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Zinc Oxide Based Coatings for the UV-Protection of Wood for Outdoor Applications

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Summary: Nano-sized zinc oxide (ZnO) was chosen as a suitable candidate for the UV-protection of coatings. ZnO-based acrylate coatings were applied to polycarbonate plates, glass plates and impregnated wood. Coated samples were artificially weathered (Xenon test) for at least 1500 hours and studied with regards to their optical and mechanical properties, such as color shifts (yellowing), as well as to changes in brightness, transparency or hydrophobicity. The prepared wood coatings showed reduced yellowing and improved optical properties.

Keywords: coatings; nanocomposites; UV-protection; wood; ZnO

Introduction

It is well known that wood, being exposed to natural weathering conditions, turns yellow or brown and brittle during time (Figure 1).[1–5] The yellowing of wood is a result of the photochemical decomposition of lignin triggered by UV-irradiation, while the brittleness is caused by rain and moisture.[3,4,6,7] Lignin is an amorphous, phenylpropanoid macromolecule and, besides cellulose, one of the main components of wood.[8] Its has not a single uniform structure, but is composed of a collection of compounds with similar properties and molecular weights.[8,9] Due to its aromatic structure, lignin is able to absorb irradiation below 440 nm, having an absorption maximum at 282 nm.[4,7] Its degradation finally leads to brown products of decomposition – the humic acids.[4]

Moisture and oxygen can further accelerate the degradation of lignin, which finally leads to the loss of the coating adhesion. For the customer, in general, it is important to keep the natural look of the coated wood, so that transparent UV-protective coatings are desirable.[4,10] An ideal protective coating for wood for outdoor applications must therefore possess a sufficient filter efficiency up to 440 nm, a high barrier for oxygen and moisture as well as a high transparency in the visible range.[11,12]

Commonly used additives for the UV-protection of wood species are either organic compounds, e.g. the so called hindered amine light stabilizers (HALS) or inorganic additives, such as pigments and/or dyes.[5,6] However, they have the disadvantage that coatings thereof are often not fully transparent.

Zinc oxide (ZnO) is a well known low cost material, which is easy to synthesize, chemically inert and non-toxic. Since it shows an excellent ultraviolet and infrared absorption as well as a high transparency in the visible range, it was therefore chosen as a promising candidate for the UV-protection of wood for outdoor use.[13–15]

Experimental Part

Materials

Acrylates, methacrylates and the reactive thinner (isobornyl acrylate (IBOA)) were

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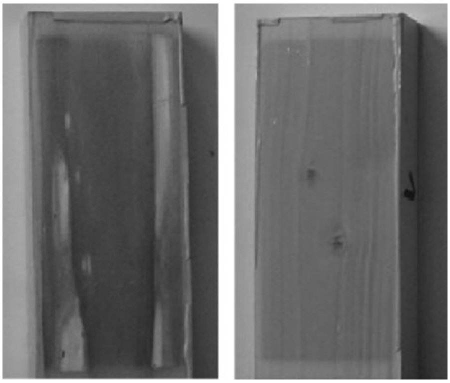

Figure 1.
Coatings on wood without (left) and with nano-sized ZnO (right) after 1500 hours of artificial weathering.

purchased from CYTEC Surface Specialities (Cray Valley, USA) or BASF (Ludwigshafen, Germany). The photoinitiator Darocure 4265 was obtained by Ciba (Lampertheim, Germany) and is composed of a 1:1 mixture of 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocure 1173). This photoinitiator shows a second absorption maximum around 380 nm and is especially suited for UV-curing of pigmented wood finishes as well as of white UV-inks. The effect of ZnO on the curing rate was investigated by measuring the content of residual double bonds and residual photoinitiator after the UV-curing. A residual double bond content and an amount of residual photoinitiator of 2.7-2.9% and 21.5%, respectively, was obtained for ZnO-based coatings, which were only slightly higher as measured for an unmodified coating (2.5% and 19.5% of residual double bond and photoinitiator content, respectively). Therefore, we concluded that the addition of ZnO did not affect the polymerization process. Spruce and pine wood samples were pre-treated with an aqueous wood impregnation H5100 (3H-Lacke, Hiddenhausen, Germany) containing 5 wt.-% of a water-based lignin protection agent. Nano-sized ZnO was provided by three suppliers (Degussa, Nanobyk and Benefit), where one ZnO was provided as a 40 wt.-% dispersion in organic solvent and the other two ZnO species were provided as powders. According to the product information of the suppliers, the ZnO species had a primary particle size of 20 nm.

