LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES
2006, N 2

SYNTHESIS OF LIGNIN-BASED HYBRID MATERIALS USING α-KEGGIN'S TYPE POLYOXOMETALATES AS INORGANIC BUILDING BLOCKS

G. Telysheva[1], T. Dizhbite[1]*, L. Jashina[1], A. Andersone[1],
N. Mironova-Ulmane[2]

[1]Latvian State Institute of Wood Chemistry,
27 Dzerbenes St., Riga, LV-1006, LATVIA
[2]Institute of Solids State Physics of University of Latvia
8 Kengaraga St., Riga, LATVIA
*e-mail: ligno@edi.lv

A new hybrid organic–inorganic material was synthesized using the solid-phase interaction between the plant-originated polymer lignin (an electron-rich donor with developed π-conjugated aromatic structure inclined to form supramolecular associations) and the $[SiMo_{12}O_{40}]^{4-}$ – a Keggin-type heteropolyanion (an electron acceptor). The structure of the new material was studied by the FTIR spectroscopy, electron paramagnetic resonance (EPR), Raman microscopy, elemental analysis, and by the thermogravimetry and N_2 sorption-desorption techniques. To synthesize the hybrid material a quaternized lignin was used, which was produced at the Institute of Wood Chemistry from Curan – a commercial craft lignin (a multi-tonnage by-product of sulfate cellulose production).

1. INTRODUCTION

In the last decade, polyoxometalates (POMs), long-known for their magnetic, electroionic and photoelectrochemical properties, have begun their evolution as inorganic building blocks in the synthesis of multifunctional hybrid materials. Integration of POMs into polymeric organic matrices improves their stability and opens a wide variety of novel applications in medicine, analytical chemistry, nanoscience, catalysis, optics, *etc*.. Recently, new strategies for POM modification have been reported [1, 2], which rest on the exchange of the POM counteractions with suitable surfactants [1] or, alternatively, with cationic macromolecules [2], resulting in the POM/polyelectrolyte dispersed nanocomposite hybrid material of a new type.

In this work, we report on the structure and properties of hybrid organic-inorganic materials based on the lacunary POM, which presents a Keggin's-type heteropolyanion molybdosilicate $[SiMo_{12}O_{40}]^{4-}$ and a cationic surface active polymer – the so-called quaternized lignin. The "Keggin" anions, being good electron acceptors, are attractive as inorganic precursors owing to their reactivity towards organic groups [3]. A plant-originated lignin polymer was chosen as an organic moiety for building up the organic-inorganic material. As is known, lignin is the second after cellulose most abundant biopolymer found in lignocellulosic biomass; it is characterized with developed π-conjugated aromatic structure (Fig. 1),

