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Controlling the water uptake of wood by polyelectrolyte adsorption

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ABSTRACT

National and European legal rules and regulations require the replacement of solvent paints by water-born paints. Water on wood surfaces leads to significant problems because water can penetrate the pore system of wood and causes a swelling of the wood. The aim of our work was the reduction of water uptake of wood by polyelectrolytes with the surface polarity and wetting behavior of the wood surfaces should not be significantly changed. Cellulose materials, such as wood show in presence of moderately acidic, neutral or basic aqueous solutions a negative net surface charge. Therefore, for surface modifications of wood samples different commercially available cationic polyelectrolytes were used. In particular, weak polyelectrolytes were likely to reduce the water uptake of wood. They also slightly decrease the surface polarity of wood surfaces, which was advantageous for the rapid wetting of wood. Moreover, the reactive functional groups of the weak polyelectrolytes were used for subsequent cross-linking reactions to form irreversibly anchored polyelectrolyte networks on the wood surfaces.

1. Introduction

Wood, a natural material is one of the oldest materials used by the mankind. In addition to rocks, thousands of years, wood was the main material to build accommodation and equip them with pieces of furniture. Machinery, transportation vehicles, domestic appliances, tools and toys were made from wood. In the course of time, new materials having more favorable properties to fulfill technologic and reasonable public demands partially substituted the original applications of wood. However, during the last decades many people in industrially developed countries oriented their lifestyle to be more ecological, green and substantial. Wood and wood-basing materials have undergone a renaissance. They have re-substituted plastic materials especially in the toy and furnisher industries. Wooden articles indicate quality, solidness and a high living standard. Hence, wooden parts can be found as interior in upper-class cars, modernly furnished flats, and catalogs offering high-quality and expensive tools and household utensils. This trend in lifestyle corresponds to political and scientific statements and disclosures about the world's climate and the dire necessity to protect it. Wooden materials can be considered as CO_2 neutral and do not harm the environment after the end of their use. In order to retain and further the high acceptance of wooden materials it seems to be necessary to establish substantial and environment-friendly technologies in wood processing. One step in this important matter was the VOC (volatile organic compound) directive of the European Commission [1], which was enacted in 1999 and which is being valid by German laws. Together with the *Decopaint* regulation [2], which is being valid since 2007, it requires the substitution of solvent-containing lacquer systems by such, which do not emit volatile organic compounds. During the last years economically working processing techniques, such as vacuum-spraying of UV-curing lacquers, spraying of water-born lacquers, powder or calender coating have been developed and established in the furniture and other wood processing industries. However, water-born lacquers, which are particularly compatible to environment and cost-efficient for small and medium-sized companies, penetrate the wooden materials. The water soaked up causes a swelling and roughening of the wood fibers. Expensive drying processes and additional sandpapering are unavoidable to produce wooden parts of required accurate fit and quality.

The aim of our work was the modification of wood samples to minimize the water penetration and avoid the wood's swelling. Modification substances and their application had to be consistent with the VOC directive and comparable regulations. Furthermore, the modified wood surfaces should be easily wet by water-born lacquers, what means they should kept their hydrophilic character.

In paper industry polyelectrolytes are widely applied as so-called retention agents. Polyelectrolytes adsorb onto the surface of pigment and filler particles, change their net surface charge to the opposite polarity and keep them in the pulp. Additionally, their adsorption along the cellulose fibers increases the rate of dewatering the pulp because the adsorbing macromolecules display water molecules, which are bonded to the cellulose fiber

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surface via weak hydrogen bridge linkages. Hence, the application of polyelectrolytes from their aqueous solutions seemed to be suitable to reduce the water uptake of wood. However, during application the aqueous polyelectrolyte solution on wood, water and polyelectrolyte molecules are in competition to be adsorbed onto the wood surface. The equilibrium and rate of the polyelectrolyte adsorption can be supported by the selection of positively charged macromolecules. The most natural materials, such as cellulose, wood or inorganic particles have a negative net surface charge in moderately acidic or neutral environment. Beside the adsorption entropy, which mainly controls adsorption free enthalpy of macromolecules cationically charged polyelectrolytes obtain an additional enthalpic contribution (via Coulomb interactions between negatively charged surface sites and positive charges along the polymer chain) to the adsorption free enthalpy driving the force of polyelectrolyte adsorption. In particular, for cellulose it was found that the adsorbed amount of strong cationic polyelectrolytes depends on the molecular weight of polyelectrolytes, while the adsorption on inorganic fillers is not significantly influenced by the molecular weight of the polyelectrolyte sample [3]. Cationic polyelectrolytes were also successfully employed to control the wettability and net surface charge of kaolin (china clay), cotton and further cellulose-based materials [4,5]. In former works it was found that the surface properties of inorganic and cellulose-based materials can be more efficiently adjusted and optimized by using polyelectrolyte complexes, which are made from mixed polycations and polyanions or polycations and anionic surfactants [4,5].

