

RIGA TECHNICAL UNIVERSITY
Faculty of Material Science and Applied Chemistry
Department of Chemical Technology and Biological
Active Compounds

Anrijs VEROVKINS

Doctoral student of the Chemical technology program

**MODIFICATION OF WOOD BARK WITH
NITROGEN-CONTAINING FUNCTIONS**

Summary of Doctoral Thesis

Scientific supervisors:

Dr. habil. chem. Ģ. ZAKIS
Dr. habil. chem. F. AVOTIŅŠ

Riga 2013

UDK 630*81+ 661.728](043.2)

Ve 667 m

Anrijs Verovkins „Modification of wood bark with nitrogen-containing functions”. Summary of Doctoral Thesis.-R.:RTU, 2013.- 36 p.

Printed in accordance with the resolution of RTU P01 January 2, 2013, protocol No. 1

This work has been partly supported by the European Social Fund project „Importance of Genetic Factors in Formation of Forest Stands with High Adaptability and Qualitative Wood Properties”.



IEGULDĪJUMS TAVĀ NĀKOTNĒ



Doctoral thesis accomplished in:
Latvian State Institute of Wood Chemistry,
Riga Technical University Department of
Chemical Technology and Biological Active
Compounds.



ISBN 978-9934-8258-9-7

**DOCTORAL THESIS SUBMITTED
AT THE RIGA TECHNICAL UNIVERSITY FOR
ACQUISITION OF THE DOCTORAL DEGREE IN CHEMISTRY**

The Doctoral thesis is openly defended on 7 of March 2013 at 14:00 at the Riga Technical University, Faculty of Material Science Applied Chemistry, 14/24 Azenes Street, lecture room 272.

The Doctoral thesis is available at the library of Riga Technical University, 10 Kipsalas Street, Riga, LV-1659 and the National Library of Latvia, 5 Anglikanu Street, Riga, LV-1050.

OFFICIAL REVIEWERS

Dr.chem. Bruno Andersons
Latvijas Valsts Koksnes ķīmijas institūts

Professor, Dr. sc. Ing. Māris Daugavietis
Latvijas Valsts Mežzinātnes institūts „Silava”

Asoc. profesors Dr. chem. Andris Morozovs
Latvijas Lauksaimniecības Universitāte

APSTIPRINĀJUMS

Hereby I confirm that I have worked out the current Doctoral Thesis, which is submitted for consideration at the Riga Technical University for acquisition of Doctoral degree. The current scientific thesis is not submitted at others scientific institutions for acquisition of scientific degrees.

Anrijs Verovkins

Date: 02.02.2013.

The scientific thesis consists of introduction, literature review (chapters), experimental part (chapters), and evaluation of results (chapters), conclusions and list of references. The thesis is written in Latvian and consists of 129 pages. There are 48 figures, 32 tables, 9 formulas in the thesis. It covers list of 129 references.

ACKNOWLEDGEMENTS

My gratitude to Doctoral thesis supervisors Dr. habil. chem. Ģirts Zaķis and Dr. habil. chem. Fricis Avotiņš for the guidance, useful advices and understanding during the development of the work.

Special thanks go to researchers of Laboratory of Lignin Chemistry in Latvian State Institute of Wood Chemistry, especially to Brigita Neiberte for introducing me to science and wood chemistry, for sharing her experiences, and scientific discussions during the development of work and during the experiments and analysis. Big thanks also to Dr. habil. chem. Galiņa Šulga for scientific advice while mastering the new direction in polymer chemistry field.

I would like to thank my colleagues for practical support during the development of the thesis, for making the necessary analyses and helping to understand the results.

Thanks to my fellow-students Jānis Rižikovs, Vladimirs Biziks, Māris Puķe and Uldis Grīnfelds for setting the example in development of the doctoral thesis.

Thanks to Dr. chem. Bruno Andersons the Chairman of the scientific council of Latvian State Institute of Wood Chemistry for support and attracting the interest of young scientists to the institute.

Thanks to the director of Latvian State Institute of Wood Chemistry Dr. ing. sci. Aivars Žūriņš for trust and providing resources during the development of the thesis at Latvian State Institute of Wood Chemistry.

Sincere thanks to my family for their understanding, faith and moral support.

CONTENTS

ESSENCE AND URGENCY OF THE PROBLEM	6
SUMMARY OF THE DOCTORAL THESIS.....	12
RESULTS AND DISCUSSION	13
CONCLUSIONS	32
REFERENCES	34

LIST OF ABBREVIATIONS

DEEPA	- diethylepoxypropylamine
KL	- Klason lignin
hot H ₂ O	- hot water
Et-OH	- ethanol
C ₆ H ₆	- benzene
N	- nitrogen
N- bark yield	- yield of nitrogen containing bark
FTIR	- Fourier transform infrared spectroscopy
[O]	- active oxygen
PP	- polypropylen
Me	- metal

ESSENCE AND URGENCY OF THE PROBLEM

The mass of bark in standing timber volume is quite significant (10-20 %). Therefore, when speaking about complex and full value usage of tree organic matter, there must be knowledge about chemical composition of components in bark.

In terms of chemical composition bark is very unique biopolymer with various extractives content – soluble in organic solvents and water-soluble. Extractives are characterized by high content of phenolic functional groups; therefore bark can be modified by various chemical reactions and new derivatives can be obtained. For this reason bark of three different species caught our attention as the object of chemical (especially with nitrogen (N) containing functions) modifications

This thesis is a base for given dissertation which is based on studies previously carried out by LS Institute of Wood Chemistry Laboratory of Lignin Chemistry. Previous studies have showed that by modifying wood lignin with N containing functional groups, it is possible to obtain natural polymer derivatives with new qualities, including qualities with practical application [1-4]. Similar studies in bark chemistry have not been carried out yet.

In mechanical processing of wood timber is barked. Barks as residue are not completely managed yet, bark leftovers accumulate next to the processing plants, a portion of barks is exported, but mainly barks are used for energy needs. Those are potential raw material sources which could be industrially fully processed in the future. Only well-considered and thoughtful usage of wood resources could increase the economic efficiency of forest sector.

The diversity of organic matter in the bark (extractives and main components – lignin, cellulose) determines their potential application in various modifications in order to obtain new materials with new properties. Lignin in the bark can have different content of extractives which can interfere or promote the course of modifications and influence the results of modification methods which are based on pure wood lignin. That also will be investigated in the doctoral thesis.

Methods of obtaining amino-derivatives from lignin have been described in literature; up to 1.60 % N is introduced in form of amines when reducing its nitro compounds [5, 6]. Due to polyfunctionality of lignin, fixation of amine function is absolutely justified when lignin is directly treated with ammonia [7].

Different authors working in different temperature regimes have introduced, for example, 2.6-8.2 % nitrogen into hydrolysis lignin [8-12]. To obtain N containing lignin reactions with alkylamines are already known [13, 14]; active reagent, regarding different functional groups present in lignin, is ethyleneimine [15], up to 9 % N is introduced.

At the Latvian State Institute of Wood Chemistry under leadership of Dr. habil. chem. Ģ. Zaķis, methodology – patent [1] have been developed for lignin oxyalkylation with N,N-diethyl-2,3-epoxypropylamine (DEEPA), which

is obtained from epichlorohydrin and diethylamine. Amino derivatives are formed when diethylaminoepoxypropylamine and lignin are heated at 98°C in water solution. It has been calculated and experimentally proved that DEEPA reacts almost only with phenolic hydroxyl groups of lignin.

There is little work about N fixation in organic compounds in the presence of oxidants at low temperatures. In organic chemistry the formation of oligomers and polymers by way of oxidative coupling of phenols have been studied comparatively widely, while study about N containing compounds which are formed by reaction of lignin (also phenol) in presence of persulfate oxidant in ammonia-water solution as a discovery have been stated in Ģ. Zaķa inventor's certificate [16, 17]. It is known that persulfate oxidizes lignin destructively at acidic media. When reaction is carried out at alkaline (ammoniacal) media, already at room temperature high molecular weight compounds with organically contained N within it are formed.

Information found in the literature reports about different lignocellulose materials with reactive hydroxyl groups (wood, bark etc.) refining with nitrogen, mainly using ammonia (in autoclaves, at high temperatures, with or without atmosphere of oxygen or air). This is so-called oxidative ammonolysis – samples are treated with ammonia and oxygen at higher (200–250°C) or lower (100–150°C) temperatures, sometimes catalyst is also applied [18-25].

The study has been carried out about oxidative ammonolysis (1 hour in autoclave at 90-110°C) of individual parts of bark, outer bark and inner bark, after which N-content reaches 1.8 % in inner bark, 2.41 % in outer bark [19].

Urgency of the issue

In wood chemistry bark as a raw material for obtainment of various organic compounds has been studied scarcely. Therefore, when speaking about full and complex use of tree organic mass, there must be knowledge about the chemical composition of bark [26]. Bark is a material which is rich in phenolic compounds, containing active OH_{phen} (oxycarbonacids, phenolglycosides, lignans, flavanoids, flavanols, tannins etc.). The bark can be used for various modification reactions. For expanded study of bark application there was a number of modification techniques applied for introducing N. For the first time the bark was modified *in situ* with two different methods which allows obtaining nitrogen containing bark with new, practical qualities.

The aim of the work

The aim of the work is to modify the bark of the most common tree species in Latvia in order to find a wider range of application areas. For the first time, lignin will be modified *in situ* with two different modification methods, without isolating it from lignocellulose complex – bark. It would allow obtaining N-containing derivatives with new, practical characteristics, including development of environmentally friendly composite materials.

For the development of the thesis, the following goals were set out:

1. To experimentally establish the chemical composition of the components in bark of 5 most common tree species.
2. To develop optimal modification conditions which correspond to bark's maximum functionalization with highest yield of aminated product.
3. To obtain new amino-containing lignocellulose products and to investigate their properties.
4. To propose innovative applications for new products.

Scientific novelty of the work

For the first time study has been carried out about chemical composition of components in bark, as well as modification of lignin present in bark without isolating it from lignocellulose complex in 5 most popular tree species in Latvia - pine (*Pinus sylvestris* L.), spruce (*Picea abies* (L.) H.Karst.), aspen (*Populus tremula* L.), black alder (*Alnus glutinosa* (L.) Gaertn.) and grey alder (*Alnus incana* (L.) Moench). Possibility of increasing nitrogen content in wood bark using desoxyamination and oxyammonolysis reaction has been studied. Optimal modification conditions have been developed. New scientific knowledge has been acquired. New environmentally friendly materials suitable for development of composite sorbent materials have been synthesized. Usage of modified and unmodified bark in recycled polymer systems has been compared.

Practical importance of the Research

By-products of chemical processing of wood - lignin, cellolignin, also bark as wood processing residues (sawdust, bark), can be used as a raw material for new, and improved by modification, efficient, environmentally friendly product development.

One of the modified bark applications is the development of new, environmentally friendly composite materials. It would decrease the environmental pollution with non-biodegradable and polymeric materials produced from non-renewables.

Formation of the compositions with secondary polyolefins and with modified lignocellulose by different modification methods, using different output ratios of components, allows obtaining materials with a range of properties that are suitable for manufacturing wide range of products.

These compositions can be used for production of finishing materials and in a production of materials useful for household.