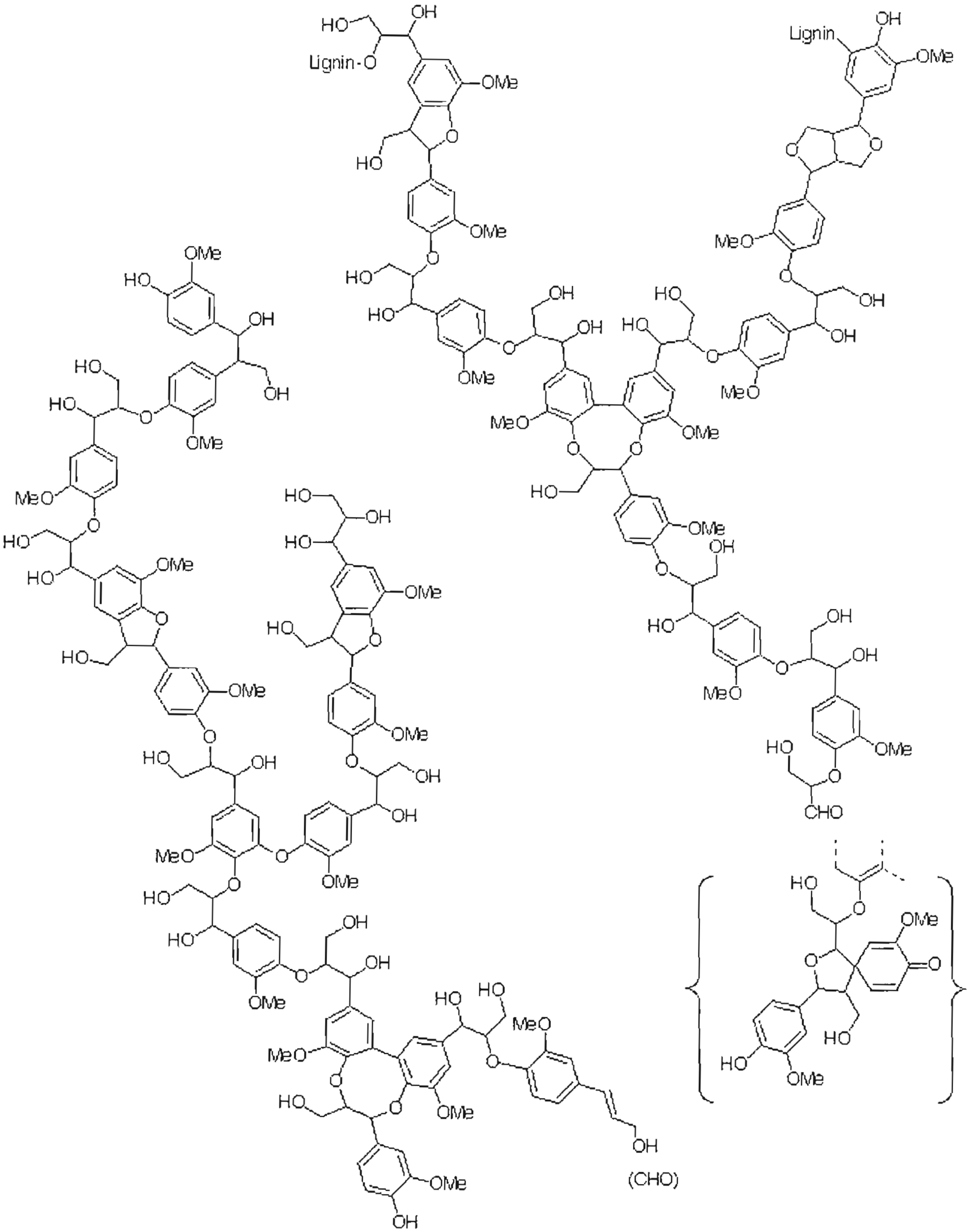

Fig. 1. Structural model of softwood lignin [4].

possesses hydrophobic properties and a high inclination to electron donation, charge transfer complexing and supramolecular associations. Commercial lignins are available in large quantities as by-products from chemical processing of lingocellulosic biomass (e.g. from pulp or ethanol production). Lignocellulose and its constituent biopolymers are among the most abundant biological raw materials, which are structurally based on nanofibrillar self-assembling/self-healing systems with a high degree of molecular fidelity. Fundamental understanding and control of these systems is essential when new nanoscale multifunctional materials and electronic devices on their basis, bioagents and composites are concerned. The use of lignin for the development of new nanostructure devices and systems has now been recognized among the major tasks of research associated with production of the next-generation forest-based materials [5].

The solid-state RT interaction of molybdosilicate with the quaternized lignin obtained from the commercial Curan craft lignin (a multi-tonnage by-product of sulfate cellulose production) proceeded as described in the literature [6]. The structure and properties of the product obtained were examined by X-ray spectroscopy, FT-IR, Raman microscopy, electron paramagnetic resonance (EPR) spectroscopy and nitrogen adsorption technique.

2. EXPERIMENTAL

Preparation of $H_4SiMo_{12}O_{40}\cdot 13H_2O$ was performed using Fournier's method [7].

Quaternized lignin was obtained by processing commercial craft lignin Curan-100 (kindly put at our disposal by Borreggard LignoTech, Norway) with 3-Chloro-2-hydroxypropyl-trimethylammonium chloride in 1 M NaOH at 40 °C for two 2 hours [8].

The solid-state RT interaction of quaternized lignin with $H_4SiMo_{12}O_{40}\cdot 13H_2O$ proceeded by the method [6] adapted as follows. Molybdosilicate and quaternized lignin were mixed at a molar ratio 1:4 and ground in an agate mortar for about 40 min and then the product obtained was washed in an ultrasonic bath with ethanol, centrifuged 10 times and dried under vacuum at 50 °C.