Zinc acetate dihydrate (Fluka), sodium hydroxide (Fluka) and ethanol (Merck) were used without any further purification. Distilled water was used throughout the synthesis.

Synthesis of ZnO

ZnO was prepared as follows. Zinc acetate dihydrate (252 g, 1.15 mol) was dissolved in 3.8 L of ethanol and the solution was heated to reflux in a Normag 6 L batch reactor equipped with a condenser, a thermometer and a stirrer. A solution of sodium hydroxide (92 g, 2.3 mol) in 115 mL of ethanol and 345 mL of water was added via a peristaltic pump (starting velocity: 300 rpm for 10 min, then increase to 600 rpm for 60 min). During that time, a white precipitate formed. The dispersion was allowed to cool to room temperature. The precipitate was filtered over a glass frit (pore size 4), thoroughly washed with a mixture of water and ethanol and dried at 90 °C over night. Finally, the nanopowder was calcined in a muffle furnace at 350 °C for 1 hour.

Preparation of the Coatings

A typical lacquer, which was composed of 89.5-91.5 wt.-% organic matrix (70 wt.-% aliphatic urethane diacrylate and 30 wt.-% of a reactive thinner), up to 2 wt.-% of each surface additive and 2-4 wt.-% nano-sized ZnO, was treated in a disperser at 4000 rpm for 30 minutes and, when needed, additionally ball-milled in a planetary ball mill (Pulverisette 5, Fritsch GmbH, Idar-Oberstein, Germany) at 350 rpm for 30 minutes. 2 wt.-% of the photoinitiator Darocure 4265 was added just before application of the coatings. To obtain a superior adhesion of the coatings, all wood samples were treated with fine sand paper (400 grit). Wood samples were coated using a Buerkle roller coater. The coating weight was in the range of 60-70 g/m^2, realized by applying

Table 1.
Summary of the used ZnO species and their primary particle sizes and crystallite sizes.

Sample	obtained as	Primary particle size* [nm]	Crystallite size (obtained by XRD) [nm]
ZnO-1	40 wt.-% dispersion in organic solvent	20	n.d.
ZnO-2	powder	20	34
ZnO-3	powder	20	15
ZnO-4	powder	20 to 60	31

*according to the product information of the providers

two layers. The first layer was typically 5-10% heavier than the second. Curing of the first layer under a N_2-atmosphere led to adhesion problems of the second layer. Therefore, the first layer was cured under air, while the second was cured under a N_2-atmosphere (residual O_2-concentration < 100 ppm). An overall dose of 4500 mJ/cm^2 for each layer was reached by a 3-fold curing at a conveyor speed of 4 m/min applying full power (120 W·cm^{-1}) to the Hg lamp. Samples on glass and polycarbonate plates were coated using a 100 μm doctor blade and cured in one step applying an overall dose of 1525 mJ/cm^2 by 1-fold curing applying half power (dose of 185 mJ/cm^2) and a 2-fold curing at full power (dose of 670 mJ/cm^2) both at a conveyor speed of 6 m/min under a N_2-atmosphere (residual O_2-concentration < 100 ppm). Low gloss samples could be achieved curing the second layer under the action of a 172 nm excimer lamp followed by curing with a Hg lamp. This effect is called physical matting, the set-up is described elsewhere.[16–23]