Approbation of the Research

The main scientific achievements and the results of the thesis were presented at 13 scientific international conferences, with a positive assessment. The results of the thesis theme is published in 25 printed works, including 12 articles (1.-2., 8., 13., 15.-17., 20.-24.) in scientific journals, 6 papers in conference proceedings (4.-5., 10.-12., 25).

1. Verovkins A., Neiberte B., Zaķis Ģ., Avotiņš F., Šulga G. Lignocelulozes slāpekļa atvasinājumi. 1. Mizu dezoksiaminēšana ar dietilepoksipropilamīnu // Latvijas Ķīmijas Žurnāls - 2012. - 3.
2. Verovkins A., Neiberte B., Zaķis Ģ., Avotiņš F., Šulga G. Lignocelulozes slāpekļa atvasinājumi. 2. Mizu oksiamonolīze // Latvijas Ķīmijas Žurnāls - 2012. - 4.
3. Verovkins A., Neiberte B., Shulga G., Zakis G., Shapovalov V., Valenkov A., Tavroginskaya M. The composites based on secondary polymers and amine containing bark as a filler // 11th Baltic polymer symposium (BPS-2011) - Pärnu, Estonia, September 21-24, 2011. Book of abstract, p. 55
4. Verovkins A., Neiberte B., Shulga G., Shapovalov V., Valenkov A., Tavroginskaya M. Modified bark as a filler in polymer composites // 11th European Workshop on Lignocellulosics and Pulp (EWLP-2010) - Hamburg, Germany. - August 16-19, 2010, 235-238. p.
5. Shulga G., Neiberte B., Verovkins A., Laka M., Chernyavskaya S., Shapovalov V., Valenkov A., Tavroginskaya M. Functionalization of wood by-products and their application in polymer composites // 14th European Conference on composite materials (ECCM-14) - Budapest, Hungary. - June 7-11, 2010. CD-version 1-5. p.
6. Shulga G., Neiberte B., Verovkins A., Laka M., Chernyavskaya S., Shapovalov V., Valenkov A., Tavroginskaya M. Effect of the modified wood based products on characteristics of the polypropylene composites // XVI International conference (MCM-2010) - Riga, Latvia. - May 24-28, 2010, Book of abstract, p. 181.
7. Verovkins A., Neiberte B., Shulga G., Shapovalov V., Valenkov A., Tavroginskaya M. Modified bark as a filler in polymer composites // Lignobiotech One, 1-st Symposium on Biotechnology Applied to Lignocelluloses - Reims, France. 28. march-1. april, 2010, Book of abstract, p. 136.
8. Zakis Ģ., Neiberte B., Verovkins A., Šāble I. Smago metālu sorbenti no baltalkšņa koksnes pārstrādes blakusproduktiem // Lapu koku audzēšanas un racionālas izmantošanas pamatojums, jauni produkti un tehnoloģijas: Valsts pētījumu programma, 2005-2009: rakstu krājums, LVMI „Silava”, LLU Meža fakultāte, LV koksnes ķīmijas institūts, SIA „Tipogrāfija „Pērse””, 2009, 175-179. lpp.
9. Verovkins A., Neiberte B., Zakis G., Sable I. Nitrogen-containing grey alder bark as a sorbent and filler // 9th Baltic polymer symposium (BPS-2009). – Ventspils, Latvia. – September 22-25, 2009, Book of abstract, p. 105.

10. Shulga G., Neiberte B., Verovkins A., Laka M., Chernyavskaya S., Shapovalov V., Valenkov A., Tavroginskaya M. The new polymer composites integrating modified wood originated products // *Italic5 -Science & Technology of Biomass: Advances and Challenges*. - Villa Monastero, Varenna (Lecco), Italy. - September 1-4, 2009, 185-188 p.
11. Shapovalov V.M., Valenkov A.M., Tavroginskaya M.G., Timoshenko V.V., Shulga G., Neyberte B., Verovkins A., Laka M., Chernyavskaya S., Shakels V. Composite Materials Made of Secondary Polymers and Modified Wood Wastes to Produce Moulded Strips and Sheetings // *Cooperation for Solution of Problem of Waste. Materials of VI International Conference*. - Kharkov, EcoInform, Ukraine. - April 8-9, 2009. 104-108 p. (In Russian).
12. Шульга Г., Нейберте Б., Веровкинс А., Лака М., Чернявская С., Шакелс В., Шаповалов В.М., Валенков А.М., Таврогинская М.Г., Тимошенко В.В. Модифицированные лигноцеллюлозные материалы для создания древеснополимерных композитов // *Материалы IV всероссийской научной конференции, Новые достижения в химии и химической технологии растительного сырья*. - Барнаул, Изд. Алтайского государственного университета. – 2009. - 204-207. с.
13. Шаповалов В.М., Валенков А.М., Таврогинская М.Г., Тимошенко В.В., Шульга Г., Нейберте Б., Веровкинс А., Лака М., Чернявская С., Шакелс В. Композиционные материалы на основе вторичных полимеров и модифицированных отходов переработки древесины, *Экологический вестник России*, 2009, N 10, 14-17.
14. Shulga G., Betkers T., Shakels V., Verovkins A., Neiberte B., Kolesnikovs G. Effect of wood species on the properties of lignocellulosic composites obtained with a lignin-based glue // 15th International conference, *Mechanics of composite materials 2008 (MCM-2008)*. Riga, Latvia, - May 26–30, 2008, Book of abstract, 242-243. p.
15. Verovkins A., Neiberte B., Shulga G., Sable I., Zakis G. Modifying of bark of wood as natural polymer by nitrogen containing functions // 8th Baltic polymer symposium 2008 (BPS2008) - Otepaa, Estonia. - May 13-16, 2008, Book of abstract, 71 p.
16. Verovkins A., Sable I., Neiberte B., Zakis G. Concerning determination of lignin in bark // *Latvian Journal of Chemistry*. - 2008. - 3. - 303-306. p.
17. Verovkins A., Neiberte B., Šāble I., Zaķis G., Shulga G. Latvijas raksturīgāko koku sugu mizas ķīmiskais komponentsastāvs // *Latvijas Ķīmijas Žurnāls*. - 2008. - 2. - 195-201. lpp.
18. Sapovalov V., Tavroginskaya M., Timoshenko V., Shulga G., Verovkins A., Laka M. Processing technologies for composite materials based on using waste polymers and lignocellulosics // *The Latvian-Belarus Bilateral Forum: Science. Innovation. Investments*. – Minsk, Belarus. - December 18-19, 2007, - 82-84 p.
19. Shulga G., Neiberte B., Verovkins A., Sable I., Brovkina J., Laka M., Chernavskaya S., Sapovalov V., Tavroginskaya M., Timoshenko V. Modified

- technical lignins and lignocellulosic wastes for obtaining of novel polymeric products // The Latvian-Belarus Bilateral Forum: Science. Innovation. Investments. - Minsk, Belarus. - December 18-19, 2007, - 72-74 p.
20. Šāble I., Zaķis Ģ., Neiberte B., Verovkins A. Ekstraktvielas Latvijas melnalkšņa (*Alnus glutinosa*) mizā // Latvijas Ķīmijas Žurnāls. - 2007, - 3. - 274-278. lpp.
 21. Verovkins A., Neiberte B., Zaķis Ģ. Latvijas apses (*Populus tremula*) koksnes kā celulozes ieguves izejvielas un tās delignifikācijas blakusprodukta - lignīna ķīmiskais raksturojums // Latvijas Ķīmijas Žurnāls. - 2007, - 2. - 189-193. lpp.
 22. Закис Г., Нейберте Б., Веровкин А. О методике аминирования лигнина диетил-эпоксипропиламином (ДЭЭПА) // Латвийский Химический Журнал. - 2006. - 4. - 395-396 с.
 23. Zaķis G., Neiberte B., Verovkins A., Smogol V. Amino derivatives of lignin. 4. Amination of lignin in composition of lignocellulose complex – obtaining of bile acid sorbent // Latvian Journal of Chemistry. - 2006. - 3. - 287-291 p.
 24. Shulga G., Nestore O., Neiberte B., Verovkins A., Betkers T., Belous O., Žukauskaite A., Ambrazaitene D., Lukošius M.. Collaboration research on a modified biopolymer as a soil stabiliser and amendment. – In Book: „Sustainable Development in the Baltic and Beyond”, Walter Leal Filho, A Ubelis, D. Berzina (eds.), PETER LANG GmbH 2006, v.23, 397-401 p.
 25. Zaķis G., Neiberte B., Verovkins A. Nitrogen – Containing Derivatives of Lignin and Their Applicability // 8th European Workshop on Lignocellulosics and Pulp. Utilization of lignocellulosics and by-products of pulping. - Riga, Latvia. - August 22-25, 2004, 451-455 p.

SUMMARY OF THE DOCTORAL THESIS

Introduction – the urgency of the Doctoral thesis is grounded, the aim and tasks are formulated, and also the basic statements of the Doctoral thesis are outlined.

The **First Chapter** is dedicated to the literature overview of chemical composition of components in bark. The main application areas of bark and modification with nitrogen are covered.

In the **Second Chapter** experimental part is covered. The preparation of samples and methodology to determine chemical composition of bark, as well as both developed methods of amination, oxyammonolysis and desoxyamination, is described.

The experimental course of the Doctoral thesis is shown in Figure 1.

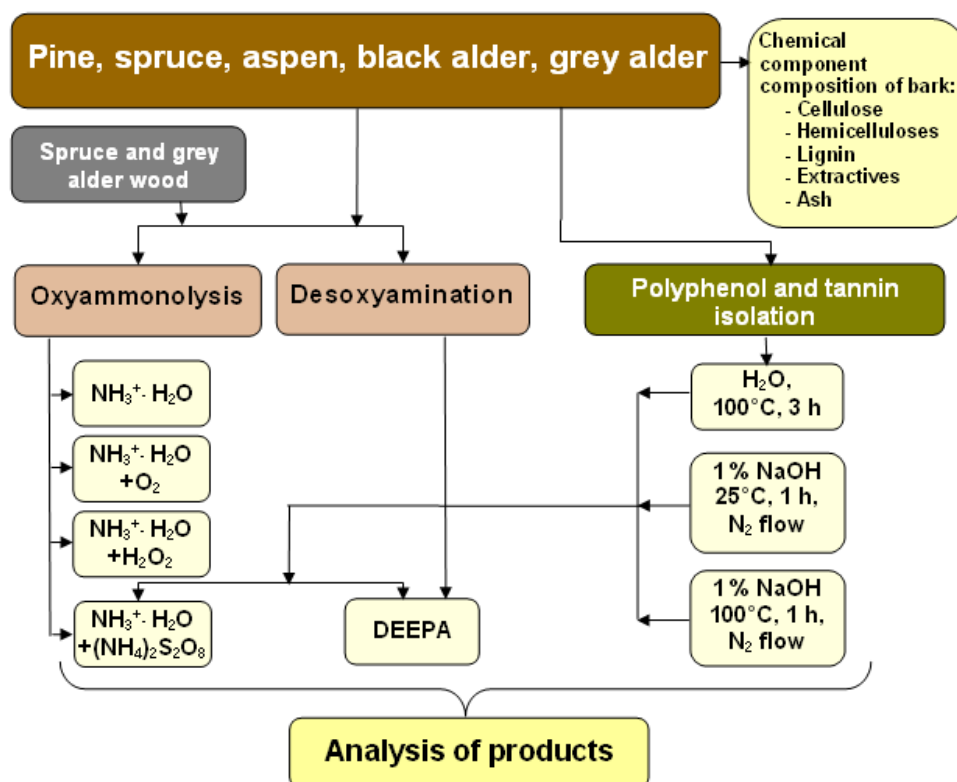


Figure 1. Course of the experimental methods applied

In the **Third Chapter** results of the experimental work about chemical composition of components in bark and amino containing lignocellulose products are analyzed and discussed.