The elemental analysis was performed on varioMacro CHNS equipment; Mo content was determined by the atomic absorption spectrometric (AAS) method.

The average diameter of particles was estimated using the adsorption characteristics of the material described by the equation [9]:

$$A = 6/\rho d,$$

where A is the specific surface area, ρ is the real lignin density (1370 kg/m^3), d is the average diameter of a spherical particle.

Specific surface areas were calculated from the nitrogen adsorption-desorption isotherm determined at 77 K using a KELVIN 1042 sorptometer.

X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with CuKα radiation (λ = 1.5418 Å).

IR spectra of the samples were obtained at room temperature with a Spectrum One (Perkin Elmers) FT-IR spectrometer in the range of 4000–400 cm^{-1} using KBr pellet technique.

Raman spectra were measured with a Nanofinder-S. The measurements were taken at room temperature using the 441.6 nm line of an argon-ion laser.

The EPR spectra were recorded by an EMX-6/1 spectrometer (BRUKER) working at X-band frequency. All measurements were taken at room temperature.

Thermogravimetric and differential thermal analyses (TGA-DTA) were carried out in air on a MOM Q-Derivatograph within the range 20–1000 °C, with a heating rate of 10 °C/min.

The data obtained at elemental analysis of the product of the solid-state interaction between quaternized lignin and molybdosilicate are in conformity with the molar ratio 4:1 of the components. The product is ethanol- and water-insoluble.

The new hybrid material obtained at the RT solid-state interaction consists of homogeneously dispersed particles with the average diameter of ~200 nm ($A = 19.5\ m^2/g$). This product can therefore be characterized as a nanocomposite material, unlike the product obtained by anion-cation interaction between the same co-reagents in aqueous solution which had a much higher polydispersity and the average particle diameter of 5 mkm ($A = 0.8\ m^2/g$).

X-ray diffraction (XRD) patterns of the solid-state interaction product and the pure molybdosilicate are presented in Fig. 2.

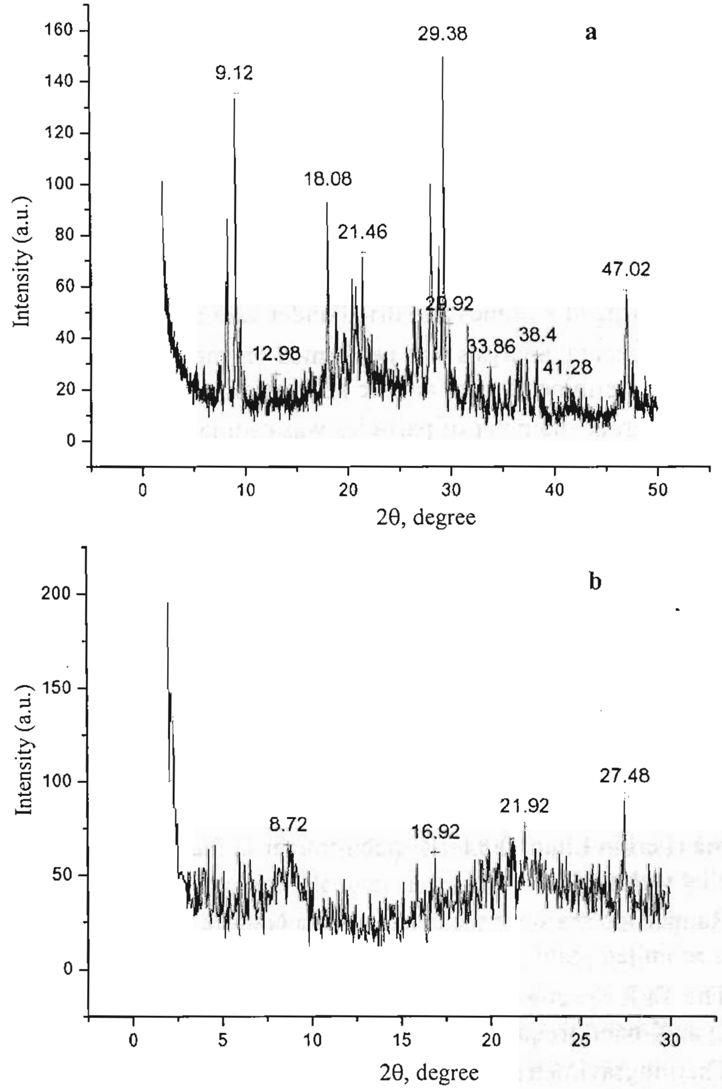

Fig. 2. XRD patterns of pure molybdosilicate (*a*) and the product (*b*) of solid-state interaction of quaternized lignin and molybdosilicate.

