Project no:SNS-97

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FINAL PROJECT REPORT

Please notice that the size of text sections in the form can be adjusted if needed.
The length of the final report should not exceed 5 pages.

1. Projekt titel	
2. Title of project	Wood hemicelluloses for surface modification of fibrils, fibers and boards
3. Project leader /coordinator (name, address, telephone, telefax. e-mail)	Coordinator: Prof. Maija Tenkanen Department of Applied Chemistry and Microbiology P.O. Box 27, FIN-00014 University of Helsinki phone: + 358-9-19158410, fax: +358-9-19158475 maija.tenkanen@helsinki.fi Reserach partners: Prof. Paul Gatenholm Chalmers University of Technology Department of Materials and Surface Chemistry, Polymer Technology Chalmers, SE-41296 Göteborg, Sweden pg@pol.chalmers.se Prof. Kristiina Oksman Norwegian University of Science and Technology Department of Engineering Design and Materials Rich. Birkelands vei 2b, 7491 Trondheim, Norway Present address: Luleå University of Technology Wood Science and Technology Forskargatan 1, SE- 93187, Skellefteå, Sweden kristiina.oksman@ltu.se
4. Time schedule	The project started 1 /1 2005 and ended 31/12 2007
5. Project cost	SNS-grant: 249 486 NOK (2005) 69 500 € (2006-2007) Total project cost: 981 481 NOK (2005) 277 492 € (2006-2007)

6. The purpose of the project/main problems/hypotheses addressed	The increased use of renewable materials is considered as one of the key issue of the sustainable development. It has been estimated by the National Research Council in the USA that 25 % of the produced organic chemicals should originate from renewable materials in 2020. Vast quantities of lignocelluloses are produced every year, constituting the main source of renewable organic material available on earth. Wood is conventionally used as a building material, for fibre production for paper, board and textiles, and energy. Due to objectives to decrease the use of fossil hydrocarbons refining of biomass into useful products is becoming an increasingly important issue. The aim of the joint project was to evaluate possibilities for conversion of hemicelluloses (xylans and mannans) separated from forest sources as well as from waste streams from the pulp and fibre production and agriculture into novel surface materials for nanocomposites, fibers and packaging materials. Hemicelluloses are the second most abundant plant polysaccharide after cellulose and they comprise about one third of wood material. However, compared with cellulose and starch, utilization of hemicelluloses has been mainly neglected. The future target is an increased utilization of these valuable polymers for example to replace some currently used oil based materials.
7. Brief description of the research plan and of possible larger deviations from the plan	The goal of this multidisciplinary project was to evaluate possibilities for conversion of hemicelluloses separated from forest and agricultural sources into novel surface materials for fibrils, fibres and packaging materials. Hemicelluloses are the second most abundant polysaccharide after cellulose and they comprise about one third of wood material. The future target is an increased utilization of hemicelluloses for example to replace some currently used oil based packaging materials. The project included experiments with different native, enzymatically or chemically modified xylan and mannan samples, in order to evaluate their potentials for further development of applications. The results provide valuable information for novel utilization of forest resources. The project partners were: Prof. Maija Tenkanen (Finland), Prof. Paul Gatenholm (Sweden) and Prof. Kristiina Oksman (Norway, moved to Sweden during the project). Novozymes provided the non-commercial enzyme for xylan modification. The project was carried out mostly according to the plan. As 67% national funding is required, the parallel national projects also influenced the execution of the project. The research carried out focused mainly on evaluation of effect of molecular structure of hemicelluloses (xylan, mannan) on the film formation and the material properties of films and composites obtained. Xylan films were studied in Prof. Gatenholm´s and Tenkanen´s group. This also included research visit between the groups. Prof. Tenkanen´s group studied films from mannans, too, and was responsible of enzymatic modifications. Production and characterization of cellulose nanocrystal (whiskers) and nanocomposites were studied in Prof. Oksman´s group. Combining hemicelluloses and cellulose nanocrystals was researched in collaboration with all three groups.