Conclusions – the achieved results of the work are formulated and the most essential statements are defined.

In the **References** all the literature sources used in this work are listed.

RESULTS AND DISCUSSION

Comparing the obtained results of chemical composition of components in bark with results described in the literature, they are both in a comparable range. Authors have had different approaches in choice of the analytical methods. Different parts of bark or bark in whole were analyzed. Variation in the results can also be caused by usage of different extraction schemes. The content of cellulose in bark is significantly lower than content of Klason lignin, variation in results between (among) different tree species is not big.

Table 1.

Chemical component composition of bark

Species	Cellulose		Hemicelluloses		Holo-cellulose by per-acetic acid method, %	Klason lignin, %	–OCH ₃		Ash, %
	by Kirshner method, %	by per-sulphate method, %	by penthosans, %	by holo-celluloses, %			in Klason lignin, %	in bark, %	
Pine	18.1	22.4	5.9	17.3	35.4	51.2	6.52	3.59	2.4
Spruce	22.1	21.0	7.1	20.6	42.7	36.3	7.08	2.49	4.3
Aspen	25.2	22.3	16.7	20.4	45.6	42.6	11.8	2.44	4.2
Black-alder	22.5	18.4	15.4	20.7	43.2	49.1	6.74	3.74	2.8
Grey-alder	20.7	21.9	12.2	23.7	44.4	36.5	9.67	2.88	4.6

Our analyzed tree bark samples of coniferous and deciduous trees have high content of lignin. Knowing that, we can better solve the question of using bark as a by-product, for example, as soil structurizer in a form of mulch, as a soil supplements in bark composting (humic substances necessary for plants are formed from lignin).

As can be seen from Table 2, bark of the spruce (after extraction with organic solvent and hot water 42.4 %, after alkaline extraction – 83.2 %) is the richest with extractives. The highest amount of extract is reached when extraction with ethanol/benzene is applied: 22.2 % for aspen, 15.8 % for black alder, 15.1 % for grey alder, 11.2 % for spruce and 7.9 % for pine.

After comparing the results of conductometric titration of bark acetone extracts and alkaline extracts it is evident, that acidic phenolic type compounds are more efficiently extracted from bark using alkaline extraction.

It is important to find out - do phenolic type compounds present in alkaline extracts aminates with DEEPA in the same way as lignin in the bark. For this purpose isolated alkaline extract and bark residues were also aminated with DEEPA.

Table 2.

Content of extracts and functional composition after sequence extraction

Extractions stage	Extract		Conductometric titration of extracts		
	Yield, %	–OCH ₃ , %	OH _{phen} , %	OH _{COOH} , %	OH _{total} , %
1	2	3	4	5	6
Pine					
Et-OH / C ₆ H ₆	7.9	3.36	2.9	3.4	6.3
Et-OH	2.8	1.88	5.2	5.7	10.9
hot H ₂ O	4.4	1.05	2.3	4.8	7.1
1 % NaOH	36.0	1.42	6.6	6.5	13.1
Acetone*	11.2	2.93	3.3	2.4	5.6
Spruce					
Et-OH / C ₆ H ₆	11.2	8.97	4.5	4.65	9.1
Et-OH	3.8	5.34	5.8	5.3	11.1
hot H ₂ O	27.4	1.93	3.5	4.3	7.8
1 % NaOH	40.8	1.27	4.9	6.4	11.3
Acetone*	18.7	2.07	4.6	2.7	7.3
Aspen					
Et-OH / C ₆ H ₆	22.2	4.58	4.8	4.4	9.2
Et-OH	4.3	4.36	5.2	4.3	9.5
hot H ₂ O	7.3	2.72	4.2	3.2	7.4
1 % NaOH	30.5	2.31	5.1	8.4	13.5
Acetone*	21.0	2.30	2.5	2.9	5.4
Black alder					
Et-OH / C ₆ H ₆	15.8	5.09	5.5	5.5	11.0
Et-OH	10.7	3.49	6.4	5.9	12.3
hot H ₂ O	6.4	1.52	5.6	4.4	10.0
1 % NaOH	22.5	1.94	5.0	6.9	11.9
Acetone*	23.2	1.52	4.3	3.7	8.0
Grey alder					
Et-OH / C ₆ H ₆	15.1	2.51	2.7	7.7	10.4
Et-OH	4.2	5.39	3.0	9.0	12.0
hot H ₂ O	5.6	1.79	7.0	3.3	10.3
1 % NaOH	29.7	1.15	5.5	7.4	12.9
Acetone*	15.2	1.02	3.5	3.6	7.1

Remark: * previously not extracted material

Bark as a material rich in phenolic type substances (oxycarbonacids, phenolglycosides, lignans, flavanoids, flavanols, tannins etc.) can be used for various modification reactions with N introduction function. As we found out, the reaction environment can play important role. Oxidative process of phenols, including lignin can occur in strong alkaline media, which have an effect on yield and result of the modified product.

Wood and wood bark are closely related natural polymeric materials, and for this reason their chemistry is discussed together in general [27–30]. There are significant differences, particularly in aspect of organic and analytical chemistry, when composition of components of wood and bark is determined. The issue of lignin definition in bark and its quantitative determination is problematic and widely discussed. Using Klason method the analyzed material is hydrolyzed with 72 % H₂SO₄ at 25°C and gives the true content of lignin *in situ* in the case of wood, but it is not so when bark is analyzed as the presence of diverse extractives influence the course of the analysis.

One of the criteria to describe the „ligninic” criteria of isolated preparation could be the content of methoxy groups, as, in the case of wood, when lignin is unequivocally formed by guaiacyl (C₆H₄OH(OCH₃)) and syringil (C₆H₃OH(OCH₃)₂) elementary units. The content of the functional groups most typically for lignin is 17–22 % and 14–16 % in deciduous wood lignin and coniferous wood lignin, respectively [30].

Thus, attempts to assess the "true" lignin content by these parameters have been made. In conclusion, the content of OCH₃ is not adequate in wood and bark lignin and cannot be the foundation for the definition of lignin. Apparently it can be explained by the presence of other compounds containing OCH₃, for example lignans.

It can be seen from Table 3 that after bark extraction with organic solvents (ethanol-benzene, ethanol) and hot water, using Klason method the content of isolated preparation varies. Essential changes in the yield are observed after the additional extraction of bark with 1 % NaOH at the temperature 100°C. Additional extraction of aspen and black alder bark alone did not give any noticeable changes.

Table 3.

Residues of bark non-hydrolysable with 72 % H₂SO₄ after extraction

Species	Non-extracted bark, %	After extraction with organic solvent and hot water, %	After extraction with 1 % NaOH, %	After extraction with organic solvent, hot water and 1 % NaOH, %
1	2	3	4	5
Pine	67.4 (3.96)	65.3 (3.96)	56.0 (6.08)	51.2 (6.52)
Spruce	44.2 (8.31)	44.8 (4.18)	30.0 (7.83)	36.3 (7.08)
Aspen	45.6 (4.66)	39.9 (10.4)	31.8 (9.70)	42.6 (11.8)
Black alder	52.7 (7.13)	50.0 (7.58)	50.0 (9.64)	49.1 (6.74)
Grey alder	48.8 (6.63)	46.7 (2.78)	47.9 (2.70)	36.5 (9.67)

Note: in brackets is given –OCH₃ groups content, %

The polyphenols part that is insoluble in organic solvents and hot water passes in the alkali extract, and remains in the residue, non-hydrolyzable with 72 % H₂SO₄, by sorption on it (Table 3 Column 3 and 5, Table 2 Column 2).

By isolating lignin from unhydrolyzed residue using Klason method, the apparent lignin with increased yield is obtained. The content of $-\text{OCH}_3$ (Table 3 Column 3) is lower than in lignins isolated from bark after extraction with organic solvents and 1 % NaOH (Table 3 Column 5).

When carrying out additional extraction with 1 % NaOH, it is possible to increase the amount of the substances extractable from bark, which are represented mainly by phenols and polyphenol type compounds (phenolic acids, condensed tannins, as well as flavonoids and lignans). That is indicated by the results of conductometric titration listed in Table 2, namely, 1 % NaOH bark extracts contain much more $\text{OH}_{\text{phen-}}$ and OH_{COOH} groups containing substances than the extracted residue (Table 4).

Table 4.

Residues of bark after after extractions with 1 % NaOH (after extraction with organic solvent and hot water) and their conductometric titration

Species	Yield, %	$-\text{OCH}_3$, %	Conductometric titration		
			OH_{phen} , %	OH_{COOH} , %	OH_{kop} , %
1	2	3	4	5	6
Pine	54.6	4.26	6.0	0.9	6.9
Spruce	57.0	3.02	4.7	-	4.7
Aspen	69.6	3.28	3.2	1.0	4.2
Black alder	69.6	3.55	4.8	-	4.8
Grey alder	68.6	3.72	2.8	0.7	3.5

Therefore we recommend additional extraction of bark with 1 % NaOH, to eliminate the compounds that interfere with quantitative and correct determination of lignin.

Oxyammonolysis

Dynamics of nitrogen fixation in bark of the spruce was initially determined in ammoniacal media, with no oxidant, depending on exposure time. It was found that over 24 h bark of the spruce captures $\text{N}=2.61$ %, but after 48, 72 and 120 hours increase of nitrogen is progressive, but slow – up to 3.51 %.

When bark material was suspended in ammonia aqueous solution, the results of fixed N were lower than withstanding in gaseous ammonia (Table 5). Obviously, to fixate N there is a need for presence of oxygen, even at minimal level, which is less available for materials in liquid phase. After fixation of N from $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ without oxidant, weight loss is only 4–20 %.

In the case of both peroxide and persulfate the oxidant is active oxygen. In the case of peroxide when sample contacts with $\text{NH}_3^+ \cdot \text{H}_2\text{O}$, a rapid reaction takes place. Knowing that hydrogen peroxide in ammoniacal media at elevated temperature is used for obtainment of cellulose (wood delignification) [23], it is clear that also at room temperature peroxide as oxidant can act destructively on

lignin as it was observed in the experiment. It is showed in both fixation of N and yield of polymer (Table 5).

Table 5.

Fixation of nitrogen in wood bark when treated with 20 % $\text{NH}_3^+ \cdot \text{H}_2\text{O}$
(at presence of atmospheric oxygen)

Treatment time, h	in atmosphere		in vacuum		suspended in 50ml	
	N-bark yield, %	N content, %	N-bark yield, %	N content, %	N-bark yield, %	N content, %
Pine						
24	96	2.66	96	2.76	93	1.36
48	86	4.13	97	4.23	92	1.40
Spruce						
24	92	2.39	93	2.84	71	1.27
48	84	2.97	84	3.11	70	1.29
Aspen						
24	80	1.38	80	1.76	80	1.16
48	73	1.63	83	1.85	78	1.20
Black alder						
24	84	2.37	92	2.41	72	2.10
48	86	3.66	96	3.69	74	2.14
Grey alder						
24	84	2.75	84	2.84	62	1.33
48	77	2.80	83	3.11	61	1.36
Spruce wood						
24	99	0.32	99	0.34	99	0.38
48	97	0.33	98	0.36	99	0.42
Grey alder wood						
24	99	0.75	96	0.79	96	0.68
48	99	0.84	97	0.86	94	0.70

Consequently H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, which oxidizing effect is linked through active oxygen [O], in ammoniacal media act destructively on active component of bark matrix – lignin.