Characterization Methods

Scanning electron microscopic (SEM) images were obtained on a Zeiss Ultra 55 field-emission (FEG) SEM device (Carl Zeiss SMT, Germany) at 1.0 keV. ICP-OES measurements were done on a Spectro ciros vision (Spectro Analytical Instruments GmbH&Co. KG, Germany). Powder X-ray diffraction (XRD) was performed on a Philips X'Pert wide-angle diffractometer with slit optics, Cu Kα radiation ($\lambda = 1.54$ Å) and Ni Kβ filter. The powder was applied to the specimen holder using double faced-adhesive tape, where the upper site was covered with a thin layer of the powder. Measurements were carried out at a voltage of 40 kV and a current of 30 mA in the 2Θ-range of 20-80° with a step size of 0.05 and 1.00 seconds per step. For the wood samples, artificial weathering was performed in accordance with DIN EN ISO 11341 applying a CI 3000 XENONTEST device (Atlas MTT, Chicago, USA). UV-Vis measurements were carried out using a Shimadzu UV-Vis scanning spectrophotometer UV-2101PC. Color measurements were carried out according to DIN 5033-7 using a CM 3601d spectrophotometer (Minolta, Japan). The gloss was determined according to DIN 67530 using a reflectometer REFO 3-D (Dr. Bruno Lange GmbH, Berlin, Germany). The conversion of the -C=C- double bonds was determined by FT-IR spectroscopy measuring the absorbance at 810 cm^{-1} on a Bruker Vector 22 using ATR technology. The residual photoinitiator content was determined by means of HPLC analysis after its extraction from the cured coatings with acetonitrile. For this purpose, a 0.200 g sample of the cured coating was placed in 2 mL of acetonitrile and sonicated for 10 minutes at 25 °C in an ultrasonic bath. The sample was filtered and subjected to HPLC. Quantification of the photoinitiators was achieved on a Varian Pursuit x Rs Ultra C-18 reversed phase column using acetonitrile:water (80:20 vol.-%) as a mobile phase at a flow rate of 0.4 mL/min using UV-detection at 255 nm. Contact angles were measured on a Contact Angle System OCA 20 (Data Physics Instruments GmbH, Filderstadt, Germany).

Results and Discussion

Self-synthesized ZnO (**ZnO-4**) was obtained by precipitation reaction in ethanolic solution. The XRD spectra showed the typical reflexes of the Wurtzite crystallite structure without any impurities. A crystallite size of 31 nm was calculated using the Scherrer equation. ICP-OES measurements revealed a Zn-content of 81.8% (calculated 80.3%) and no remaining Na was detected (below detection limit).

The SEM images of **ZnO-1** to **ZnO-4** are shown in Figure 2. For the commercially available ZnO species, a primary particle size of 20 nm was indicated by the suppliers. For **ZnO-3**, this is in agreement with the SEM results. **ZnO-1** was composed of agglomerates of spherical nanoparticles with particle sizes of 20 to 70 nm, while **ZnO-2** showed aggregates of rod-like nanoparticles with lengths of around 200 nm and aspect ratios of 15-20. SEM images of the self-synthesized **ZnO-4** showed agglomerates of spherical nanoparticles with primary particle sizes of 20-60 nm.

A lacquer with **ZnO-1**, available as dispersion in organic solvent, was homogeneous and did not show any agglomerates and was therefore used as such without any ball milling or filtration. Lacquers with **ZnO-2**, **ZnO-3** and **ZnO-4** where additionally ball-milled in a planetary ball mill at 350 rpm for 30 minutes when applied on glass or polycarbonate plates and filtered through a 30 μm nylon filter when applied on wood. **ZnO-2**-based coatings were very homogeneous and the optical appearance of the cured coatings was equally good for the lacquer with or without filtration/ball milling. The coatings made of a lacquer based on **ZnO-3** or **ZnO-4** were inhomogeneous and big agglomerates were still visible after dispersion in the dissolver. After additional application of ball-milling, the lacquers were homogeneous and did not show any visible agglomerates.

