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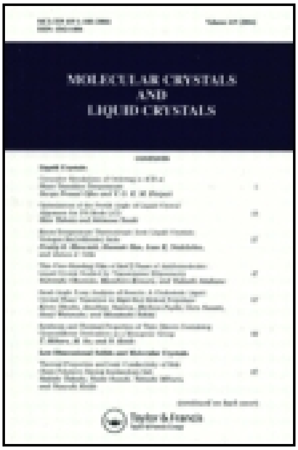

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Development of Modified Wood Products Based on Furan Chemistry

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Development of Modified Wood Products Based on Furan Chemistry

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The first processes for "furfurylation" of wood (wood modification with furfuryl alcohol) were developed several decades ago. Furfuryl alcohol is a renewable chemical since it is derived from furfural, produced from hydrolysed biomass waste. Over the last decade modernised processes for furfurylation of wood have been developed. These new processes are based on completely new catalytic systems and process additives. The properties of furfurylated wood depend on the retention of grafted/polymerised furfuryl alcohol (PFA) in the wood. At high modification levels (high retention of PFA) the enhancement of a wide variety of properties are achieved: an exceptional hardness increase, exceptional resistance to microbial decay and insect attack, high resistance to chemical degradation, increase in MOR and MOE, and high dimensional stability. At lower modification levels many property enhancements also occur, however to slightly lower extent. Notable are resistance to microbial decay and insect attack, increase in MOR and MOE, and relatively high dimensional stability. Two main processes for production of furfurylated wood have been developed for Kebony ASA (Former Wood Polymer Technology ASA) by the authors. Kebony™ for hardwood modification and VisorWood™ for soft wood modification, where the name reflects the colour of the material produced by the process. Commercial production according to the Kebony process has been running since October 2003, mainly for flooring. A small Kebony production plant is now in operation in Lithuania. A Kebony/VisorWood production plant was started during of 2003 in Porsgrunn, Norway. There are now planed for an expansion of this plant, and plans for a large Visorwood plant is ongoing. Further commercialisation of the technology will be done through licences issued by Kebony ASA.

Keywords: commercialisation; decay resistance; furfuryl alcohol; wood modification

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HISTORY OF FURFURYLATION

Early research with furfuryl alcohol (FA) concerned FA-resins as a substitute to phenol formaldehyde resins (PF resins) for adhesives, moulding compounds and inorganic composites. In the 1930's and 1940's several processes and patents concerning paper laminates, grinding wheels and metal casting moulds from FA-resin impregnated paper or inorganic compounds such as silicon carbide, were developed [1]. Metal casting moulds and grinding wheels are still the main commercial applications for furfuryl alcohol. Research concerning modification of wood with furfuryl alcohol, hereafter referred to as "furfurylation" of wood, was initiated by the "pioneer of wood modification", Dr. Alfred Stamm, in the early 1950's. Additional early work on wood furfurylation was done by Irving Goldstein [2–4]. Goldstein's process employed zinc chloride as a catalyst and mainly modified wood veneers. He reported that treatment with 90% (weight/volume) olume) solutions of FA resulted in products with high dimensional stability, and increased resistance to fungal decay, alkali and acids [2,4]. This research lead to a small-scale production of furfurylated wood in the 1960's by Koppers Wood Inc. (USA). Among these products were laboratory bench tops, pulp mixer rotor-blades and knife handles [5]. Anaya developed a process very similar to the Stamm/Goldstein process [6,7]. However, this process was never commercialized. The major problem with these processes was that zinc chloride used as a catalyst depolymerised the cellulose, which consequently reduced the strength properties of the modified wood.

Professor Marc Schneider and Dr. Mats Westin developed, separately and more or less simultaneously during the early 1990's, alternative catalysts for the furfurylation process. They both based their polymerization process on similar paths of chemistry using cyclic carboxylic anhydrides, mainly maleic anhydride, as key catalysts [8–10]. These novel systems lead to solutions that are chemically stable at room temperature and have good properties with regard to the impregnation process. The final furfurylated wood products, shown to be of high quality, are described in this chapter. The properties of this second generation of furfurylated wood are generally superior to those wood modified by the first-generation processes developed by Stamm and Goldstein [8].