In all cases along with fixation of N, the weight loss of bark is observed which mainly is promoted by destructive effect of oxidant. Weight loss (49–54 %) is more distinguishable after impregnating with H_2O_2 and withstanding in ammoniacal media, also difference between withstanding in vacuum and in atmospheric pressure is not so pronounced (see Table 6).

When the bark of fast-growing aspen hybrid is treated in ammoniacal media with or without oxidants, the nitrogen yield was lower in comparison to aspen, for example, when treated with oxidant H_2O_2 in vacuum, the N-content was 1.03 %, in atmosphere 0.79 %. Also, at other treatment regimens the N-content was lower than for aspen. This is the evidence that nitrogen in the bark mainly fixates to lignin component in the cases we examined, but in particular hybrid

of aspen the content of nitrogen in the bark was lower – 32.8 % (against of 42.6 %).

Table 6.

Fixation of nitrogen in wood bark treated with 20 % $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ with oxidizers

Treat- ment time, h	$\text{NH}_3^+ \cdot \text{H}_2\text{O}$ (without oxidizer)		$\text{NH}_3^+ \cdot \text{H}_2\text{O}$ + O_2		$\text{NH}_3^+ \cdot \text{H}_2\text{O} +$ H_2O_2		$\text{NH}_3^+ \cdot \text{H}_2\text{O} +$ $(\text{NH}_4)_2\text{S}_2\text{O}_8$		
	N-bark yield, %	N content, %	N-bark yield, %	N content, %	N-bark yield, %	N content, %	Treat- ment time, h	N-bark yield, %	N content, %
Pine									
24	96	2.66	98	4.06	47	0.89	120	55	14.23
48	86	4.13	96	5.17					
Spruce									
24	92	2.39	90	3.00	47	0.87	120	46	9.20
48	84	2.97	89	3.24					
Aspen									
24	80	1.38	79	1.58	59	0.84	120	52	8.73
48	73	1.63	79	2.01					
Black alder									
24	84	2.37	94	3.70	54	1.36	120	59	11.85
48	86	3.66	92	4.78					
Grey alder									
24	84	2.75	78	2.71	52	0.98	120	37	8.67
48	77	2.80	76	5.02					
Spruce wood									
24	99	0.32	98	0.33	97	0.22	120	64	7.35
48	97	0.33	98	0.37					
Grey alder wood									
24	99	0.75	98	0.74	86	0.54	120	48	6.39
48	99	0.84	97	0.95					

Treatment with $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ / $(\text{NH}_4)_2\text{S}_2\text{O}_8$

Phenolic compounds can oxidize through phenoxy radicals and quinones to oligomers and polymers in acidic and neutral media. In alkaline media (in our case with $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ and persulfate as oxidant) process has been little-studied; dark, insoluble (or poorly soluble) precipitates similar to humic acids are formed. At the same time few benzene rings are splitted, accompanied with release of carbon dioxide, which can be more pronounced if temperature is allowed to increase.

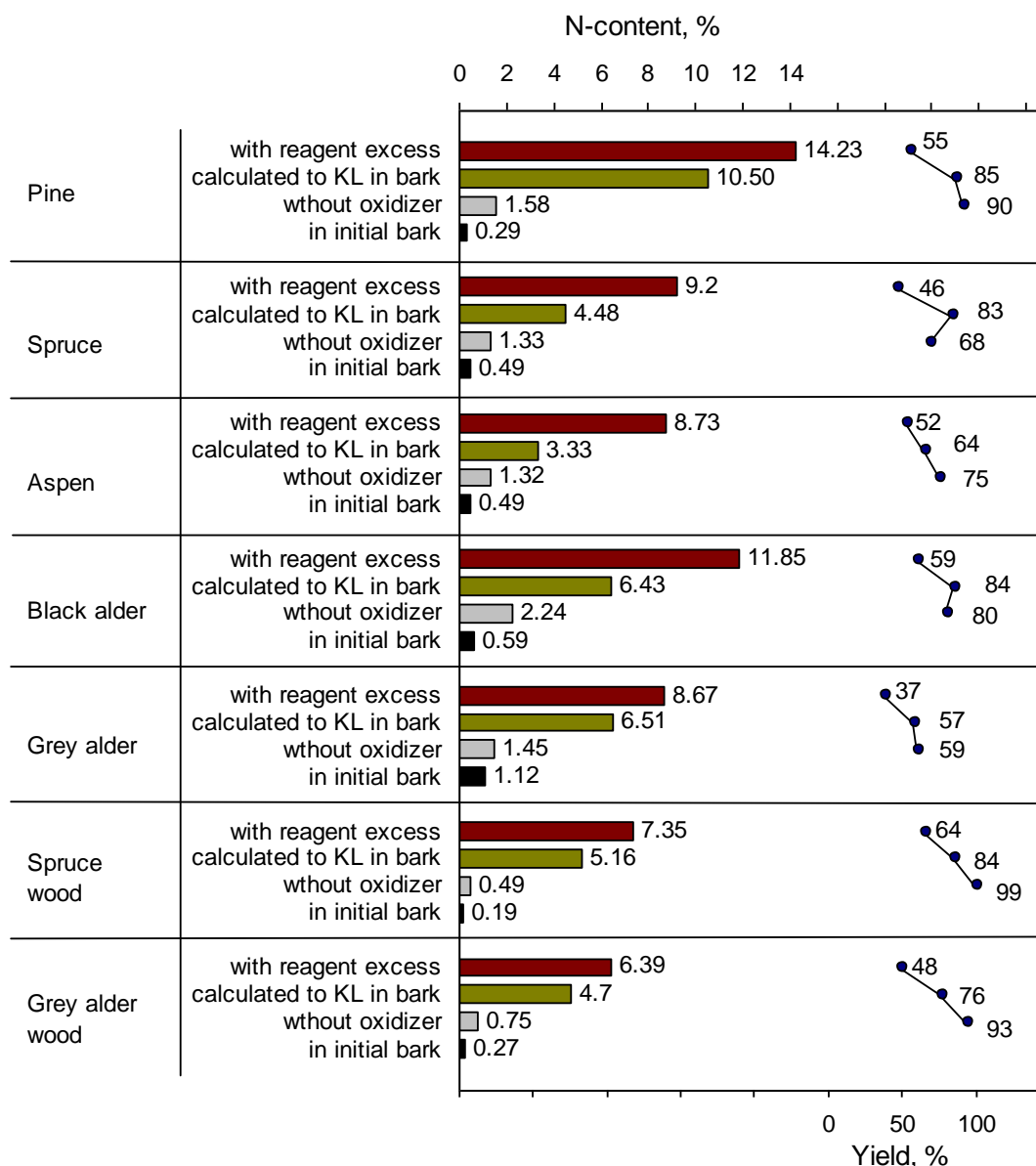


Figure 2. Schematic connection between nitrogen content and yield, bark treated with persulfate at ammoniacal media

Reagents required to perform ammoxydation in bark are calculated by module which is applied to 1 g of bark : 50 ml of 20 % $\text{NH}_3^+ \cdot \text{H}_2\text{O}$: 0.5 g [O] of $[\text{NH}_4]_2\text{S}_2\text{O}_8$ (with a concentration of 98 %). Sample is suspended in respective amount of $\text{NH}_3^+ \cdot \text{H}_2\text{O}$, with stirring and cooling applied, so the temperature does not exceed 20–22°C (if necessary flask can be cooled with water), then calculated amount of persulfate is added. Mixture is left for 120 hours with periodical mixing. Following by filtration of the polymeric product, treatment with solution of ammonia sulfate to prevent peptization of precipitate, and washing with water, drying and elemental analysis.

Treating bark material with $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ / $(\text{NH}_4)_2\text{S}_2\text{O}_8$, better results (higher N-content) were reached for pine and black alder, 14.23 and 11.85 % respectively (see Figure 2). Warming as well as foaming (this kind of bark contains higher content of lignin) were observed for this kind of bark when

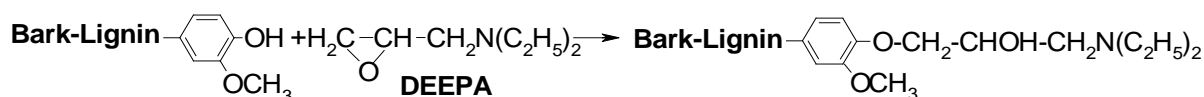
oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added. Exactly this type of bark shows the highest N-content when treated with DEEPA.

The possibilities of reducing the amount of reagents were also studied. Previously determined amount of reagents was taken on 1 g „pure” lignin, therefore, when bark is treated with respective amount of oxidant, there is excess amount of oxidant. The amount of oxidant is also enough to aminate low molecular weight phenols. After treatment with the amount of reagents that was precisely calculated in relation of Klason lignin in bark, the N-content decreases, but bark yield increases.

Overall, results show that the best fixation of nitrogen takes place in the system $\text{NH}_3^+ \cdot \text{H}_2\text{O}$ and oxidant, as well as the yield of obtained polymers is the most optimal

Desoxyamination reaction with diethylepoxypropylamine (DEEPA)

The reaction of lignin oxyalkylation with N,N-diethyl-2,3-epoxypropylamine (DEEPA) is suitable and improved for lignin amination in bark where the active amination component DEEPA reacts according to this scheme:



There is a good correlation observed between the content of phenolic hydroxyl group in raw material and N-content in obtained amino compounds.

The amount of active component needed for modification can be accurately calculated by Klason lignin content in bark. Also low molecular weight phenols existent in bark are capable to aminate. They can increase the balance of introduced N and yield of product. For this reason for bark amination the hydromodule where active component DEEPA is taken with excess (1 g bark: 1.5 ml DEEPA: 15 ml H_2O) was used. For comparison bark amination was also carried out using method that was developed for lignin when bark is treated with alkaline amination mixture [32].

Bark treatment with DEEPA was carried out using 3 methods:

Method 1. Sample treatment with synthesis mixture, active component DEEPA was not isolated from synthesis.

Method 2. After the synthesis using separating funnel active component DEEPA was separated. The ratio of 1 g bark: 1.5 ml DEEPA: 15 ml H_2O was used [32].

Method 3. The amount of active component DEEPA was precisely calculated to content of Klason lignin in bark.

Synthesis of amination agent diethylaminoepoxypropylamine (DEEPA)

At the first stage, 2 ml of water was added to diethylamine (71 ml) and epichlorohydrin (54 ml) to initiate the reaction. The mixture was stirred for 5–6 h at a temperature of 28–30°C to form diethylamino-oxy-propoxy-chloride. At the second stage, sodium hydroxide (32.5 g) and water (53 ml) were added.

DEEPA – the active component for amination reagent was formed. In the next day ~ 50 ml of water was added to dissolve the residue.