8. Results (max 2 pages)	Xylans were extracted from several raw materials (hardwoods and cereals) and their features were investigated in detail. Spruce galactoglucmannan (GGM) was obtained from Åbo Akademi, Finland. Some xylans and mannans used were of commercial origin. Xylan and mannan films were prepared by casting from aqueous solution and their mechanical properties, morphology, equilibrium moisture content, and permeability properties were measured. The films were homogeneous and the mechanical properties could be controlled by an addition of plasticizers, such as glycerol and sorbitol. Tensile testing showed that barley husk arabinoxylan films had a higher stress at break and strain at break as compared to aspen glucuronoxylan films at corresponding plasticizer contents. Arabinoxylan from oat spelts formed weaker films. It was also shown that water is a good plasticizer for highly substituted arabinoxylans, which formed self-supporting films without external polyol. The water content of the films depends on the chemical structure of xylan, such as branching and type of substituents. The films from less substituted xylans (aspen, oat spelts) were semicrystalline, whereas films from highly substituted arabinoxylans were mostly amorphous. Spruce GGM did not form cohesive films without addition of polyol as a plasticizer. The GGM films were weak showing low mechanical properties. This is most probably due to the low molecular weight of GGM. Other mannans (konjac glucomannan, locust bean and guar galactomanannas) studied as comparison showed much better mechanical properties, the best being konjac glucomannan, which forms strong and transparent films also without external polyol. GGM films were semicrystalline and had somewhat higher crystallinity than films from konjac glucomannan. Both xylan and mannan films showed rather low oxygen gas permeability and are thus potential in packaging of oxygen-sensitive products. The lowest oxygen permeability was measured with barley arabinoxylan and sorbitol plasticized hardwood xylan. Content and selection of plasticizer affected the permeability properties as films with high content of glycerol possessed highest oxygen permeability. The same was also noticed with water vapour permeability as the use of sorbitol resulted in more effective water vapour barrier properties than the use of glycerol. It was also noticed that mechanical softening of xylan films occurred at higher relative humidity when sorbitol was used instead of glycerol. The water vapour permeability of xylan films was moderate and higher than that of films from synthetic polymers. Permeation of sunflower oil through the films was not detected. In order to get information on how polymer structure (degree of branching, degree of polymerization) affects properties of xylan and mannan films, specific modifications were carried out. Acid and enzyme hydrolysis were compared for controlled debranching of arabinoxylan. Acid hydrolysis resulted in concomitant xylan depolymerization with arabinose removal whereas enzymatic modification with alpha-arabinofuranosidase was specific and modified only the degree of branching. Degree of branching of galactomannans was also modified enzymatically with a specific alpha-galactosidase. In addition mannanase was used for controlled decrease of polymerization of galactomannans. All modified xylans and mannans formed cohesive films. Debranching resulted in clear increase in the crystallinity of arabinoxylan films. The decrease in arabinose content also resulted in lower oxygen permeability of the films. All films were strong and relatively stiff, but showed variations in strain at break.

8. Results (max 2 pages)	The moderately debranched film with an Ara/Xyl ratio of 0.37 had highest strain at break among all the films tested, yet was stiff and strong. This material also exhibited yielding, and had stress/strain behaviour similar to synthetic semi-crystalline polymers, with a tendency to strain induced crystallization. Such combination of mechanical properties combined with oxygen barrier properties is very attractive for packaging applications. Films from debranched galactomannans (from guar gum) showed also higher mechanical properties than films from highly branched galactomannans analogously to the behaviour of arabinoxylan films. Interestingly, moderate reduction of the degree of polymerization of high molecular weight galactomannans resulted in improved mechanical properties. The stability of arabinoxylan films was followed for 5 months. The tensile properties of glycerol-plasticized films clearly changed during storage, whereas those of sorbitol-plasticized films were more stable. Work on cellulose nanocomposites was targeted on the production methods of cellulose nanocrystals, characterisation of nanostructured materials and to develop nanocomposites for different uses. The results from process optimization of nanocrystals showed that acid hydrolysis with sulphuric acid resulted in nanocrystals with negative charged surfaces and that it was difficult to neutralize these crystals. Acid hydrolysis with hydrochloric acid resulted in crystals which were easier to neutralize and these crystals also showed better thermal stability compared to sulphuric acid hydrolysed crystals. To be able to characterize the produced nanocrystals and nanocomposites different characterisations methods were tested. Birefringence between crossed polarized films was found to be a suitable method to determine if the process of nanocrystals was successful. Transmission electron microscopy (TEM) was found to be the best method for characterization of the size of nanocrystals (diameter 5 nm, length of 200 nm). Field emission scanning electron microscopy (FE-SEM) was a suitable method for a quick overview of the materials to visualize how nanocrystal agglomerated in different polymers. Atomic force microscopy (AFM) was also a potential characterization method for the prepared nanocrystals and composites. The sample preparation of nanostructured materials for microscopy was found to be difficult especially for the composites materials in which the nanocrystals are imbedded in a polymer matrix. It was found that a cryo-ultramicrotome was needed for that purpose as a common ultra-microtome diamond knife smeared the polymer on the surface and thus covering the nanocrystals in the sample. The nanocomposites produced were mixtures of cellulose nanocrystals with starch, cellulose acetate butyrate, polyvinyl acetate and mannan as matrix materials. Mixing of cellulose nanocrystals (5 and 15%) to mannans did not significantly change the mechanical properties of films. However, microscopy observations (optical microscope, SEM) revealed clear morphological changes compared to the pure mannan films. New methods of compounding nanocellulose (long bacterial cellulose) with xylans were also developed. The dispersion of nanocellulose in xylan matrix is critical for mechanical properties of nanocomposites. Nanocellulose was found toreinforce xylan and films/composites with good flexibility were prepared using arabinoxylans as matrix.