CHEMISTRY OF FURFURYLATION

The acid catalyzed polymerization of FA in wood has a very complex chemistry. The resulting polymer is a highly branched and cross-linked furan polymer that is chemically bonded to the wood

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structural components. However, the reaction parameters (i.e., type of and concentration of catalyst, the pH of the solution, processing temperature and time, and the presence of water) highly affect the final product by the degree and type of chemical bonds to wood, the major type of polymer units, and the degradation of wood components (mainly depolymerisation of cellulose and hemicelluloses by acid hydrolysis). The reaction types can be divided into three categories: a) homo-polymerization of FA, b) co-polymerization of FA and additives or wood extractive substances, and c) grafting of FA or polymerized FA to wood cell wall polymers [11,12].

HOMO-POLYMERIZATION OF FA

Early studies stated that the reaction rate is a simple function of the pH in aqueous furfuryl alcohol solutions [1]. However, there are several competing reactions and the rate of the dominating reaction mechanism is affected by factors other than pH. These factors include temperature, FA/water-ratio, and the presence of oxygen and/or weak organic bases. In the presence of a powerful acid catalyst, such as para-toluene sulphonic acid (PTSA), the dominating reaction is a very rapid radical polymerization which results in a high degree of ring-opening reactions [13]. However, these kinds of systems are not suitable to use for impregnation and modification of wood since they are not stable at room temperature. Solutions used for impregnation of wood must be stable during storage and during impregnation of wood, but should react readily when the impregnated wood is heated. In the initial phase of the polymerization of these stable systems, there are two competing condensation reactions as are illustrated in Figure 1: Reactions 1 and 2a [14]. The reaction products according to reaction 1 normally dominate. High reaction temperatures and high concentration of furfuryl alcohol further suppress the formation of the ether bridges in reaction 2a [14].

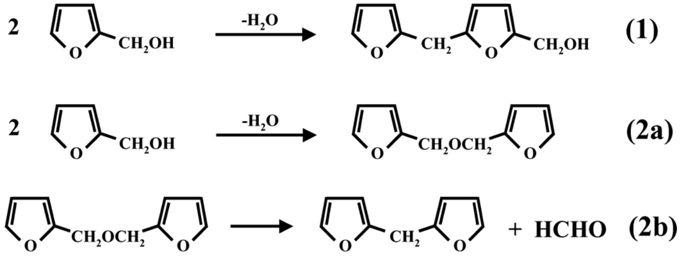

FIGURE 1 Initial polymerization of FA (acid catalyzed condensation reaction).

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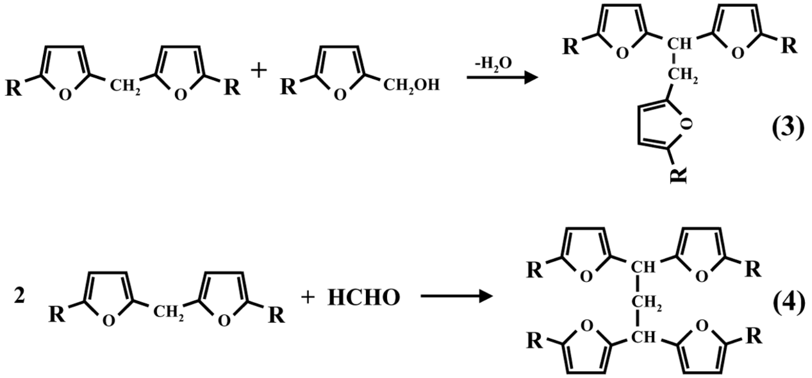
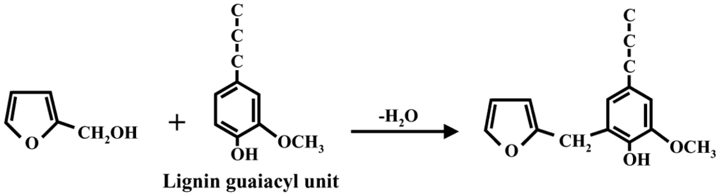


FIGURE 2 Branching (reaction 3) and cross-linking (reaction 4) of FA-polymer chains.