The quaternized lignin exhibits amorphous structure. The pattern for pure POM coincides well with the known structure of $H_4SiMo_{12}O_{40}\cdot 13H_2O$ [10] with the crystal data: P1, $a = 14.096(1)$ Å, $b = 13.499(1)$ Å, $c = 13.976(1)$ Å, $\alpha = 109.3(1)°$, $\beta = 119.1(1)°$, $\gamma = 67.8(1)°$, $V = 2115.74$ Å^3. Ball-and-stick representation of the heteropolymolybdosilicate is shown in Fig. 3.

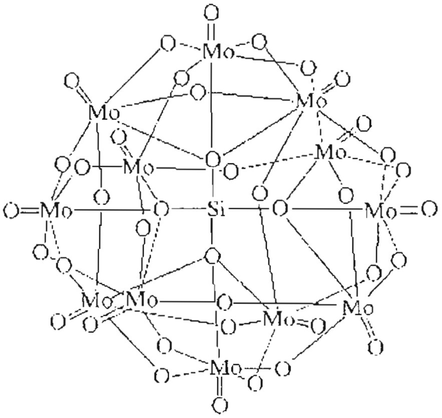

Fig. 3. Structure of heteropolymolybdosilicate $H_4SiMo_{12}O_{40}\cdot 13H_2O$.

A good crystalline structure was observed for the initial $H_4SiMo_{12}O_{40}\cdot 13H_2O$ only. For the product of lignin-$SiMo_{12}O_{40}$ interaction a low crystallinity is revealed, obviously owing to dispersion of molybdosilicate anions inside the amorphous lignin matrix; however, the peaks presented in XRD pattern of the interaction product indicate that a $SiMo_{12}O_{40}^{4-}$ anion retains the Keggin structure also in this case.

For stability determination of the product of solid state interaction lignin – $H_4SiMo_{12}O_{40}\cdot\cdot 13H_2O$, the TGA measurements were carried out. The results obtained (Table 1) show that the thermal stability of the hybrid material is slightly higher than that for the initial quaternized lignin: the mass losses were, respectively, about 2 and 9 % at 200 °C, and 33 and 37% at 500 °C. Thermal decomposition of pure parent compounds begins, respectively, at 200 and 160 °C, exhibiting the exothermic peak at 195 °C and the endothermic – at 155 °C. The data for the thermal decomposition of the hybrid product are: the temperature of the destruction beginning 237 °C, and two exothermic peaks on the DTA curve at 270 and 370 °C, which could be attributed to the decomposition of lignin and POM fractions.

Table 1

The results of TGA-DTA study of lignin-POM interaction products

Sample	Temperature of decomposition beginning, °C	Mass loss at 200 °C, %	Mass loss at 500 °C, %	Peak temperature on DTA curve, °C	
				endothermic	exothermic
Quaternized lignin	200	9.1	36.7	135	195
$H_4SiMo_{12}O_{40}\cdot 13H_2O$	160	10.7	13.7	155	370
Product of solid state interaction of lignin – $H_4SiMo_{12}O_{40}\cdot 13H_2O$	237	1.8	32.1	200	270 370

The FT-IR spectra of the hybrid material and the corresponding pure parent compounds are shown in Fig. 4. In the spectrum of pure $H_4SiMo_{12}O_{40}\cdot 13H_2O$ the main peaks at 956, 908, 859 and 778 cm^{-1} are presented, which are characteristic of a Keggin-type heteropolyanion [11].