Synthesis scheme for active component DEEPA from diethylamine and epichlorohydrin:

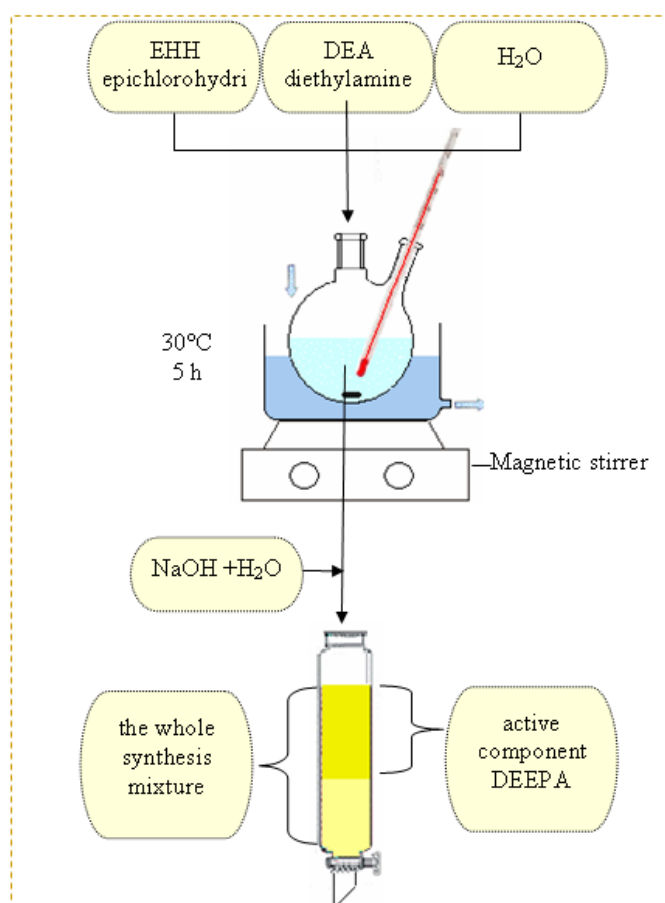
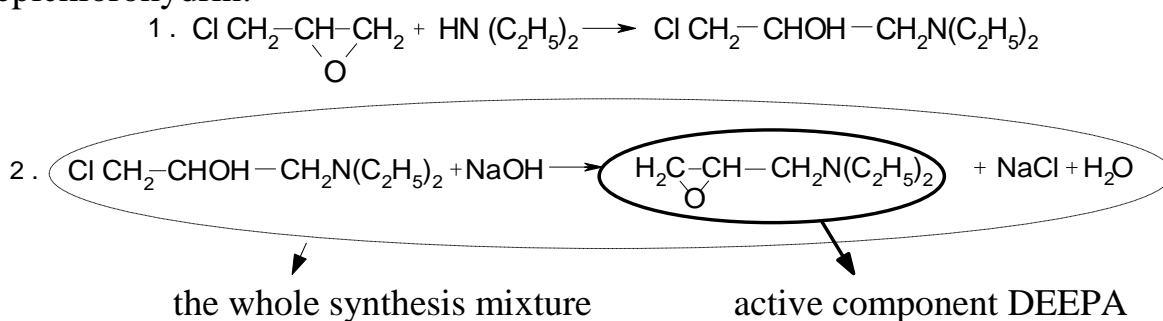


Figure 3. Synthesis scheme of amination reagent DEEPA

Sample treatment – modification: bark material with DEEPA was heated for 1 hour at 98°C in water bath. When the sample has cooled, it is washed with small amount of water, 1 % acetic acid and one more time with water. Afterwards the sample is air dried; further drying is carried out in a vacuum oven over P₂O₅ at 40°C. Then the yield of reaction is weighted and fixed N-content is analyzed.

Significant weight loss in range from 76 % to 50 % was observed when bark was reacted with alkaline amination synthesis mixture. Also the values of introduced N-content were low. The most suitable amination method with DEEPA was found. It is when the active component DEEPA was separated

from the whole synthesis mixture and bark was treated with excess of amination reagent DEEPA. As can be seen in Figure 4, the yield in many cases significantly increases.

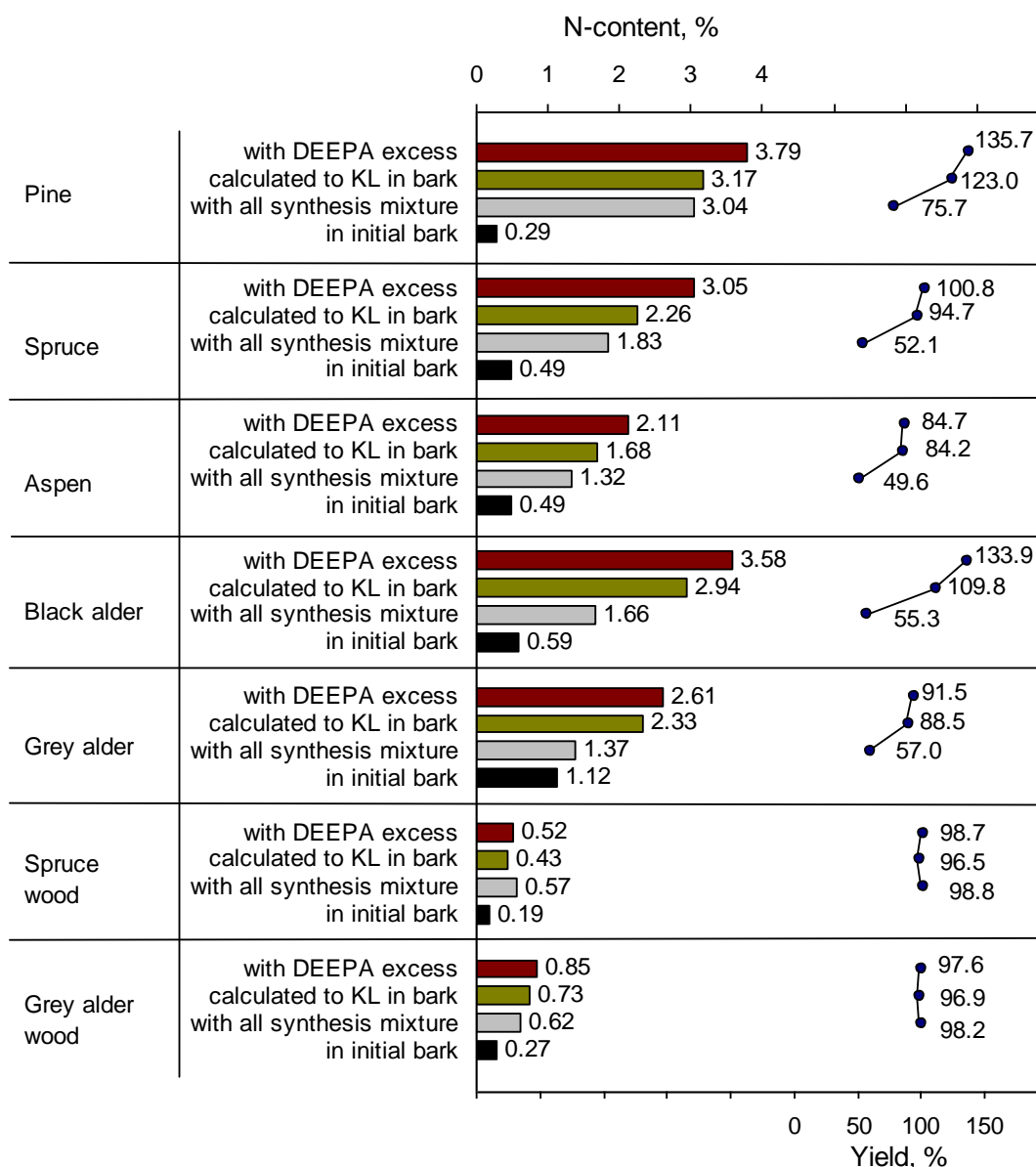


Figure 4. Schematic connection between nitrogen content and yield, bark treated with DEEPA

Effect of bark particle size on fixed N-content was studied when mulch of pine bark aminated with DEEPA was prepared. When bark particle size significantly increases, the introduced N-content decreases from 3.84 % (bark particle size < 1mm) to 3.35 % (2–5 mm) and 2.9 % (5–7 mm). It is planned to continue this study by increasing the duration of treatment.

Bark of aspen hybrid was treated with DEEPA where active component was taken with excess: 1.5 ml DEEPA: 15 ml H₂O. The introduced N-content was only 1.36 % in comparison to bark of aspen 2.11 %, because the aspen hybrid bark and aspen bark have different contents of lignin.

The results of modification indicate that there are significant differences in the main parameters of wood and bark – the yield of aminated product and N-content introduced by using different methodologies. Wood shows lower results but more stable.

Along with the N-content also the C, H and O changes. So in the result of bark amination with DEEPA also wide range of N-containing functional groups in form of amide, imide, imine, ammonium and nitrile can be introduced in bark.

The presence of amino groups in lignin products treated with diethylaminoepoxypropylamine is proved using conductometric titration when on direct and reverse titration curves the titration region of amino groups appears in accordance with the ongoing reactions [32]:

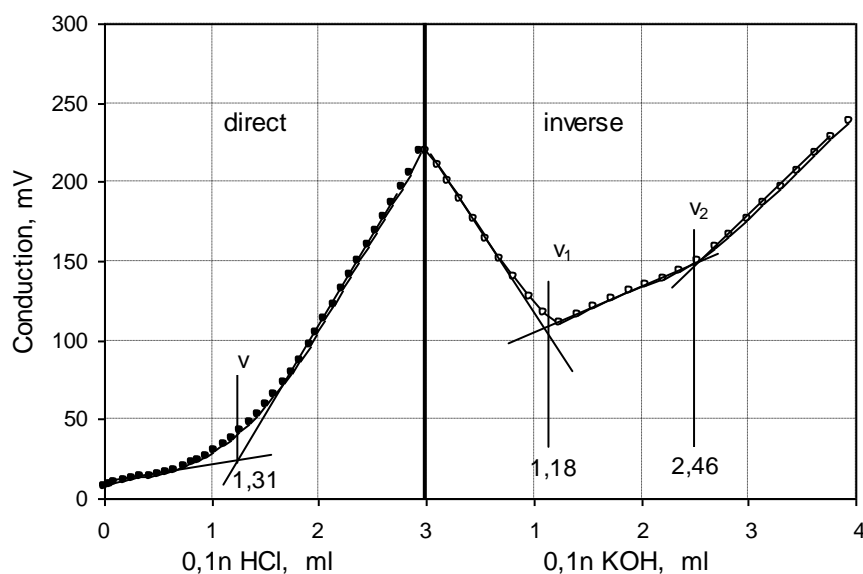
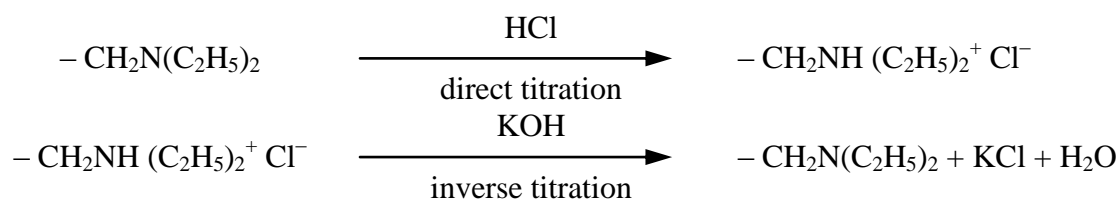


Figure 5. Direct and inverse titration of pine bark aminated with DEEPA

Lignin that has not been isolated from bark, but has been treated with DEEPA in relation to other components has constrained condition. Therefore the titration curves are not so accurate. The inverse titration curves are more precise (Table 7, column 4). Titration curves display a plateau which characterizes the titration region of amino groups.

