

## Using the Methods of Molecular Optical Spectral Analysis of Modified Plant Polymer Structure

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### ABSTRACT

Using computer-based monitoring systems that rely on tests could be the most effective way of knowledge evaluation. The problem of objective knowledge assessment by means of testing takes on a new dimension in the context of new paradigms in education. The analysis of the existing test methods enabled us to conclude that tests with selected response and expandable selected response do not always allow for evaluating students' knowledge objectively and this undercuts the effect of pedagogical evaluation of their cognitive activity as well as the teaching and learning processes generally. Authors propose an expert knowledge monitoring and evaluation system based on an integral method of knowledge evaluation. This method is built on a new approach to constructing test items and responses to them, which give students an opportunity to freely construct their responses, and presupposes a set of criteria for their assessment. Proposed method makes it possible to expand the functions of tests and in this way approximate the test grade to the real level of students' knowledge. Theoretical and empirical data presented in the paper can be used for improving the monitoring and evaluation of knowledge in social sciences and the humanities and thus raising the quality of education.

### KEYWORDS

infrared spectroscopy; molecular optical spectroscopy; structural and functional changes; natural polymer; bark waste.

### ARTICLE HISTORY

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### Introduction

Currently, much attention is paid to the study of wood-polymer composites' properties (Islam et al., 2014; Teuber et al., Matveev et al., 2016). This is due to their increasing role in motor and building industries. There is growing relevance of the study on biodegradable composites, which are wood-polymer composites (Rodriguez et al., Mogoşanu and Grumezescu, 2014; Wegst et al., 2015), because the European Union has adopted a number of resolutions to limit the use of non-biodegradable materials, including their use in motor industry.

Wood-polymer composites have a high-quality exterior and texture properties that allow grinding (Gong et al., 2012; Haider et al., Srubar et al.,

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2014). WPC have properties that are better than some characteristics of a tree (Deka, 2013; Yanna et al., 2014).

Strong chemical modification of wood waste accompanied with low-molecular compounds abstraction caused significant structural and functional changes of the plant polymer molecules (Kononova, 1963; Orlov, 1974; Sjutkin, 1996). Incomplete functional group conversion was observed because of steric hindrances. It was resulted in unpredictable process of macromolecules modification and in getting final products that require deep structural and functional research.

The most difficult thing when analyzing modifying compounds is identification and determination of functional groups content (phenolic, carboxylic, aldehydic, cetonic, ster) (Shvecova, Hmelinin et al., 1993; Grehova and Romanchuk, 2008). Polydispersity, large molecular weight, irregular structure, variety of bond types make it difficult to analyze compounds chemical structure using the most known chemical and physical methods.

Thus, the use of infrared spectroscopy in organic biogenic samples' analysis may help to study natural polymers' properties and behavior. This, in turn, will help to improve the quality of wood-plastic composites, to increase the duration of their use, to make them more environmentally clean.

### **Aim of the Study**

Consider the nature of plant polymers components' activity by means of infrared spectroscopy

### **Research questions**

How does the valence line change?

### **Method**

Methods of molecular optical spectroscopy as well as traditional chemical methods for functional group content determination are widely used when analyzing chemical structure of modified natural polymers.

The basic raw material for modificant making was hydrolyzed lignin of hydrolyzed-barmy production (it is a paste-like, dark-brown substance, of acid reaction, with humidity 65-70%) and bark waste.

Modificant was powder or granules of grey-brown to dark-brown color with humidity no more than 20% and with the water-insoluble content no less than 13%; pH no less than 5,0. According to element composition compounds contained: phosphorus no more than 15-16 % (appr. 46%  $P_2O_5$ ); kalium 11 % (8-12 %  $K_2O$ ); total nitrogen 10-12 %. Functional composition was: carbonyl group (CO) – from 1,1 % to 3,0 %; carboxy group (COOH) – from 1,6 to 3,3 %.

There are also used scientific methods of analysis, synthesis, systematicity, domestic and foreign researchers' experience generalization on the issues under consideration.

## Data, Analysis, and Results

Wood waste was processed in acid-salting system. After reaction ending reaction mass was saturated by ammonium carbonates.

Then process of chemical modification of natural polymer in the acid-salting system was made under varied acid strength (from 25% to 85%) and exposure time.

Changes in macromolecule structure of natural polymer modified in acid-salting system were analyzed by infrared spectroscopy. Infrared spectra were observed by famous methods (Zakis, 1975).

On the infrared spectra of the specimens processed in the acid-salting system one can see functional groups which were influenced by oxidative reactant. This is a cycle of the aromatic ring changes ( $1510\text{ cm}^{-1}$ ,  $1460\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$ ), a cycle of valent changes of carboxy groups ( $1730\text{ cm}^{-1}$ ), phenolic changes ( $1220\text{ cm}^{-1}$ ) and phenol etherous changes ( $1270\text{ cm}^{-1}$ ). Peaks in the cycle of  $1000 - 1100\text{ cm}^{-1}$ , i.e. the cycle of aliphatic alcohol group, remain almost unchanged (Zakis, 1975).