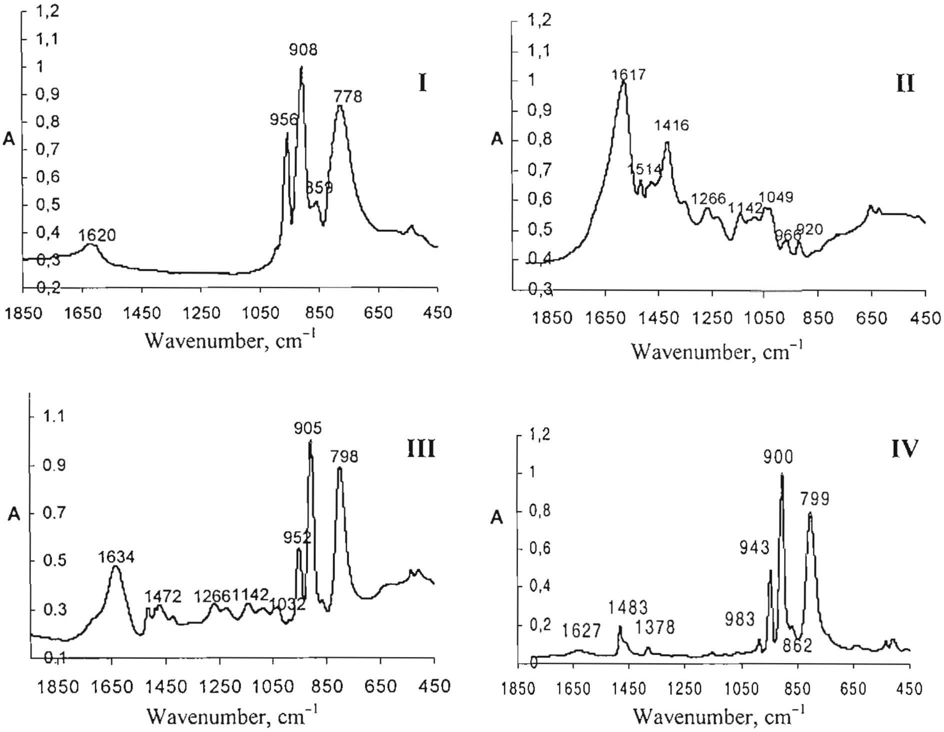

Fig. 4. FT-IR spectra of pure parent compounds and hybrid materials:
I – $H_4SiMo_{12}O_{40}\cdot 13H_2O$; II – quaternized lignin; III – product of solid-state quaternized lignin – $H_4SiMo_{12}O_{40}\cdot 13H_2O$ interaction; IV – $[(C_4H_9)_4N]_4SiMo_{12}O_{40}\cdot 4H_2O$.

The bands in the FTIR spectrum of the new product associated with the $[SiMo_{12}O_{40}]^{4-}$ anions are all shifted by only several inverse centimeters as compared with the pure POM, which indicates that the Keggin geometry of polyanions is still preserved inside the lignin matrix, though being slightly distorted due to the influence of coordination with quaternized lignin cations (red shift of the band ν (Mo = $O_{terminal}$) from 956 to 952 cm^{-1} and ν (Si–O) from 908 cm^{-1} to 905 cm^{-1}; blue shift of bridge bonds Mo–O–Mo: ν (Mo–O–Mo, angle-sharing octahedral bridge) from 859 to 867 cm^{-1} and ν (Mo–O–Mo, edge-sharing bridge) from 778 cm^{-1} to 798 cm^{-1}). The considerable shifts of bands associated with quaternized lignin, e.g. 1617 cm^{-1} – ν (C=O) in carboxyl and carbonyl groups and 1416 cm^{-1} – ν (C=O) in carboxylate ions, evidence that the lignin carbonyl groups interact as ligands with $[SiMo_{12}O_{40}]^{4-}$. For comparison, Fig. 4 also shows the IR spectrum of $[(C_4H_9)_4N]_4SiMo_{12}O_{40}\cdot 4H_2O$ considered in the literature as the reference compound for isolated anions in the crystal lattice [12]. The comparison of I, III and IV spectra of Fig. 4 indicates that cations of quaternized lignin are large enough to keep the polyanions far apart so that the anion-anion interactions can be neglected [12].