Nitrogen amine content calculated by it is not equal to the total elemental nitrogen content; consequently not all nitrogen is fixated in form of amine functions.

Table 7.

Distribution of nitrogen introduced with DEEPA in bark samples

Species	N-total elemental, %	N-amine by titration		N in other form, % (2–4)	OH _{phen} (by hemo- sorption method), %	OH _{phen} (calculated by N total)*, %	OH _{phen} (calculated by N amine)*, %
		direct, %	inverse, %				
1	2	3	4	5	6	7	8
Pine	3.84	1.83	1.79	2.05	4.70	4.68	2.20
Spruce	3.10	1.28	1.51	1.59	3.94	3.78	1.00
Aspen	2.11	0.81	0.81	1.30	2.77	2.57	0.98
Black alder	3.58	1.67	1.88	1.70	4.30	4.36	2.21
Grey alder	2.61	0.86	1.12	1.49	4.49	3.18	1.20

Note: $N = 1,4 [OH] / 1,7 + 0,129 [OH]$ [32],

$$\text{or } [OH]^* = \frac{1,7[N]}{1,4 - 0,129[N]}, \% .$$

In the case of pure lignin there is a good correlation between OH_{phen} and introduced N-content.

$$[OH]^* = \frac{1,7 \cdot [3,84 / 100]}{1,4 - 0,129 \cdot [0,0384]} = 4,68\% \quad (\text{after N-total});$$

$$[OH]^* = \frac{1,7 \cdot [0,0181] \cdot 100}{1,4 - 0,129 \cdot [0,0181]} = \frac{3,077}{1,3977} = 2,20\% \quad (\text{after N-amine}).$$

Results in Table 7 (Columns 6 and 7) suggest a good correlation between content of phenolic hydroxyl groups in output bark (Column 6) where content of phenolic hydroxyl groups has been determined experimentally using chemisorption method, and theoretically calculated OH_{phen} (Column 7) using total nitrogen content introduced in bark (Column 2). Knowing that phenolic hydroxyl groups mainly react with DEEPA and knowing the content of OH_{phen} in bark lignin, it is possible to calculate the amount of nitrogen introduced in other monomeric phenols (Table 7 Column 5).

It is evident that in all the procedures related to the alkaline treatment of bark, reaction environment plays significant role. The best fixation of nitrogen and yield of obtained polymer product is the most optimal in bark amination system where active component DEEPA was taken with excess (1 g bark : 1.5 ml DEEPA : 15 ml H₂O). The results demonstrate complex content of bark rich in extractives requires an adjustment in existing methodologies and to develop new methodologies for chemical analysis and modification of bark.

FTIR spectra taken for bark treated with different modification methods show changes in obtained products. The presence of diethylaminooxypropoxy group in aminated bark is monitored by the appearance of new peaks in 3000-2800 cm⁻¹ region (C–H bonds fluctuation band) characteristic to methyl, methylene-groups which are included in propyl and ethyl groups.

In comparing spectra of modified pine bark and spectra of unmodified sample, it is evident that in spectra for sample treated with DEEPA, as well as in sample obtained by ammoxydation with persulfate, the fluctuations corresponding to C=O in the intensity $\sim 1735\text{ cm}^{-1}$ region do not appear anymore. We believe that this part is related to soluble aminated compounds which aminated product does not contain anymore. An analogous picture is observed in the spectra of modified wood samples.

In all bark samples treated with ammonia / persulfate there is decrease in absorption intensity at $\sim 1270\text{ cm}^{-1}$ which is characteristic for lignin guaiacyl structure. In oxidative ammonolysis that is associated with the formation of new N hetero-function in the result of demethoxylation. Also, the author has observed previously described occurrences [34].

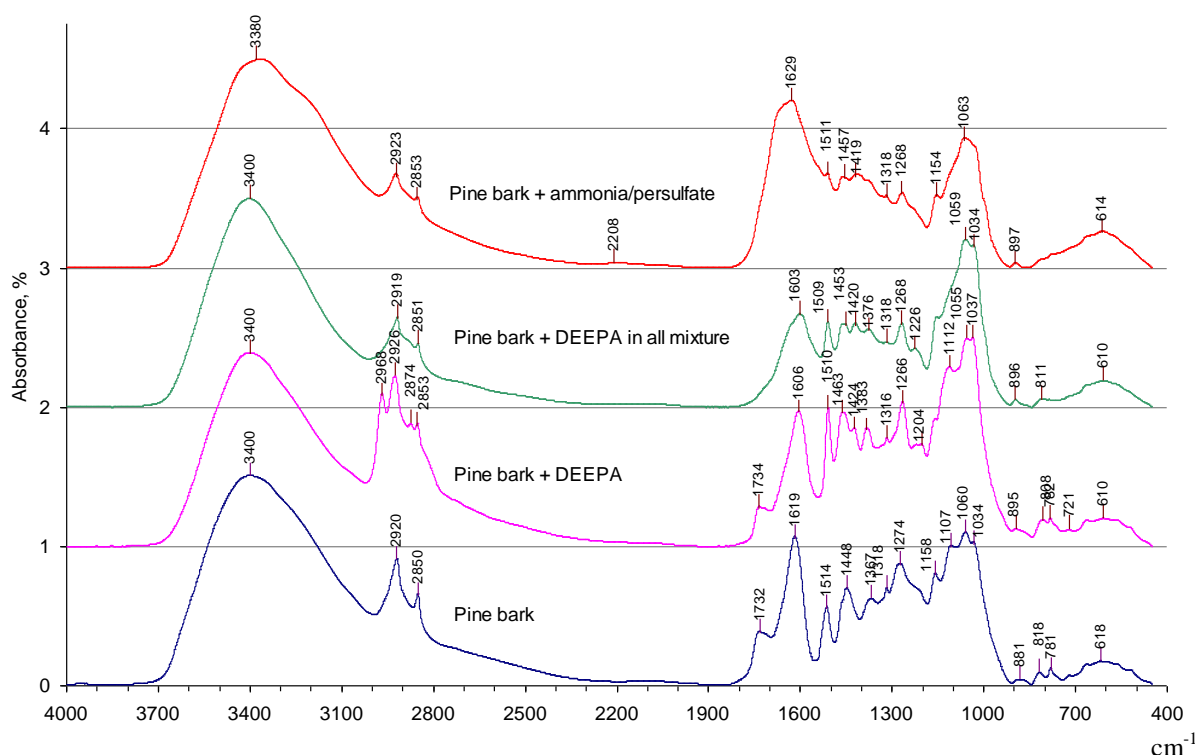


Figure 6. FTIR spectrum of pine bark for modified and initial sample

Comparing the spectrums of initial and modified spruce and grey alder wood spectrum bands in the region $3000\text{--}2800\text{ cm}^{-1}$, no changes or shifts in peaks are observed. Significant decrease of absorption intensity at 1300 cm^{-1} is observed for pine sample modified with ammonia / persulfate.

FTIR spectrum reveals that as the result of modification some of the absorption bands typical for lignin are lost. Instead there are wide bands of aminated lignin in the region $4000\text{--}2000\text{ cm}^{-1}$ and $1700\text{--}600\text{ cm}^{-1}$ (with weakly expressed maximums) which are characteristic for heterocyclic compounds (very stable and are not hydrolyzed by acids).

Nitrogen containing polyphenols and tannins

Tannins are rich in OH_{phen} groups which are reactive groups in formation of N functions as we have proved before. Tannins are physiologically-active compounds with medical properties. It is possible that their amino derivatives, similarly as “Deapolin” from lignin”, will show increased activity as enterosorbents [2, 3].

The yields of preparations extracted from bark of spruce and black alder with different regimes, as well as results of analysis are summarized in Table 8.

Table 8.

The yield and functional characterization of polyphenols extracted from bark with different extraction regimes

Extractions regime	Polyphenols extract			Klason lignin in insoluble part or in residue after extraction %
	Yield, %	OCH ₃ , %	Tannin, %	
Spruce				
H ₂ O-100°C-3 h	37.4	2.00	36.2	32.63
1 % NaOH-25°C-1 h	38.8	1.58	30.9	29.11
1 % NaOH-100°C-1 h	39.5	0.84	29.2	30.03
Black alder				
H ₂ O-100°C-3 h	22.3	1.51	19.2	49.73
1 % NaOH-25°C-1 h	30.1	0.93	26.1	49.94
1 % NaOH-100°C-1 h	33.4	1.21	36.1	49.84

The results show that the polyphenols from the bark can be equally well extracted using neutral solvent - bark is boiled for 3 hours in hot H₂O or with 1 % NaOH for 1 hour at 100°C. 1 % alkali is effective solvent for polyphenols extraction. Practically in 1 hour at room temperature (with mixing and N₂ flow) all polyphenols are extracted from the bark.

In a lot of industrially used bark the content of tannin usually is in a range of 10-20% [35].

Table 9.

Fixation of nitrogen in bark polyphenols by treating them with DEEPA

Extractions regime	Polyphenols extract		Insoluble part or residue after extraction	
	Yield, %	N-total, %	Yield, %	N-total, %
1	2	3	4	5
Spruce				
H ₂ O-100°C-3 h	98.9	4.08	103.3	1.35
1 % NaOH-25°C-1 h	98.3	3.95	102.8	1.37
1 % NaOH-100°C-1 h	97.9	3.79	100.6	1.22

Black alder				
H ₂ O-100°C-3 h	99.6	4.74	108.1	2.94
1 % NaOH-25°C-1 h	99.4	4.96	105.3	2.72
1 % NaOH-100°C-1 h	99.1	4.80	111.1	2.55

Polyphenols extract extracted using different methods presents the same chemical composition (Table 9). This is indicated by the equal N-content in fractions that have been aminated with DEEPA, as well as similar yields.

Table 10.

Titration of amines in polyphenols extracts treated with DEEPA

Extractions regime	N-total, %	N-amine by titration	
		direct, %	inverse, %
1	2	3	4
Spruce			
H ₂ O-100°C-3 h	4.08	3.42	4.56
1 % NaOH-25°C-1 h	3.95	2.41	3.75
1 % NaOH-100°C-1 h	3.79	2.18	4.56
Black alder			
H ₂ O-100°C-3 h	4.74	3.36	4.79
1 % NaOH-25°C-1 h	4.96	2.46	3.50
1 % NaOH-100°C-1 h	4.80	2.07	3.70

The results of Table 10 show:

1) Fixed N in the form of amines can be determined in water and alkali extracts treated with DEEPA using conductometric titration method. In direct titration (water) the dissociation of amino groups is weak and their titration does not happen quantitatively. In reverse titration the formed amine salt form releases an equivalent amount of HCl, which more accurately reflects the titration curves and results. In future other aminated bark preparations (raw bark ~100 mg) firstly will be treated with a fixed amount of 5.0 ml of 0.1 N HCl, with frequent stirring will be left for 24 hours and the salt formed will be titrated with 0.1 N KOH.

2) Almost all introduced N is fixed in a form of amine function in water extracts of spruce and black alder (Table 10, Columns 2 and 4) during amination. Introduced N can also be found in other forms of N fixation in alkali extracts of black alder bark.

3) It is evident that after the total introduced N-content aminated alkali and water extracts contain significant amount of phenolic type compounds with non-ligninic character that are capable to aminate. Alkali extracts could also contain a small amount of aminated lignin component.

