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Improving the mechanical resistance of waterborne wood coatings by adding cellulose nanofibres

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ABSTRACT

In the present study, microfibrillated cellulose (MFC) and nanocrystalline cellulose (NCC) were applied as additives for a waterborne acrylate/polyurethane-based wood coating in order to improve the mechanical resistance of coated wood surfaces. Coating mixtures containing up to 5 wt% nanocellulose were prepared by high-shear mixing and applied to wood substrates. The optical, mechanical and chemical properties of cured coatings were characterized. Surface roughness, gloss, scratch resistance, abrasion resistance and resistance against chemicals were determined according to the relevant European standards. Additionally, nanoindentation (NI) was used to assess the micromechanical properties of modified and unmodified coatings. Owing to a higher surface roughness, cellulose-filled coatings showed significantly lower levels of gloss than the unmodified coating indicating that nanocellulose acts as a matting agent. NI experiments revealed a slightly positive effect of nanocellulose addition on the hardness and modulus of the coatings. While scratch resistance improved consistently with increasing nanocellulose addition, abrasion resistance was found to improve only sporadically. Tensile tests on free-standing coating films revealed a significantly higher tensile strength and modulus for cellulose-filled coatings. Overall, the results suggest that the addition of cellulose nanofibres primarily improves the internal cohesion of the coating layer whereby MFC was more effective than NCC.

1. Introduction

Constructional wood is exposed to a number of detrimental factors like moisture, UV-radiation or mechanical stresses in both, interior and exterior applications. Apart from providing a way to specifically design the optical and haptic characteristics of a wood surface (e.g. colour, gloss, etc.), protection against physical and chemical influences can be obtained by a surface treatment of the wooden structure. Depending on the considered field of application, especially the mechanical-technological coating properties like surface hardness, deformability as well as abrasion and scratch resistance are of prime importance for wood in indoor areas. These mechanical properties strongly depend on the binder of the coating material used but can be improved by the use of additives such as fillers.

Currently, predominantly inorganic fillers such as silicon dioxide, aluminum oxide or the carbonates, silicates and sulfates of various metals are applied in the formulation of coating materials for wood [1]. Due to their high hardness, these minerals induce a significant increase in the abrasion and scratch resistance of the coated surface. This is why for instance in parquet industry it is quite common to add around 10% of fine-grained corundum to the clear coat in order to improve the abrasion resistance [2]. An extremely scratch resistant coating can be achieved by using nanoscale filler particles. Sow et al. [3], for instance, considerably improved the scratch resistance of a UV-hardening waterborne wood coating by the addition of aluminum and silicon nanoparticles. With the latter, scratch resistance was improved by around 200% at an addition of only 1 wt%. Furthermore, the adhesion strength of the coating and its glass transition temperature were increased. Apart from the mechanical properties, also the optical coating characteristics were affected by the addition of nanofillers.

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Due to their higher surface roughness, the filled coatings showed significantly reduced gloss levels. In another study [4] nanocomposite coatings were produced by mixing silane-modified zirconia nanocrystals with a polymeric matrix on a polyurethane/polyacrylate basis. Also in this study, the addition of a nanofiller resulted in a distinct increase of abrasion and scratch resistance as well as pendulum hardness according to König. The optical transparency of the coating remained fairly unchanged up to a filler content of around 20 wt%. As described above, the application of inorganic nanoparticles enables the preparation of remarkably hard and scratch resistant coating layers. However, the processing of such coating materials appears to be not without problems. The poor sanding behaviour of the hard coatings has a detrimental effect, and, for instance, limits the reparability of pre-finished parquet flooring [5].

Apart from improving the mechanical coating resistance, nanoscale fillers may be used to impart specific functionalities to a coating material, including for instance antimicrobial [6,7] and flame retardant properties [8] hydrophobicity [9], UV-protection [10–12] and enhanced barrier properties [13,14]. While in the past, primarily the processing and performance characteristics as well as the price have been the determining factors for advancements of coating materials, ecological and health aspects became increasingly important in the last two decades. Induced by the European VOC-directive (1999/13/EG), a massive replacement of conventional solvent-based wood coatings by UV-hardening and waterborne coating systems has taken place during the last years [1]. Currently, polyacrylates and polyurethanes are considered as the most important binders in the formulation of waterborne coating materials for wood in indoor applications.