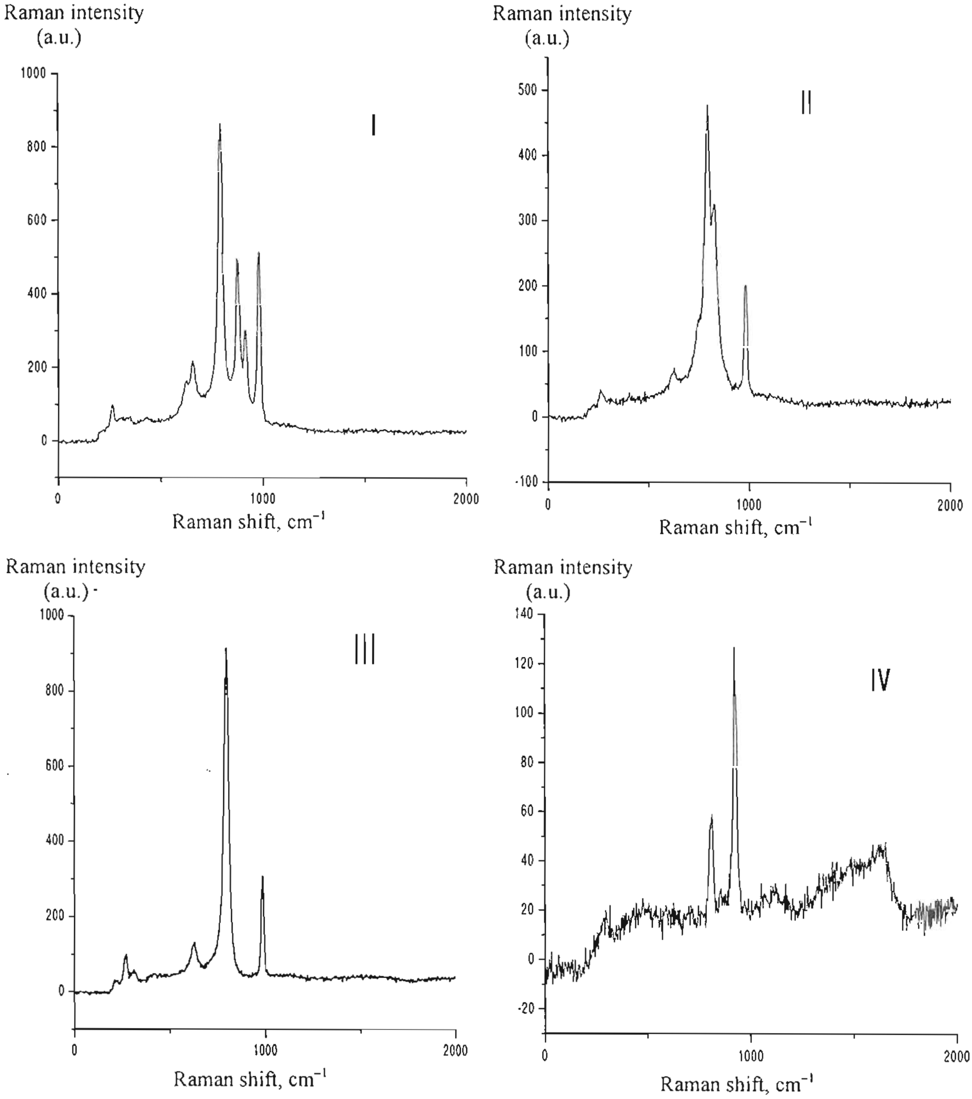

Fig. 5. Raman spectra: I – pure molybdosilicate immediately after its synthesis; II – the same sample after one-week storage under vacuum; III – the products of solid-state interaction of $H_4SiMo_{12}O_{40}\cdot 13H_2O$ with quaternized lignin; IV – tetra-butyl ammonium bromide.

Similarly to FT-IR spectra, despite the broad and low-intensity Raman spectra bands for lignin-containing compound, the influence of lignin cation on the $H_4SiMo_{12}O_{40}$ spectrum is close to that for tetra-butyl ammonium cation.

Comparison of the Raman spectra of molybdosilicate crystals measured immediately after they were obtained and stored (I and II, respectively, in Fig. 5) reveals some instability of the POM.