Since the ether-bridge in reaction 2a is an unstable intermediate, it is believed that it undergoes reaction 2b to form formaldehyde as an intermediate product. The terminal methylol group could later split off as formaldehyde. The latter reaction is highly temperature dependant. Initially, a linear polymer is formed. But as the polymerization progresses, cross-linking via reactions 3 and 4 occur more frequently and the polymer becomes infusible. It is believed that formaldehyde, formed according to reaction 2b and by splitting off of terminal methylol groups, acts as a cross-linking agent according to reaction 4. However, the dominating cross-linking reaction is by condensation reaction 3, shown in Figure 2 [1,14]. Furthermore, it is commonly assumed that some cross-linking in the late stages of polymerization occurs through ring-opening reactions. A competing reaction to the FA ring-opening reaction is formation of levulic acid. This reaction, and oxidation reactions, can be suppressed by the presence of a weak organic base, e.g. triethanolamine [1,15]. However, no significant difference in the polymer structure was found between polymerization carried out in the presence or absence of oxygen [14].

Co-Polymerisation and Reactions with Cell Wall Components

The high degree of permanent bulking of the furfurylated wood cell wall is considered evidence of reactions between polymer and wood at an early reaction stage. Similarly to low-molecular weight phenol formaldehyde resins (PF-resin), FA impregnation leads to super-swelling of the cell wall (i.e. a slightly higher degree of swelling than for



(5)

FIGURE 3 Suggested reaction between FA and a lignin unit.

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water). However, as PF-oligomers become more and more hydrophobic during polymerization, they begin to migrate out of the cell wall. This results in a maximum anti-shrink efficiency (ASE) of approximately 50% for PF resins. Since FA-oligomers are even more hydrophobic than PF-oligomers at the same degree of polymerization (DP), one would expect anti-shrink efficiencies below 50% for furfurylated wood. Instead, the ASE for FA-modified wood can be as high as 80%. This is a strong indication that grafting reactions occur between the FA-polymer and wood during the early stages of polymerization.

Grafting of poly-FA onto cellulose was previously accomplished using ferric salts and peroxides as catalysts [16]. However, these types of catalysts are too reactive to be use. Therefore, by using cyclic anhydrides, as described in this chapter, grafting reactions likely occur between the poly-FA and cellulose, hemicelluloses and principally, the lignin in wood. Reaction 5 (Fig. 3) is a possible reaction between FA and a guaiacyl unit of lignin (the predominant monomeric lignin unit in softwood lignin).

An ongoing study on a liquid system of partly polymerized furfuryl alcohol and lignin model compounds creosol was subject to different experiments based on ^{1}H NMR spectroscopy. The study is to be published later this year, but initial results by H-NMR confirm covalent bindings between polymer of FA and creosol [17]. This study strengthens the hypothesis of reactions between FA and guaiacyl units of lignin. The suggested reaction is presented in Figure 4.

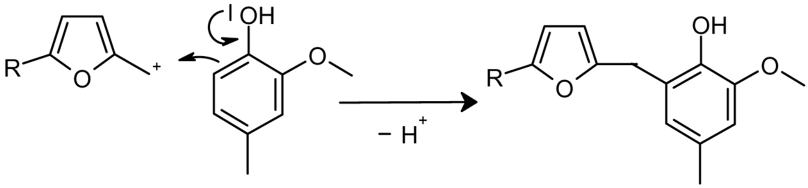

FIGURE 4 Suggested reactions between FA and Creosol investigated by H-NMR spectroscopy.

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BIOLOGICAL RESISTANCE

Furfurylation of wood can be done with different FA levels to obtain wood with varying degrees of modification, expressed as Weight Percent Gain (WPG). WPG is thereby an essential parameter when discussing the effects of furfurylation. The major property improvement observed with a moderate WPG (30%) is increased resistance to biological degradation. Moderate WPG will only have a minor effect on the physical properties of the modified wood. Furfurylation has been shown to be a good method to increase the resistance against biological deterioration of wood using non-toxic chemicals. Various research groups have carried out laboratory and field tests on FA-modified wood. Irving Goldstein was the first to show that furfurylated wood has an increased resistance to biological decay. His formulation was based on high concentration of FA (90%) that resulted in a high WPG. For commercial applications it is important to know the minimum treatment level required to achieve a desired property, to minimize the cost of the process. The studies reported in this chapter are published in international journals [18,19] and some tests conducted for Kebony ASA (Porsgrunn, Norway).