Instead of inorganic fillers, cellulose nanofibres, i.e. microfibrillated cellulose (MFC) and nanocrystalline cellulose (NCC), have been used in the present study. As compared to inorganic nanoparticles, cellulose nanofibres show a substantially lower hardness, strength and stiffness, which should positively affect the processing characteristics of the coating material. Since the density of cellulose is substantially lower too, its specific properties are comparable with those of inorganic fillers. Another benefit of cellulose nanofibres is their polar and reactive fibre surface that enables an enhanced formation of secondary valence forces between the fibres and the matrix polymer [15]. In literature, a number of studies [16–20] can be found, in which the addition of cellulose nanofibres to polyacrylate or polyurethane resins resulted in a significant improvement of mechanical properties of the respective matrix polymers. In contrast, literature on the use of cellulose nanofibres as an additive for wood coatings is quite scarce. Very recently, Poaty et al. [21] dispersed chemically modified cellulose nanocrystals in a waterborne acrylic wood coating with the aim of improving the mechanical properties of the matrix polymer. In order to enhance the dispersion of nanocrystals in the varnish, surface chemical modifications using alkyl quaternary amines or acryloyl chloride in simple conditions were performed. Abrasion tests carried out on coated wood specimens indicated that the abrasion resistance increased by up to 38% due to the addition of 2 wt% of surface modified cellulose nanocrystals.

The present study investigates the possibility of using cellulose nanofibres as functional filler in waterborne wood coatings in order to improve the mechanical resistance of the respective coating layers. For this purpose, up to 5 wt% cellulose nanofibres (MFC and NCC) were added to a commercially available acrylate-/polyurethane-based furniture varnish. The resulting nanocellulose-filled coating materials were subsequently applied to wooden substrates. The optical, mechanical and chemical properties of coated wood surfaces were analyzed using well established standard test methods for wood coatings. Furthermore, a micromechanical characterization of the nanocomposite coatings was performed using nanoindentation (NI) technique. Apart from coated wood samples, free-standing coating films have been prepared and characterized in tensile tests.

2. Experimental

2.1. Preparation and characterization of nanocellulose suspensions

For the preparation of a homogeneous MFC suspension, commercially available MFC (Celish KY100G, Daicel FineChem Ltd., Japan) with a solid content of 13.8% was initially diluted to 0.86% with distilled water. The diluted cellulose suspension was then fibrillated by 10 passes through a high-pressure laboratory homogenizer (APV 1000, APV Manufacturing Poland) operated at a pressure of 700 bar in order to improve fibril dispersion and to disintegrate any remaining fibril aggregates. The homogenized suspension was air-dried at 80 °C for about 12 h resulting in a final solid content of 1.69%. Apart from MFC, carboxylated NCC was prepared by surface carboxylation of commercially available NCC (University of Maine, USA) from wood pulp. The carboxylation was performed according to Saito et al. [22] using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) as a catalyst. After completion of the reaction the modified nanocrystals were filtered off, repeatedly washed with distilled water and diluted to a dry content of around 2%. Finally, the NCC suspension was subjected to the same homogenization procedure as MFC and air-dried at 80 °C for 3–4 h to a dry content of 2.52%. For the preparation of the coating mixture containing 5 wt% NCC, a small amount of the NCC suspension was further dried to a final solid content of 12.3%. In order to determine the fibre dimensions and their aspect ratio, AFM imaging of dried MFC and NCC suspensions was performed on a Bruker Dimension Icon AFM (Bruker, USA) whereby 10 randomly selected fibres were measured for each type of nanocellulose.

2.2. Preparation of test specimens

Coating mixtures with a cellulose content of 1%, 2% and 5% by weight of solid resin were prepared by adding the respective amount of the aqueous MFC/NCC-suspension to a water-based clear coat as used in furniture production (AquaRapid CFB, Adler Lacke, Austria). The cellulose content of the coating mixtures was determined according to Eq. (1).

$$\%\ \text{Cellulose} = \frac{m_S \times SC_S}{m_C \times SC_C} \times 100 \qquad (1)$$

where m_S is the mass of the cellulose suspension, SC_S is the solid content of the cellulose suspension, m_C is the mass and SC_C is the solid content of the base coat. SC_S and SC_C were calculated by dividing the dry mass of the respective material (after drying at 120 °C for 2 h) by its mass in the wet state. The composition of the individual coating mixtures is apparent from Table 1. The acrylic/polyurethane-based coating was applied without the addition of a hardener, i.e. as one-component system. According to the manufacturer's instructions, the base coat (solid content 33.5%, viscosity ~820 mPa s) was diluted with 10 wt% water in order to get a sprayable coating with a viscosity of about 480 mPa s which was used as a reference. The viscosity of all cellulose containing coating mixtures was adjusted to approximately the same value (530 ± 60 mPa s) by the addition of water. To achieve an almost homogeneous dispersion of nanofibres, the coatings were mixed with a laboratory mixer (T10 basic Ultra-Turrax, IKA-Werke, Germany) operated at 30000 min^{-1} for 3 min. Viscosity measurements were performed on a Bohlin CVO Rheometer (Bohlin Instruments, Germany) using a cone/plate measuring system with