Figure 6 shows the EPR spectrum for the product of quaternized lignin – $H_4SiMo_{12}O_{40}\cdot 13H_2O$ solid-state interaction. A strong single line at $g = 1.93$ and six equidistant lines are observed. No EPR signal was obtained for $H_4SiMo_{12}O_{40}\cdot 13H_2O$ and for $[(C_4H_9)_4N]_4SiMo_{12}O_{40}\cdot 4H_2O$ due to the EPR silence of Mo (VI) ions. For pure quaternized lignin and the product of its interaction with molybdosilicate in solution only weak singlet signals were observed at $g = 2.00$, which are due to lignin aroxyl radicals [13].

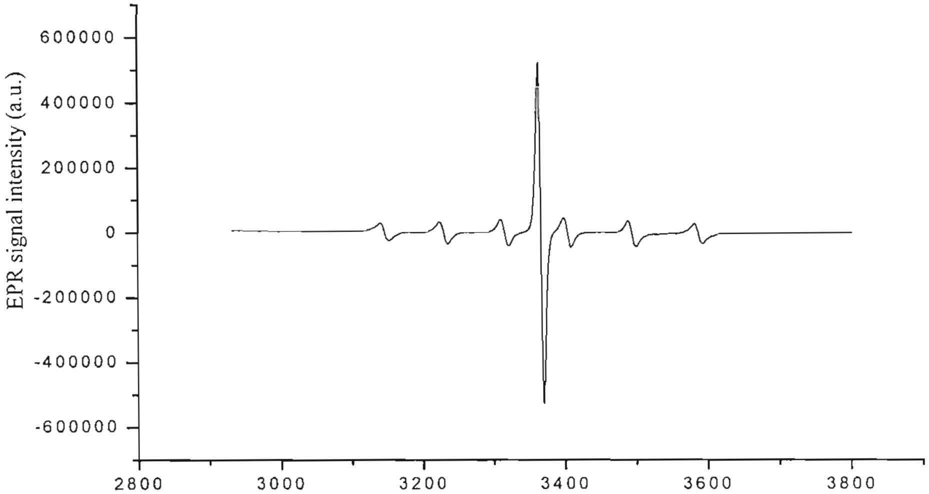

Fig. 6. EPR spectrum of the lignin-molybdosilicate solid-state interaction product.

The EPR spectrum shown in Fig. 6 is ascribed to the appearance of Mo(V) ions in the product of the solid-state interaction. Naturally occurring molybdenum is a mixture of isotopes of which 75% have zero nuclear spin (even mass-numbered isotopes) and 25% are odd mass-numbered (15% Mo^{95} and 9.6% Mo^{97}). The EPR spectrum expected for Mo(V) ions is, therefore, a strong single line with six much weaker lines superimposed upon it. Not only Mo(V) but also Mo(IV) and Mo(III) could give rise to the EPR signal, however it is not expected under ambient conditions [14]. The EPR spectra parameters obtained for the product ($g = 1.93$, $A = 6.7$ mT) are close to the data of [15] for the one-electron-reduced α-$[SiMo_{12}O_{40}]^{5-}$ ion. Therefore, the EPR spectrum of the synthesized product gives evidence for the formation of stable paramagnetic complexes of lignin with Mo^{5+} (resulting from reduction of a part of Mo^{6+} (acceptor) by lignin electron donor substructures) and the stabilization of mixed-valence heteropolyanion in the lignin matrix. The spectrum did not change at least during 6-month storage under ambient conditions. In the case of $H_4SiMo_{12}O_{40}\cdot 13H_2O$ solid-state interaction with a low molecular quarternary ammonium compound – the tetra-butyl ammonium bromide, reduction of Mo (VI) obviously does not occur and the hybrid material obtained remains the EPR silent. Developing further the present research, electroionic and photoelectrochemical properties of the lignin-based hybrid inorganic-organic material will be studied with the aim of its possible application as a bulk modifier for composite electrodes.

4. CONCLUSIONS

Hybrid inorganic–organic material (nanoparticles) containing milybdosilicate heteropolyanions was prepared from naturally originated polymer lignin by its solid-state interaction with the mentioned co-reagent. Based on XRD, FT-IR, Raman and ESR characteristics of the hybrid material, a mixed valence of Mo ions and the formation of complexes between lignin and polyoxometalate have been established. The obtained hybrid material is characterized with good storage and thermal stability properties.

ACKNOWLEDGEMENT

The financial support from the EU 6th Framework Programme, Contract IRRISEASOIL, and the Latvian budget, Research grant 1564 and 05-1716, is gratefully acknowledged.