The hydrophobicity of the coatings was studied by measurement of their water

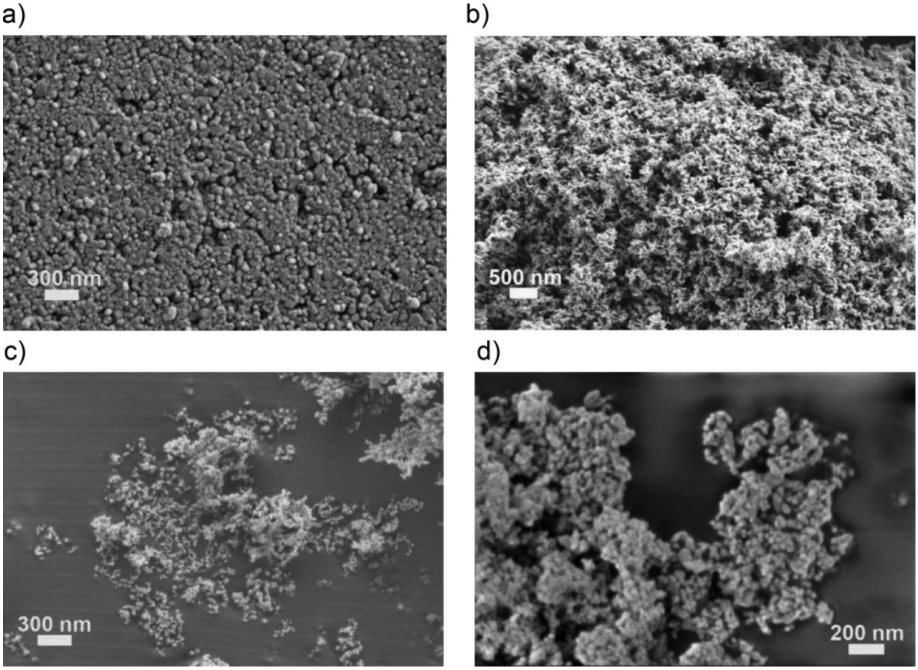

Figure 2.
SEM images of ZnO samples **ZnO-1** (a), **ZnO-2** (b), **ZnO-3** (c) and **ZnO-4** (d).

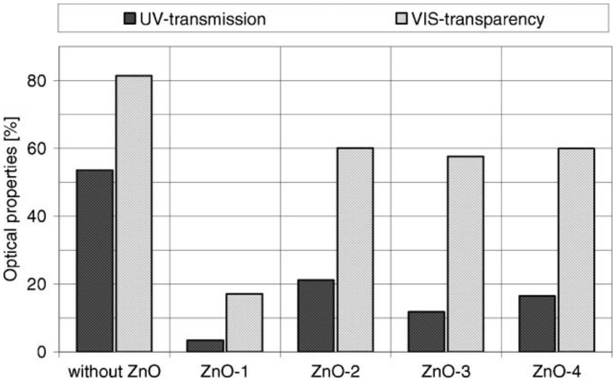

Figure 3.
Calculated values of UV-transmission and VIS-transparency (according to the directive ift-R5 of the IFT Rosenheim) of coatings (thickness of 60 μm) without and with different nano-sized ZnO species.

contact angles. Comparable contact angles around 100° were obtained for all coatings with and without ZnO. After artificial weathering for 1000 hours, the contact angles of all samples decreased. However, the contact angles of the ZnO-based coatings (81-85°) generally were up to 6-12% higher as compared to a coating without ZnO (76°). Therefore, the ZnO-based coatings were more hydrophobic, i. e. showed a better water repelling behavior, which is an important property for coatings applied outdoors.