When processing specimens of lignin and other wood waste in the system of  $\text{KNO}_3\text{-H}_3\text{PO}_4$  (85%) under different time duration one can see changes in their specific optical density. One can suppose that the decrease of specific optical density in  $1510\text{ cm}^{-1}$  and time increase of oxidative system influence is connected with either the aromatic ring gap or bonds redistribution. Flattening of the peak in  $1510\text{ cm}^{-1}$  shows the changes in the chemical structure of aromatic fragments in the tested specimens (Table 1).

As Table 1 shows, increasing time duration of lignin specimen process leads to increasing of specific optical density in  $1720\text{ cm}^{-1}$ . It appears that at the beginning of oxidative nitration there is demethylation and formation of quinines which in their own turn are oxidized. After having been oxidized they form carboxyl groups (their content increase was seen on the infrared spectra of the derived specimens) and split the benzene ring. The amount of macromolecule phenolic groups during oxidative nitration decreases up to 0,8 – 1,0%. It appears to be caused by changes during the process of demethylation of structure elements of guaiacyl type and during the process of quinine formation (the lines of average intensity in  $1660\text{ cm}^{-1}$ ). Quinoid structures have high reaction capacity. Therefore they are oxidized thus forming carboxy groups ( $1720\text{ cm}^{-1}$ ) and gapping the benzene ring (low specific optical density in  $1510\text{ cm}^{-1}$ ).

**Table 1.** Specific optical density dependence of lignin specimens in the cycle  $1510\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$  on processing time duration in the system  $\text{KNO}_3\text{-H}_3\text{PO}_4$  (85%)

| Characteristic features                        | Processing time duration (min) |      |      |      |      |
|--|--------------------------------|------|------|------|------|
|  | 0                              | 10   | 20   | 30   | 40   |
| Specific optical density $1510\text{ cm}^{-1}$ | 1,05                           | 0,70 | 0,69 | 0,66 | 0,60 |
| Specific optical density $1720\text{ cm}^{-1}$ | 0,21                           | 1,54 | 1,65 | 1,89 | 1,90 |

Analysis of infrared spectra also shows direct correlation of functional groups conversion depth to phosphorus acid concentration. These changes are particularly seen in the cycle of aromatic ring variations. For example, if the



acid concentration is higher in the specimens, the peak in the cycle of  $1510\text{ cm}^{-1}$  on the spectra almost disappears, and in the cycle of  $1470$  and  $1610\text{ cm}^{-1}$  aromatic power is partially lost. Peak in the cycle of  $1720\text{ cm}^{-1}$  rises.

When the acid concentration is lower, the process slows down, aromatic rings do not almost break (specific optical density in  $1610\text{ cm}^{-1}$  remains at the same level). This greatly influences on structural and functional composition of modified lignins. Carboxyl group mass content is not high.

### Discussion and Conclusion

Analysis of phosphorus acid concentration influence and time process of structural lignin molecule changes helps to make a conclusion that in the system  $\text{KNO}_3\text{-H}_3\text{PO}_4$  aromatic cycles with a free phenolic group are broken forming the aliphatic carboxylated structures. At the same time the reaction of electrophilic nitration occurs.

In the acid-salting system  $\text{KNO}_3\text{-H}_3\text{PO}_4$  together with oxidative changes of lignin molecule the reaction of electrophilic nitration occurs. This is proved when intensive absorption line of valent variations of nitration group appears adjoined to the aromatic ring ( $1360\text{ cm}^{-1}$ ). Nitration groups by means of hydroxyl groups etherification are not formed. There is no line in  $1642\text{ cm}^{-1}$  on infrared spectra. Internal spectrochemical line correlation in  $870\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  is in favor of nitration mechanism with aromatic nitration groups forming (Zakis, 1975).

Comparing the infrared spectra of original lignin and spectra of modified specimens formed by oxidation original lignin in the system  $\text{KNO}_3\text{-H}_3\text{PO}_4$  one can make a conclusion that lignin oxidation is accompanied by large structural changes.

Gained data prove that the destruction depth and degree of aromatic fragments of the natural polymer depend on acid concentration and system time duration influence on lignin. Analysis of specimens infrared spectra shows that structural and functional changes of lignin molecule influenced by acid-salting system form the specimens which, according to the structural – group composition, do not differ from humic substance.

### Implications and Recommendations

The factor that limits wide using of natural organic material is that it is difficult to determine the composition and structure of specimens formed. Methods of molecular spectroscopy, infrared spectroscopy particularly, are widely used for analyzing the organic biogenic specimens. It helps to find out structural and functional changes of natural polymers that were broken up chemically.

According to the data of infrared spectroscopy of chemically modified lignin specimens, molecules of modified lignin have few aromatic structures and many carboxyl groups. Infrared spectroscopy of all specimens is characterized by feebly marked absorption in the cycle  $1660\text{ cm}^{-1}$ . This proves that there are few quinone groups or  $\text{C=O}$  in aliphatic 6-membered cycles. In the whole the well-defined line of valence changes in the cycle  $1720\text{ cm}^{-1}$  ( $\text{COOH}$  groups changes) and weak-intensified absorption lines in  $1510\text{ cm}^{-1}$ ,  $1460\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$

(changes of the aromatic ring) on infrared spectra of modified specimens show deep structural and functional changes of lignin molecule.

The results of this paper can be used in the studies in order to increase the biological stability of natural polymers to a wide range of microorganisms.

### Disclosure statement

No potential conflict of interest was reported by the authors.

### Notes on contributors

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