9. What advantages has been gained by the Nordic collaboration (i.e. by the cooperating partners, use of the project results)	New research collaboration between the project partners was established. Novozymes´s role was to supply specific non-commercial enzyme for xylan modifications. The student exchange visits between the research partners were very successful and productive. Erik Sternemalm from Chalmers visited Prof. Tenkanen´s group in summer 2007 and Kirsi Mikkonen from Helsinki visited Prof. Oksman´s group in autumn 2007. Both visits resulted in joint publication of which one is published and the other one is under preparation. The collaboration in the SNS-97 project resulted in also a new joint three year project (2008-2010) between Prof. Gatenholm and Prof. Tenkanen in the WoodWisdom-Net – programme. Collaboration with Prof. Oksman will be continued regarding the cellulose nanocrystal (whiskers) and nanocomposites. Prof. Oksman and Prof. Gatenholm have also a new national collaboration project on nanocomposites (2008-2009) financed by Kempe Stiftelserna. In Finland the plan is to continue research on the utilization of hemicelluloses in packaging and coating applications in the new national Forest Cluster project starting in 2009.
10. Publications and other communication activities (please list scientific reports, more popular reports and other communication activities)	<u>Presentations</u> *Results (including those obtained in the preproject) presented in in the 229th ACS Nat. Meet., San Diego, California, USA, 13-17 March, 2005:* Mikkonen, K., Helén, H., Hyvönen, L. & Tenkanen, M. Effect of chemical structure on mannan-based films (talk) Gröndahl, M.H. & Gatenholm, P. Modulation of the molecular structure of arabinoxylans for optimal barrier films (talk) Karlsson, P. & Gatenholm, P. Formation and diffusion of xylan nanoparticles into cellulose fibril networks (talk) Oksman,K., Bengtsson, M, Gatenholm, P. & Dammstrom, S., Green composites: The latest development from micro to nanoscale (talk) *Presentations in the Workshop on Innovative Biopolymers, Fiskebäckskil, Sweden, August 20-21, 2006:* Tenkanen M, Using enzymes for tailoring plant polysaccharides - xylans and mannans (talk) Oksman K, Nanocomposites based on cellulose (talk) Bengtsson M, LeBaillif M & Oksman K, Extrusion and Mechanical Properties of Highly Filled Cellulose Fibers-Polypropylene Composites (poster) *Other presentations:* Mikkonen, K., Helén, H., Talja, R., Willför, S., Holmbom, B., Hyvönen, L. & Tenkanen, M. Biodegradable films from mannans, 9th European Workshop on Lignocellulosic and Pulp (EWLP), Vienna, Austria, 27-30 August 2006, pp.130-133 (talk and proceedings) Tenkanen, M., Soovre, A., Heikkinen, S., Jouhtimäki, S., Talja, R., Helen, H. & Hyvönen, L. Production and properties of films from cereal arabinoxylans, Italic 4 – Science & Technology of Biomass: Advances and Challenges, Roma, Italy, 8-10 May 2007, pp. 70-73 (talk and proceedings) Mikkonen, K., Yasav, M., Willför, S., Hicks, K. & Tenkanen, M. Blend films from spruce galactoglucomannan and konjac glucomannan, Production, Functionalization and Analysis of Hemicelluloses for Sustainable Advanced Products, March 19-20, 2007, Hamburg, Germany, pp. 57-58 (talk and extended abstract) Mikkonen, K.S., Yasav, M.P., Willför, S., Hicks, K.B. & Tenkanen, M. Films from spruce galactoglucomannans blended with poly(vinyl alcohol), corn arabinoxylan and konjac glucomannan, (Bio)degradable Poly-mers from Renewable Resources, Wien, Austria, November 18-21, 2007 (poster) Mathew, A., Oksman Niska, K., Nanocomposites Based on Renewable Materials, 1st International conference on composites materials, Port Elisabeth, South Africa, December 6-9, 2007.