4) If we compare the results of Table 10 and 11, it is obvious that total N in aminated extracts of hot water and 1 % NaOH is several times higher than the total N in aminated residuals, which confirms the presence of polyphenols in extracts.

5) Water and alkali at elevated temperature are equally good phenolic type compound extractant. It is indicated by stable N-content in obtained aminated extracts and residues.

Table 11.

Fixation of nitrogen with DEEPA in aminated bark residue

Extractions regime	N amine by titration, %	N total (by elemental analyze), %	N in sample (by another connection way), %	KL in residue, %
1	2	3	4	5
Spruce				
H ₂ O-100°C-3 h	1.39	1.35	0.04	32.63
1 % NaOH-25°C-1 h	1.07	1.37	0.30	29.11
1 % NaOH-100°C-1 h	0.78	1.22	0.44	30.03
Black alder				
H ₂ O-100°C-3 h	1.22	2.94	1.72	49.73
1 % NaOH-25°C-1 h	1.24	2.72	1.48	49.94
1 % NaOH-100°C-1 h	1.11	2.55	1.44	49.84

Sorption experiments of heavy metals using grey alder and pine bark aminated with DEEPA (practical application)

Due to retained submicroscopic structure (physical sorption) and the ability of aminated bark to form inner coordination complexes with heavy metals (chemical sorption), the bark can be used to absorb the heavy metals systems containing them (for sewage, for sorption of heavy metals in rainfall through mulch in top layers of soil in city greenery).

The ability of sorption of grey alder`s and pine`s bark modified with DEEPA heavy metals ions Cr^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} (using water solutions of metal salts $\text{CrN}_3\text{O}_9 \cdot 9 \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$) individually and in a mixture Cr^{3+} , Cu^{2+} , Zn^{2+} has been analyzed and compared to modified wood using atomic absorption spectrophotometer Shimadzu (Figure 7).

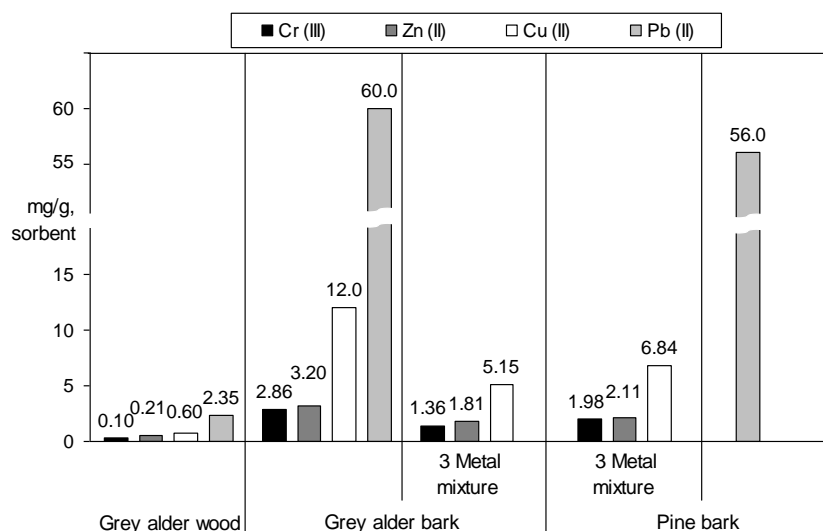


Figure 7. Sorption of heavy metals using aminated wood and bark sorbents

Note that not always there is maximal ion concentration in purified objects. There is also sorption competition between ions. In sorption competition the determining factors are pH and the presence of other contamination agents.

It has been found out that:

1) In comparison to modified wood, the activity of modified bark is significantly higher for sorption of heavy metals (see chart).

2) The ability of bark to fix metals is changing in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cr^{3+}$. Similar results were obtained in [36] and other studies.

3) Sorption materials obtained from modified bark of black alder have high sorption activity of Pb^{2+} and Cu^{2+} .

In collaboration with Institute of Mechanics of Metal-Polymer Systems, NAS of Belarus the utilization of used sorption materials is studied with emphasis in resourceful development of technology for composite material production of lignocellulosic waste and recycled polymers.

The possibility of obtaining polymer composite materials with metal containing lignocellulose filler has been practice-proven. The necessary experiments to develop the recipe for obtainment of composite materials with high filler concentration have been carried out.

Composites filled with functionalized bark and recycled polypropylene

The modification of wood, including bark and individual components using them as fillers in synthetic polymers is interesting topic from theoretical point of view, but more interesting from practical application point of view for derived products. Experience shows that even relatively less active technical lignin can be used in acquisition of synthetic resins and plastic materials. It is mainly possible due to lignin aromatic units with active phenol hydroxyl groups. In other authors point of view [37], non-isolated lignin from wood (analogously bark), linked in united ligno-hydrocarbon complex with other

reactive functional groups, is more active than isolated preparations. According to these authors proto lignin has enhanced activity related to the ability to form chemical bonds between lignin and synthetic polymer macromolecules.

In framework of bilateral Latvian-Belarus scientific project (2007–2009) the possibilities to obtain composite materials based on natural polymers were studied. In order to do that it was necessary to study the compatibility of materials in composite, to develop methods for modification of lignocellulosic materials including a method for physical-chemical modification of bark filler. Also, it is necessary to study the structural formation of filler-binder particle interfacial layer.

Bark material unmodified and modified with DEEPA was used to obtain composites, as well as wood sawdust with particle size 0.5–0.8 mm. A powder secondary polypropylene (PP) was used as binder for thermoplastic polymers at processing temperature that did not exceed the thermo-oxidizing degradation of wood. With PP content greater than 50 % there is no longer any significant improvement in physical-mechanical properties. At the same time, if composition contains less than 50 % of lignocellulose (bark, wood sawdust) filler, there is a decrease in exploitation properties and increase in product cost. For these composites 50 / 50 % was chosen as the most optimal composition PP / lignocellulosic filler ratio.

For bark composites unmodified and modified with DEEPA the following recipes:

1. Secondary PP (50 %) / unmodified bark (50 %).
2. Secondary PP (50 %) / modified bark (50 %).
3. Secondary PP (50 %) / utilized bark sorbent - 1 Me: Pb^{2+} (50 %).
4. Secondary PP (50 %) / utilized bark sorbent - 3 Me: Cr^{3+} , Cu^{2+} , Zn^{2+} (50 %).
5. Secondary PP (50 %) / modified bark (25 %) / pine wood (25 %).

As shown in the graphs (Figure 8) modified bark filler composites are characterized with relatively high physical-mechanical characteristics in comparison to samples with unmodified bark. Grey alder composites elongation at break and tensile strength increases ~ 50 % in comparison to composite from unmodified bark. The elevated values of elongation at break testify that there is an additional plasticizing of the composite materials' components. Whereas elongation at break and impact strength practically did not change for both bark composite samples. In some indicators bark of grey alder show 30–50 % higher results than pine bark, except for modulus of elasticity in tension.

It is known that physical-mechanical properties of composite, wood sawdust / bark / polymer, improve when content of wood sawdust in sample is increased [38–40]. That also reflects in our results.

The elongation at break significantly increases up to 73 % for samples obtained from modified pine bark / pine wood sawdust / PP in comparison to samples from modified pine bark / PP. Composites have been obtained from used, heavy metal containing sorbents: sorbent containing Pb^{2+} from bark of

pine and grey alder, sorbent containing Cr^{3+} , Cu^{2+} , Zn^{2+} from bark of pine and grey alder. Both these composites showed good physical-mechanical properties.