FUNGAL DECAY RESISTANCE

Results from laboratory testing according to several standards; AWPA E10, EN 113, EN 807 confirm that furfurylated wood obtain decay resistance. The mass loss due to rot of furfurylated wood of medium (30%) and high (50%) WPG are less than the mass loss of samples treated with CCA to a retention for Use class 4, ground contact. Only for the furfurylated samples with a low treatment level have mass losses slightly higher than for CCA-treated samples. The conclusion is that the resistance to brown and white rot decay fungi is high for furfurylated wood treated to a WPG of 35 or more [18]. Field tests confirm the same trend that furfurylated wood also has potential for high resistance even in ground contact [18].

In-ground exterior field tests (EN 252) are the most realistic test setup that can be performed for testing decay properties. The climate and soil type will affect the rate of degradation. Therefore, outdoor exposure tests are normally run for several years using multiple test sites to obtain realistic results. Furfurylated wood have been field tested for more than 9 years at three different locations in Sweeden; Simlångsdalen, Ultuna and Ingvallsbenning. Although the type of decay is very different in these three fields, the performance of furfurylated wood is quite similar in all three fields. At the higher modification levels, furfurylation seems to provide a performance equal to or better than CCA in the retention level approved for Use class 4 [18].

MARINE FIELD TESTS (EN 275)

Wood used in marine applications is susceptible to marine borers. Laboratory tests exist for only some marine borers; the main option is to conduct tests in an actual marine site. In Europe, marine testing is done according to European Norm EN-275. The furfurylated wood was found to perform well in marine tests. Furfurylated samples at medium (WPG 30%) to high (WPG 50%) modification levels were all rated sound after 5 years of marine exposure [18].

MECHANICAL AND PHYSICAL PROPERTIES OF FURFURYLATED WOOD

Chemical modification of wood can affect a wide range of properties. Cellulose, hemicelluloses, and lignin are intimately combined to form the anatomical structure of wood. Chemical modification introduces chemicals that react with one or more of the three wood constituents to varying amounts.

Typically, the change in wood properties is related to the degree of the treatment. A slight chemical modification will have only a minor impact on wood properties, while high treatment levels will have a greater influence. The optimum treatment level is determined by the intended use and the manufacturing costs. In furfurylation, the treatment level is conventionally expressed as WPG. By proper dilution of the impregnation solution, it is possible to obtain a WPG ranging from 10 to greater than 100% for low-density wood, with the WPG determined by the FA concentration and wood density. Low-density woods have a relatively large void volume, resulting in a high WPG compared to dense wood.

Furfurylation of wood results in polymer formation in wood cell lumens and cell walls. Polymers formed in the cell wall are fixed and will to some extent replace adsorbed moisture, resulting in a permanently swollen or bulked cell wall. This “bulking” effect reduces dimensional changes with changes in moisture content. This dimensional stabilization can be expressed as the anti-shrink efficiency (ASE). The permanent bulking and grafting of FA polymer to the cell structure will also affect the stiffness, strength and brittleness of the wood. Stiffness can be expressed as stiffness stabilization efficiency (SSE). For furfurylated wood, the volumetric ASE has been

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demonstrated to be high, even at low WPG. For example, at WPG = 32 the ASE is close to 50%, and at WPG = 47 the ASE is approximately 70% [18].

The increase in hardness is moderate at low WPGs but very high at high WPGs. The drawback is the decreased impact bending strength at medium to high WPG. Impact bending tests of furfurylated wood show a reduction of impact strength [20]. Furfurylated wood with WPG of about 30% has also been exposed to elevated temperature and humidity to investigate the long-term effect on impact bending strength. In general, this WPG level resulted in an impact bending strength loss of 25–35% after exposure [20].