10. Publications and other communication activities (please list scientific reports, more popular reports and other communication activities)	Oksman Niska, K., Nanocomposites Based on Renewable Resources, COMAT 2007, 4th International Conference on Composite Science and Technology, Rio de Janeiro, Brazil, December 9-13, 2007. Oksman Niska, K., Biobased Nanocomposites, Invited speaker, BIORESINS 2007, Atlanta, Georgia, USA, November 29-30, 2007. Oksman Niska, K., Nanocomposites Based on Renewable Materials, BIOPOL 2007, 1st International conference on biodegradable polymers and sustainable composites, Alicante, Spain, October 3-5, 2007. Mikkonen, K.S., Mathews, A., Peura, M., Xu, C., Serimaa, R., Willför, S., Tenkanen, M., & Oksman, K. Mannan-cellulose nanocomposites, 229th ACS Nat. Meet., New Orleans, Louisiana, USA, April 6-10, 2008 (talk) <u>Publications</u> Bengtsson, M., Gatenholm P., & Oksman, K., The effect of crosslinking on the properties of polyethylene/wood flour composites, *Composite Sci. Technol.* 65 (2005) 1468-1479. Damström, S., Salmén, L. & Gatenholm, P., The Effect of moisture on the dynamical mechanical properties of bacterial cellulose/glucuronoxylan nanocomposites, *Polymer* 46 (2005) 10364-10371. Gröndahl M., Gustafsson A. & Gatenholm P., Gas phase surface fluorination of arabinoxylan films, *Macromolecules* 39 (2006) 2718 – 2721. Bondeson D, Kvien I & Oksman K, Strategies for preparation cellulose whiskers from micro-crystalline cellulose (MCC) as reinforcement in nanocomposites, in *Cellulose Manocompo-sites: Processing, Characterization and Properties*. Ed. K. Oksman and M. Sain, ACS Symposium Series, Vol 938, Oxford Press, 2006. Karlsson P., Roubroeks, J.P., Glasser, W. & Gatenholm, P, Optimization of the process conditions for the extraction of heteropolysaccharides from birch, In *ACS Symposium Series 921. Feedstocks for the Future: Renewables for the Production of Chemicals and Materials, Ed:* Bozell, J and Patel, M., 321-334, (2006). Westbye, P., Svanberg, C. &Gatenholm, P., The Effect of Molecular structure of xylan extracted from birch on assembly onto bleached softwood kraft pulps, *Holzforschung* 60 (2006) 143-148. Höije A, Sandström C, Roubroeks J, Andersson R, Gohil S & Gatenholm P. Evidence on the presence of 2-O-D-xylopyranosyl-L-arabinofuranose side chains in barley husk arabinoxylan, *Carbohydr. Res.* 341 (2006) 2959-2966. Mikkonen, K.S., Rita, H., Helén, H., Talja, R., Hyvönen, L. & Tenkanen, M. Effect of polysaccharide structure on mechanical and thermal properties of galactomannan-based films, *Biomacromolecules* 8 (2007) 3198-3205. Gröndahl, M. & Gatenholm, P., Oxygen barrier films based on xylans isolated from biomass, *ACS Symposium Series 954*, Ed. Argyropoulos, D., Washington D.C., 2007, pp 137-153 **Bondeson, D. & Oksman, K. Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites, *Composite Interfaces* 14 (2007) 617-630.** Westbye, P., Köhnke, T., Glasser, W. & Gatenholm, P. The influence of lignin on the self assembly behaviour of xylan rich extracts from birch (Betula pendula). *Cellulose* 14 (2007) 603- 613. Pu, Y., Zhang, J-G., Elder, T., Deng, Y., Gatenholm, P., and Ragauskas, A., Investigation into nanocellulosics versus acacia reinforced acrylic films, Composites Part B: Engineering, 38B (2007) 360-366. Teeri, T., Brumer, H., Daniel, G., and Gatenholm, P., Biomimetic engineering of cellulose-based materials, *Trends in Biotechnolog,* 25 (2007) 299-307. Mikkonen, K.S., Yasav, M.P., Willför, S., Hicks, K.B. & Tenkanen, M. Films from spruce galactoglucomannans blended with poly(vinyl alcohol), corn arabinoxylan and konjac glucomannan, *BioResources* 3 (2008) 3198-3205. Sternemalm, E., Höije, A., & Gatenholm, P. Effects of arabinose substitution on the material properties of arabinoxylan films, *Carbohydate Research* 343 (2008) 753-757. Köhnke, T., Pujolras, C., Roubroeks, J. & Gatenholm, P. The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres. *Cellulose* 15 (2008) 537–546.

