2.2e^{-} \rightarrow 2S^{+4} \quad (2)$$

$$2CuSO_4 + 2Na_2S_2O_3 = Cu_2S + 2Na_2SO_4 + 3SO \quad (3)$$

A peak at 400 cm^{-1}, representative of the metal-oxygen ligand, was observed in the IR spectrums of modified wood flour and of modified wood fibers (Fig. 1, a,b,c).

These ligands are probably due to the coordinative connection of copper ions with oxygen atoms of cellulose -OH groups (Fig. 2) and aromatic nucleus in the lignin macromolecule (Fig. 3).

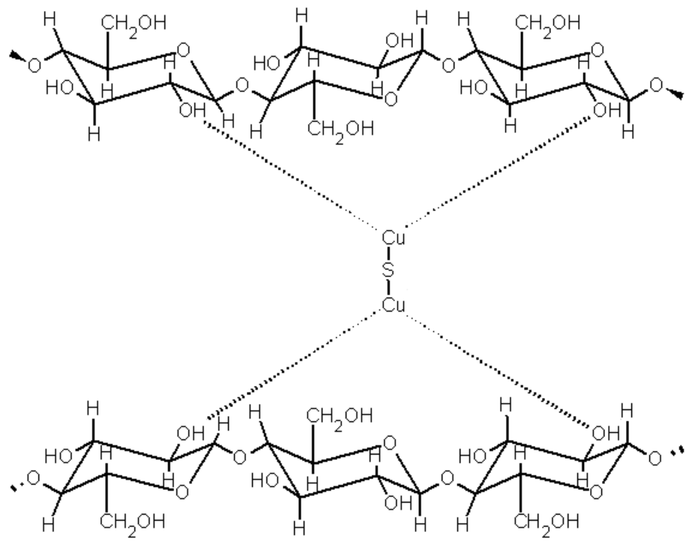
A similar model for Cu^{+2} complexes with the lignin model compound vanillin was given by Kozlevcar (2005). The connection of copper ions via methoxy oxygen atom and deprotonated hydroxy oxygen atom in nuclear species confirmed the bonding role of copper to lignin (Zhang 2005). It is possible for lignocellulose materials to give evidence of physical adsorption to copper ions.

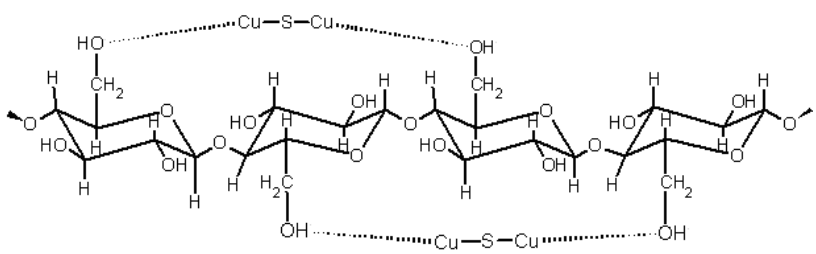


a) b) c)

Fig.1. IR spectrum of: a) non-modified (1) and modified (2) wood flour with system of three components (40% addition based on wood flour); b) non-modified (1) and modified (2) wood fibers with system of two components (30% added based on wood fibers); and c) non-modified (1) and modified (2) wood fibers with system of two components (40% added based on wood fibers)

The coordinative connection of copper ions with lignocelluloses materials may be represented by the following schemes:





and

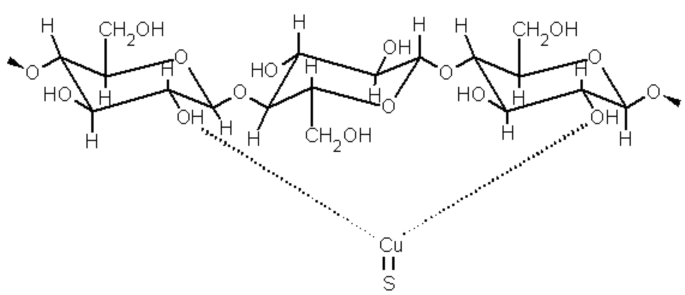


Fig.2. Copper-sulfide cellulose nanocomposites

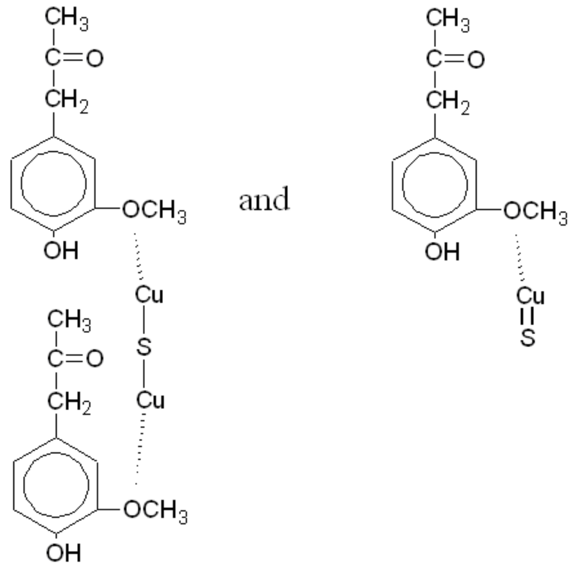


Fig.3. Copper-sulfide lignin nanocomposites

CONCLUSIONS

Treatment with a system of three components, comprising cupric sulfate pentahydrate ($CuSO_4.5H_2O$), sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$), and glyoxal (OCHCHO), at ambient pressure and 90^o C is very effective for modification of waste cellulose fibers and to some extent wood flour.

A modification of the method with a system of two components, cupric sulfate pentahydrate ($CuSO_4.5H_2O$) and sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$), is preferred for wood fibers (WF).

Original methods for modification of WF with a 2-component cupric reduction system under saturated water vapour conditions have been developed. The optimal parameters of the process were established: 40% of the 2-component system toward wood material; M=1:6; $CuSO_4.5H_2O$:$Na_2S_2O_3.5H_2O$ = 1:2.

Data from IR spectra confirmed a coordinative connection of copper ions with oxygen atoms of OH groups in cellulose and in the aromatic nucleus of the lignin macromolecule.

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