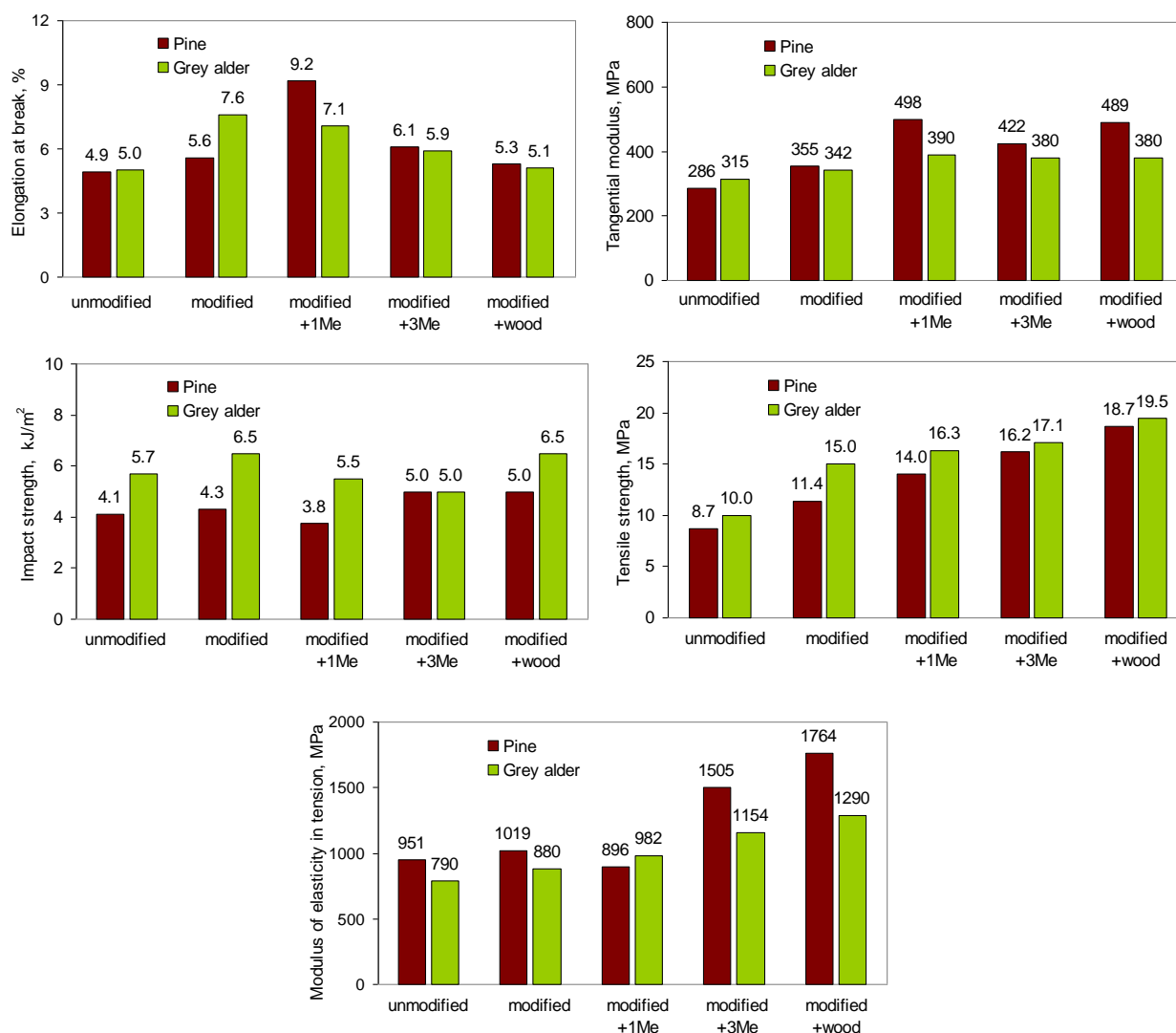


Figure 8. Physico-mechanical properties of diferent obtained polymer composites

CONCLUSIONS

1. It has been established that classical method (Klason method) for quantitative determination of wood lignin cannot be directly applied for bark analysis, because the latter contains considerable amounts of extractives, which affects the course of analysis and results. It is recommended to carry out consecutive extraction with organic solvents, hot water and additional extraction with 1 % NaOH at 100°C, mainly to isolate phenols and polyphenols in bark. After such extraction lignin content in residue in analyzed samples is: pine bark 51.2 %, black alder – 49.1 %, aspen – 42.6 %, grey alder – 36.5 %, spruce – 36.3 %.
2. For the first time bark lignin has been modified *in situ* without isolating it from lignocellulose complex. Fixation of nitrogen has been established in bark samples of five different Latvian tree species, applying treatment with ammonia without pressure and using a variety of oxidants.
3. It has been established that bark unlike wood show enhanced ability to chemically fix nitrogen. Mainly it is caused by high content of lignin in bark with active aromatic OH groups, as well as the presence of other phenolic type compounds.
4. Desoxyamination reaction with diethylepoxypropylamine (DEEPA) allows introducing tertiary diethylamino groups in bark. The impact of reaction environment has been determined: in strong alkaline media oxidation of phenols, including lignin can happen which affects the yield and properties of modified product. The ultimate bark amination regime is: 1 g bark: 1.5 ml DEEPA: 15 ml H₂O.
5. The amount of nitrogen introduced into bark is different (introduced N amount differed per tree) when modification reaction with diethylepoxypropylamine using hydromodule where active component DEEPA was taken with excess was carried out. The ability of bark to fix nitrogen is ranked in following order: pine > black alder > spruce > grey alder > aspen. N-content was the highest in bark of pine and black alder 3.84 and 3.58, respectively with product yield 135 % and 134 %, respectively.
6. Nitrogen fixation in wood bark using oxyammonolysis in ammoniacal media (20 % NH₃⁺·H₂O) has been studied; barks were treated with different oxidants at low temperatures (25°C). There are few studies in literature relating this topic. It has been found out that high content of nitrogen can be introduced in oxyammonolysis reactions when ammonia persulfate (NH₄)₂S₂O₈ is used as oxidant. The highest N-content is introduced in pine and black alder bark: 14.32 % and 11.85 %, respectively, at relatively low yield of obtained polymer.
7. The sorption properties of bark are improved in the result of modification. Carrying out modification *in situ* the bark's submicroscopic structure and

physical sorption ability have been maintained. Aminated bark has also the chemical sorption ability, i.e., ability to form inner coordination complexes with heavy metals. As a result bark can be used for heavy metal sorption from systems containing them (sewage, for sorption of heavy metals in rainfall through mulch in top layers of soil in city greenery). The ability of bark to bind heavy metal ranks in the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$.

8. Modified bark material contains nitrogen in form that can be easily taken in by plants. This kind of bark mulch can be used as soil structurizer, drainage and bio-fertilizer (as the result of biodegradation the content of humus increases in soil)
9. Modification with two different modification methods allows to obtain nitrogen containing bark materials with new qualities, including qualities with practical application, including development of environmentally friendly sorbents and composite materials.

REFERENCES

1. Zaķis Ģ., Neiberte B., Mekša M. LR Pat. P-93-422, 1993, N5213.
2. Смоголь В. А., Максимова Л. А., Майоре А.Я, Закис Г.Ф. Специфическая сорбционная активнос нового энтерального растительного сорбента // Latvijas Zinātņu Akadēmijas Vēstis. B, - 1993. - 1. - 78-79 с.
3. Neiberte B., Zaķis Ģ., Čipnīte V., Grigiškis S. Aminolignīni kā aktīvi smago metālu jonu sorbenti // Latvijas Ķīmijas Žurnāls - 2001. - 1. - 68-70. lpp.
4. Zakis G., Neiberte B., Verovkins A. Nitrogen – Containing Derivatives of Lignin and Their Applicability // 9ht European Workshop on Lignocellulosics and Pulp. Utilization of lignocellulosics and by-products of pulping. - Riga, Latvia. 2004. - 451-455 p.
5. Nachikama Y., Okabe J. Reduction of nitrolignin. Technol. Repts Osaka Univ. - 1956. - 6. - 171-177 p.
6. Мищенко Г.Л., Вацуро К.В. Синтетические методы органической химии. – Москва: Лесная промышленность, 1982. - 440 с.
7. Ковальчук Б.В., Форостян Ю.Н. Превращение гидролизного лигнина подсолнечной лузги в водно-аммиачной среде // Химия природ.соед. - 1972. - № 3. - 380-383 с.
8. Форостян Ю.Н., Ковальчук Б.В. О взаимодействии гидролизного лигнина подсолнечной лузги с аммиаком // Химия природ.соед. - 1972. - № 1. - 136-138 с.
9. Форостян Ю.Н., Кузмичева О.Н. О взаимодействии гидролизного аммонизи-рованного лигнина с бромом // Химия природ.соед. - 1976. - № 4. - 562-563 с.
10. Форостян Ю.Н., Секацкий А.А., Дубник Л.И. Аммонолиз гидролизного лигнина для получения преобразователя ржавчины // Гидролизн. и лесохим. пром-сть. - 1979. - № 2. -14-15 с.
11. Форостян Ю.Н., Широков О.В., Форостян Е.М. Аммонолиз техни-ческих лигнинов // Химия природ.соед. - 1987. - № 2. - 275-278 с.
12. Шорыгина Н.Н., Изумрудова Т.В., Хованская А.П., Тычина В.Д., Михайлов Н.П. Амминирование лигнина // Тр. ЛТА. - 1960. - Вып.91. - 211-216 с.
13. Namala S.L., Koivunen S.T., Kontturi A.K., Sarkkinen V.J. Menetelma alkanoliamiini-lignosulfonaattien valmistamiseksi. Pat. 60874 Finl. - 1981.
14. Doughty J.B. Reactions of ethylenimine with alkali lignins // Forest Prod. J. - 1963. - 13. - 9. - 413-415 p.
15. Mikawa H., Sato K., Takasaki C., Ebisawa K. Studies on the cooking mechanism of wood. XV. Mannich reaction on lignin model compounds and the estimation of the amount of the simple guaiacyl nucleus in thiolignin // Bull.Chem.Soc. - Japan. 1956. - 29. - 259-265 p.
16. Закис Г.Ф., Лудзиша А.С., Нейберте Б.Я. Действие на лигнин песульфатов. 4. Окисление некоторых простых моделей лигнина

- персульфатом в аммиачной среде // Химия древесины. - 1974. - № 15 - 110-114 с.
17. Закис Г.Ф., Нейберте Б.Я. Окисление лигнина и модельных фенолов аммиачным раствором // Химия древесины. - 1983. - № 2. - 56-59 с.
 18. Нгуэт Н.Т.М. Изизучение окислительного аммолиза коры сосны обыкновенной (*Pinus sylvestris* L.) // Автореферат. - 2004. - 161 с.
 19. Meier D., Ante R., Faix O. Catalytic hydropyrolysis of lignin: Influence of reaction conditions on the formation and composition of liquid products // Bioresource Technology. - 1992. - Vol. 40.(2) - 171-177 p.
 20. Schröder H. Bodenkunde in Stichworten. Verlag Ferdinand Hirt. Unterägeri, 1984. – 160 p.
 21. Casebier R.L., Sears K.D. Aminated sulfite derivatives of coniferous barks. US Pat. 3966708, 1976.
 22. Meier D., Zuniga-Partida V., Ramirez-Cano F., Hahn N.C, Faix O. Conversion of technical lignins into slow-release nitrogenous fertilizers by ammoxidation in liquid phase // Bioresource technology. - 1994. - Vol. 49.(2) - 121-128 p.
 23. Capanema E.A., Balakshin M.Yu, Chen C.L., Gratzl J.S., Kirkman A.G. Oxidative Ammonolysis of Technical lignins. 2. Effect of Oxygen Pressure // Holzforshung. – 2001. - 55. - 405-412 p.
 24. Efanov M.V., Averin R.Yu. Peroxide-ammonia delignification of pine wood // Chemistry of Natural Compounds. - 2004. - Vol. 40.(2) - 172-175 p.
 25. Jiang Qi-Pei, Zhang Xiao-Yong, Mo Hai-Tao, Li Zuo-Hu. Ammoxidation of Straw-Pulp alkaline lignin by Hydrogen Peroxide // Environmental Progress. - 2006. - Vol. 25.(3) - 251-256 p.
 26. Verovkins A., Neiberte B., Šāble I., Zaķis Ģ., Shulga G. Latvijas raksturīgāko koku sugu mizas ķīmiskais komponentsastāvs // Latvijas Ķīmijas Žurnāls. - 2008. - 2. - 195-201. lpp.
 27. Fengel D., Weneger G. Wood – Chemistry, Utrastructure, Reactions. - Germany: Verlag Kessel, 2003. - 613 p.
 28. Rowell R.M. Handbook. Wood chemistry and wood composites. - Routledge: USA. Taylor & Francis, 2005. - 473 p.
 29. Уайз Л.Э., Джан Э.С. Химия древесины Т.2, пер. с англ. под ред. Богомолова Б.Д. – Москва – Ленинград: Гослесбумиздат, 1960. - 356 с.
 30. Hon D.N.-S., Shiraishi N. Wood and cellulosic chemistry – 2nd ed., rev. and expanded. - New York and Basel: Marcel Dekker, Inc., 2001. - 914 p.
 31. Zakis G.F. Functional analysis of lignins and their derivatives. – Atlanta, GA: TAPPI Press. 1994. - 94 p.
 32. Закис Г.Ф., Нейберте Б.Я. Аминопроизводные лигнинов 3. Реакция лигнинов с диэтилэпоксипропиламином // Латвийский Химический Журнал.- 2000. - 4. - 89-96. с.
 33. Закис Г., Нейберте Б., Веровкин А. О методике аминирования лигнина диэтил-эпоксипропиламином (ДЭЭПА) // Латвийский Химический Журнал. - 2006.- 4. - 395-396 с.

34. Capanema E.A., Balakshin M.Yu, Chen C.L., Gratzl J.S., Kirkman A.G. Oxidative Ammonolysis of Technical lignins. 2. Effect of Oxygen Pressure // *Holzforshung*. – 2001. - 55. - 405-412 p
35. Браунинг Б.Л. Химия древесины. – Москва: Лесная промышленность, 1967. - 415 с
36. Shin E.W., Karthikeyan K.G., Tshabalala M.A. Adsorption mechanism of cadmium on juniper bark and wood // *Bioresource Technology*. - 2007. - 98. - 588-594 p.
37. Химия и использование лигнина. Коллектив авторов. - Рига: Зинатне. Акад. Наук ЛатвССР Ордена трудового красного знамени Институт Химии древесины. 1974. - 480 с.
38. Safdari V., Khodadadi H., Hosseinihashemi S.K., Ganjian E. The effects of poplar bark and wood content on the mechanical properties of wood-polypropylene composites // *Bioresources*. - 2011. - Vol. 6.(4) - 5180-5192 p.
39. Kord B. Effect of bark flour content on mechanical properties of wood plastic composites // *World Applied Sciences Journal*. - 2011. - Vol. 14.(3) - 398-401 p.
40. Pedieu R., Riedl B., Pichette A. Properties of birch outer bark panels reinforced with wood strands in the surface layers // *Bioresources*. - 2008. - Vol. 4.(2) - 771-788 p.