ENVIRONMENT AND ECO-TOXICITY

Successful commercialization requires low environmental impacts with the use and disposal of furfurylated wood. The high decay resistance of furfurylated wood is believed to be caused by inertness of the modified wood to fungal enzymes, rather than to toxicity. In an attempt to understand the protective mechanism, several studies have been performed. Information obtained included toxicity of airborne emissions, toxicity of water leachates and potential release of toxic chemicals upon disposal. As a result of these studies, furfurylated wood is not regarded as biocide treated and was therefore excepted from regulation by the European Commissions Biocide directive [21].

COMMERCIALIZATION

There is growing interest in commercial production of furfurylated wood materials due to their useful properties and good environmental profile. Kebony ASA of Norway has been strongly involved in the commercialization process and holds several patents on wood furfurylation.

Kebony ASA has based its business model on being an R&D company which licenses the furfurylation technology to wood modification plants around the world. The company offers technology to produce environmentally friendly wood products as alternative to using endangered tropical woods or heavy metal impregnated wood.

Kebony ASA was established in 1996 to take the furfurylation wood modification process from the laboratory activity to commercialization. Before the start-up of the world's first production facility in Norway, it was necessary to document and test the properties of FA modified wood. Kebony ASA cooperated with leading universities and test

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PICTURE 1 Kebony benches, Oslo Sporveier. Design – Odd Thorsen, contractor – Eurosign. (Kebony ASA, Oscars gate 30, N-0352 Oslo, Norway)

facilities around the world to secure impartial and reliable test results of the products.

These tests suggested attractive product properties and as a result, a full scale production facility was constructed by Kebony Products in Porsgrunn, Norway. At Kebony Products the autoclave and curing chamber used to furfurylate wood was adapted from an oil-based wood impregnation plant. This demonstrated that it is possible to upgrade existing impregnation plants to utilize furfurylation technology.

As the commercialization of furfurylated wood was initiated, brand names were created for the products. The name VisorWood was selected

PICTURE 2 Kebony flooring, Restaurant Le Canard Oslo. Contractor – Parkett og Idrettsgulv. (Kebony ASA, Oscars gate 30, N-0352 Oslo, Norway)

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PICTURE 3 VisorWood decking, Verdens Ende, Norway. Contractor – Arne Olav Lund. (Kebony ASA, Oscars gate 30, N-0352 Oslo, Norway)

as the brand name for furfurylated products based on pine (the sapwood is treated). Today, that market is dominated by heavy metal impregnated wood. A second brand, Kebony, is for products that will be alternatives to tropical hardwood from endangered rainforests. In these products, the whole cross section is treated. Today Kebony Products treats beech, ash, syp and maple, but other wood species, such as rubber wood and radiata pine, is being tested.

Kebony Products' first year of full operation was 2004. Since then, it has gained valuable experience with optimization of production

PICTURE 4 VisorWood cladding, Myrene school Porsgrunn, Norway. Architect – Børve & Borchenius, contractor – NCC. (Kebony ASA, Oscars gate 30, N-0352 Oslo, Norway)

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parameters and raw materials. This will be valuable information for future plants.

In 2005, there are two plants in operation using the Kebony ASA process for modification of wood. Boen Bruk is a Norwegian parquet flooring producer and Kebony ASA licensee making Kebony 100, which is used instead of the tropical hardwood Merbau in the flooring. Kebony ASA's daughter company, Kebony Products, produces Visor-Wood as an alternative to traditional heavy-metal impregnated wood and also making Kebony 30, an alternative to tropical hardwoods. Discussions are currently ongoing with potential licensees from Europe and Asia. In Europe, the focus of the possible licensees will be maintenance-free building siding and other construction materials with improved durability. The focus in Asia will be on furniture and flooring products that are currently produced from tropical timbers.

Construction of a new Kebony factory started in the spring of 2007. This factory will be operated from 2008 and have the capacity of producing 15.000–25.000 m^3 of Kebony wood.

Examples of Uses of Furfurylated Wood

Furfurylated wood has been commercially available since 2004 from Kebony Products DA, Norway. The following pictures illustrate some projects where furfurylated wood has been used.

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