REFERENCES

1. Kurth D.G., Lehmann F., Volkmer D., Muller A. and Du Chesne A. (2000) *Chem. Eur. J.* **6** 385–394.
2. Volkmer D., BredenkotterB., Tellenbroker J., Kogerler P., Kurth D.G., Lehmann P., Schnablegger H., Schwahn D., Piepenbrink M. And Krebs B. (2002) *J. Am. Chem. Soc.* **124** 10489–10496.
3. Han Z., Zhao Y., Peng J., Feng Y., Yin J. and Liu Q. (2005) *Electroanalysis* **17** 1097–1102.
4. Brunow, G. (2001) *Methods to Reveal the Structure of Lignin, in Biopolymers* Vol. **1**: Lignin, Humic Substances and Coal (Series ed.: Steinbüchel, A., volume eds: Hofrichter, M. and Steinbüchel, A.), Weinheim:Wiley-VHC, ISBN 3-527-30220-4, pp. 89–116.
5. Tsakalakos T. (2003) Nanostructures and nanotechnology: Perspectives and new trends *NATO Science Series, II: Mathematics, Physics and Chemistry* **128** 1–36.
6. Wang X., Kang Z., Wang E and Hu C. (2002) *Materials Letters* **56** 393–396.
7. Sanchez c., Livage J., Launay J.P., Fournier M. and Jeannin Y.J. (1982) *Am. Chem. Soc.* **104** 3194–3202.
8. Laszlo J.A. (1999) Solubility and dye-binding properties of quaternized and peroxidase-polymerized craft lignin *Environmental technology* **20** 607–616.
9. Карнаухов А.П. (1999) *Адсорбция. Текстура дисперсных и пористых материалов* Новосибирск: Наука, с. 175.
10. Фейст М., Молчанов В.Н., Казанский Л.П., Торченкова Е.А. и Спицын В.И. (1980) *Журн. Неорг. Хим.* **25** 733–740.
11. Nakayama M., Ii T., Komatsu H. and Ogura K. (2004) *Chem. Commun.* 4 378–379.
12. Rochiccioli C., Fourer M., Frank R. and Thouvenos R. (1983) Inorg. Chem., **22** (1983) 207–216.
13. Dizhbite T., Telysheva G., Dobele G., Rossinskaya G., Belkova L. and Degtyarev E. (June 11–14, 2001) In: *Proc. Post- Symp. Workshop of the 11th International Symp. on Wood and Pulping Chemistry "Advanced methods for Lignocellulosics and Paper Products*" Grenoble (France) pp.69–72.
14. Anwar M., Hogarth C.A. and Lott K.A.K. J. (1989) *Mater. Sci.* **24** 1660–1664.
15. Sanchez C., Livage J., Launay J.P., Fournier M. and Jeannin Y. (1982) *J. Am. Chem. Soc.* **104** 3194–3203.

HIBRĪDU MATERIĀLU SINTĒZE UZ LIGNĪNA BĀZES, IZMANTOJOT α-KEGGINA TIPA POLIOKSOMETALĀTUS KĀ NEORGANISKOS "BŪVBLOKUS"

G. Teleševa, T. Dižbite, L. Jašina,
A. Andersone, N. Mironova-Ulmane,

Kopsavilkums

Dotajā darbā jauns hibrīds organisks–neorganisks materiāls tika sintezēts cieto fāžu mijiedarbības rezultātā starp augu izcelsmes polimēru lignīnu (elektrona donors) ar attīstīto π-konjugēto aromātisko struktūru, ar spēju veidot supramolekulāros asociātus) un $[SiMo_{12}O_{40}]^{4-}$ – α-Keggina tipa heteropolianjonu (elektrona akceptors), un tā struktūra ir noraksturota ar FTIR spektroskopijas palīdzību, elektrona – paramagnētisko rezonansi (EPR), Raman-mikroskopiju, elementu analīzi, termogravimetriju un N_2 sorbciju – desorbciju. Hibrīda materiāla sintēzei izmantots četraizvietota amonija katjonu saturošais lignīns, kas iegūts KĶI no komerciāla craft-lignīna "Curan" – sulfat-celulozes ražošanas multi-tonnāžas blakus produkta.