10. Publications and other communication activities (please list scientific reports, more popular reports and other communication activities)	Höije, A., Sternemalm, E., Heikkinen, S., Tenkanen, M. & Gatenholm, P. Material properties of enzymatically tailored cereal arabinoxylans, *Biomacromolecules* 9 (2008) 2042-2047. Westbye, P., Köhnke, T. & Gatenholm, P Fractionation and characterization of xylan rich extracts from birch, *Holzforschung* 62 (2008) 31-37. Toriz, G., Gutiérrez, M.G., Gonzalez-Alvarez, V., Wendel, A., Gatenholm, P., Martinez-Gomez, A., J., Highly hydrophobic wood surfaces prepared by atmospheric pressure dielectric barrier discharges, *J. Adhesion Sci. Technol.* 22 (2008) 2059–2078. Goetz, L., Mathew, A., Oksman, K., Gatenholm, P., and Ragauskas, A.J., A novel nano-composite film prepared from crosslinked cellulosic whiskers, *Carbohydrate Polymers* 75 (2009) 85-89. <u>Thesis</u> Laine, R., Function of galactose oxidase and its effects on galactomannan film formation, Master Thesis, University of Helsinki, ETK-series 1373 (in Finnish) Auyk Etang Jackson, Cellulose based nanocomposites, Master Thesis, Luleå University of Technology Höije, A., Isolation, characterization and material propertieas of arabinoxylan from barley, Licentiate Thesis, Chalmers University of Technology The results from the project will be part of the Doctoral Thesis of Anders Höije and Kirsi Mikkonen. <u>Manuscripts</u> Mikkonen, K.S., Heikkinen, S., Soovre, A., Peura, M., Talja, R., Serimaa, R., Helen, H., Hyvönen, L. & Tenkanen, M. Films from oat spelt arabinoxylan plasticized with glycerol and sorbitol, submitted to *Journal of Applied Polymer Science* Westbye, P., Kaya, A., Esker, A., Glasser, W. & Gatenholm, P., The influence of lignin on xylan adsorption onto cellulose model surfaces, submitted to *Langmuir* Dammström, S., Salmén, L. & Gatenholm, P., On the interactions between cellulose and xylan in biomimetic bacterial cellulose/glucuronoxylan nanocomposites, submitted to *Journal of Biomacromolecular Materials* Mikkonen, K.S., Mathews, A., Peura, M., Xu, C., Serimaa, R., Willför, S., Oksman, & Tenkanen, M. Composite films from mannans and cellulose nanowhiskers, in preparation

11. Project summary (about 1/3 page) with main emphasis on results for possible use in the News & Views section of Scandinavian Journal of Forest Research	The increased use of renewable materials is considered as one of the key issue of the sustainable development. Vast quantities of lignocelluloses are produced every year, constituting the main source of renewable organic material available on earth. The project studied hemicelluloses, the second most abundant plant polysaccharides after cellulose, to evaluate their potentials for new material applications. Detailed structure-function studies of hemicelluloses were also carried out. Specific enzymatic treatments were developed and applied to achieve selective and targeted modifications. To enable the use of hemicelluloses in polymeric materials, the understanding of the effect of molecular architecture on material properties is crucial. Promising novel transparent films were prepared both from xylans and mannans. The properties of films varied according to the chemical structure of hemicellulose used. Highly branched cereal arabinoxylans and konjac glucomannan resulted in cohesive films without external plasticizer but wood-derived hemicelluloses needed addition of polyol to form self-supporting films. Presence of a plasticizer resulted in general more flexible films with higher strain at break. Branching of xylans affected also the morphology of films, and more linear xylans resulted in more crystalline films. Both xylans and mannans are potential materials for packages of oxygen-sensitive products. The best films had good mechanical properties and low oxygen permeability, but the vapour permeability and water sensitivity needs to be further improved, unless packages for moderate water vapour permeability, as with some vegetables, are a target. Cellulose nanocrystals with a diameter around 5 nm and length 200 nm were prepared from wood cellulose. Nanocomposites were obtained by mixing cellulose nanocrystals with hemicelluloses. Mixing of cellulose nanocrystals to mannans resulted in clear changes in film structure. However, no effect was observed in the mechanical properties. The addition of long nanocellulose to xylans increased stiffness and strength of films. The results obtained provide valuable information for novel utilization of forest resources. The research is continuing in the future joint projects and interactions of hemicelluloses with cellulose and production of nanocomposites and coatings will be of focus in addition to formation of self-supporing films.
12. Date and signature	Date: 24.11.2008 Signature of project leader/coordinator