Weak polyelectrolytes are characterized by functional groups, which can be partially charged in aqueous environment. Functional groups, which remain uncharged, can be used for subsequent reactions after the adsorption of the polyelectrolyte molecules on surfaces [6,7]. Cross-linkages between oppositely charged polyelectrolytes are able to stabilize the polymer layer on the solid surface [8,9]. Low molecular weight components [10–12] or nanoparticles [13] can be added to cross-link an adsorbed weak polyelectrolyte species.

With a view to industrial applications the polyelectrolytes were selected according to their commercial availability. We investigated weak polyelectrolyte molecules containing amino groups able to be protonated as well as strong polyelectrolytes characterized by quaternary ammonium salt groups along their backbone. Beside synthetically produced polyelectrolytes derivatives of polysaccharides being found in nature, such as chitosan were applied.

The polyelectrolyte adsorption was studied by XPS. The influence of the adsorbed polyelectrolytes on the water uptake was studied by wetting experiments and recording the uptake kinetics.

It was shown that cationic polyelectrolytes applied on wooden materials are able to lower the uptake of water and retard the swelling. The efficacy of modification strongly depended on the applied polyelectrolyte sample and the species of the wood substrate. It was improved by subsequent cross-linking reactions.

2. Experimental

2.1. Materials

Wood samples were descended from nature. Of course, different wood species have different chemical compositions and anatomies. However, wood samples made from the same species could also have very different properties, densities and morphologies because environmental conditions influence the growing rate of wood, the accumulation and distribution of wood components, accompanying substance, water and impurities.

For our investigations we selected veneers as well as wood pieces of English oak (*Quercus robur*) and Scots pine (*Pinus sylvestris*). Conifer wood, such as pine is characterized by a high ability to rapidly take up water. The oak samples showed very pronounced pores. In order to adjust wood moisture equilibriums all samples were stored in an environmental chamber at a temperature of 23 °C and a relative humidity of 50%. Two days before the polyelectrolyte samples were applied the wood samples were sandpapered in two steps by a belt sander equipped with sandpaper of a mesh size of 150 and 180, respectively. Just before applying the polyelectrolyte solutions a fresh sandpapering (mesh size of 220) was carried out by hand.

Table 1 summarizes the polyelectrolytes and a surfactant, which were applied to modify wood samples. Fig. 1 shows the corresponding chemical structures.

In order to produce solutions all polymer samples were dissolved in deionized water (Millipore). Typical concentrations were $0.1\,\mathrm{g\,L^{-1}}$ and $1.0\,\mathrm{g\,L^{-1}}$, respectively. Polymers with high molecular weights, such as the *PRA-630-BC* sample were intensively stirred over 24 h. The used chitosan samples were made from crab chitin by alkaline hydrolysis. They contain residual amounts of ca. 5% of acetylated amino groups. At concentrations higher than $0.5\,\mathrm{g\,L^{-1}}$ the *CHI-2500* sample was not completely soluble because the chitosan molecule is only soluble in its protonated form where the primary amino groups are converted into the corresponding ammonium salt. Hence, the chitosan samples were dissolved in diluted acetic acid. The pH value of the PEI solution was about 9.

2.1.1. Polyelectrolyte modification of veneers and wood pieces

In order to obviate warping and rejecting veneers pieces (40 mm × 25 mm) were mounted on glass plates. Then, they were brushed with aqueous polyelectrolyte solutions ($0.1\% \mathrel{\hat{=}} 1\,\mathrm{g\,L^{-1}}$) and dried at room temperature. For comparison one veneers piece was brushed with pure water and dried. Pieces of wood were modified in the same way.

2.1.2. Cross-linking reactions

Veneers pieces (40 mm × 25 mm), which were pre-treated as describe above (Section 2.1.1) were brushed with aqueous solutions of glutardialdehyde (*GA*, Merck KGaA, Darmstadt, Germany) or glutardialdehyde hydrogensulfite (*GAH*, Merck KGaA, Darmstadt, Germany). The concentration of the solutions was 1.0 wt.%.

2.2. Methods

2.2.1. Polyelectrolyte titration

In our study we used strong and weak polyelectrolytes. While the charge density of strong polyelectrolytes is fixed by the chemical structure of the polymer molecules, the charge density of weak polyelectrolytes is controlled by the pH value of their aqueous solution.

The charge densities of the polyelectrolytes were determined by polyelectrolyte titrations employing a Particle Charge Detector PCD (BTG Instruments GmbH, Herrsching, Germany). The oscillating movement of the PCD's piston moves the polyelectrolyte solution along the vessel wall and generates a streaming potential, which is tapped by two electrodes. The cationic polyelectrolyte samples were titrated by a $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ poly(ethylene sulfonate) solution. The pH value was kept constant. The anionic consumption (in $\mathrm{mmol\,L^{-1}}$) related to the mass (in g) of the cationic polyelectrolyte gives the charge density of the cationic polyelectrolyte (in $\mathrm{mequiv.\,g^{-1}}$). Table 2 summarizes the charge densities of the polyelectrolyte samples used in our studies.