Transmission and transparency measurements were carried out for the coatings on glass plates. According to the directive ift-R5 of the IFT Rosenheim, UV-transmission, T_{UV}, and VIS-transparency, T_{VIS}, can be quantitatively determined by

$$T_{UV}[\%] = \frac{\sum_{280nm}^{440nm} \tau(\lambda)\cdot\Delta\lambda}{\sum_{280nm}^{440nm} \Delta\lambda}\cdot 100$$

$$T_{VIS}[\%] = \frac{\sum_{440nm}^{720nm} \tau(\lambda)\cdot\Delta\lambda}{\sum_{440nm}^{720nm} \Delta\lambda}\cdot 100$$

with $\tau(\lambda)$ as the spectral transmission factor and $\Delta\lambda$ as the wavelength range in nm.

In general, a low UV-transmission and a high VIS-transparency is desirable, resulting in transparent coatings with high UV-filter efficiency which in turn provides an effective protection against UV-irradiation-induced photochemical decomposition of the wood. The calculated values for UV-transmission and VIS-transparency of the investigated ZnO-based coatings on glass plates in comparison with a blank sample are shown in Figure 3. In comparison to the blank sample (without ZnO), the **ZnO-1**-based coating showed an extremely low value (3.4%) for the UV-transmission, indicating a good UV-protection of the ZnO-based coating. However, also the value for VIS-transparency was low (17.1%), giving only semi-transparent coatings. The coatings based on **ZnO-2** showed only moderate UV-transmission (21.1%), but a high VIS-transparency of 60.1%. An identical VIS-transparency was obtained for a coating with **ZnO-4**, however, the UV-transmission for that sample was lower (16.5%), thus the UV-protective function was better. Finally, coatings based on **ZnO-3** revealed good UV-protection (UV-transmission of 11.8%) as well as a high transparency in the visible range (VIS-transparency of 57.6%). It can therefore be concluded that with the addition of **ZnO-2** - **ZnO-4**, transparent coatings with a high filter efficiency against UV-light could be prepared.

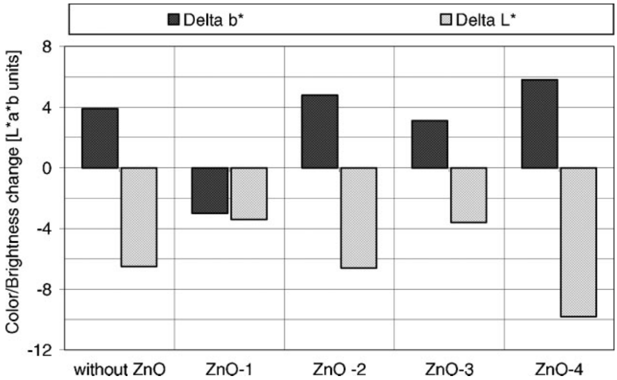

Figure 4.
Color shifts (Delta b*, Δb^*) and brightness changes (Delta L*, ΔL^*) of coatings without and with different nano-sized ZnO species after 1500 hours of artificial weathering.

The performance of ZnO-based coatings has been evaluated by comparing their resistance to artificial weathering with that of a system without ZnO. As mentioned above, the wood was pre-treated with a waterborne wood impregnation (lignin protecting formulation). In earlier studies we already investigated the effect of different UV-stabilizing measures on the discoloration of coated spruce wood.[24] A coating prepared without any UV-protective additives showed a brightness change, ΔL^*, of -20.1 after 1500 hours of artificial weathering. The sample also underwent strong yellowing ($\Delta b^* = 15.3$). The best results were obtained using a combination of lignin protecting impregnation and ZnO in the top coat. Figure 4 shows the changes of brightness and blue/yellow color changes for the investigated ZnO-based samples on wood after 1500 hours of artificial weathering. In comparison to the color shift of a blank sample ($\Delta b^* = 3.9$), the color shifts of **ZnO-1** and **ZnO-3** were lower ($\Delta b^* = 3.0$

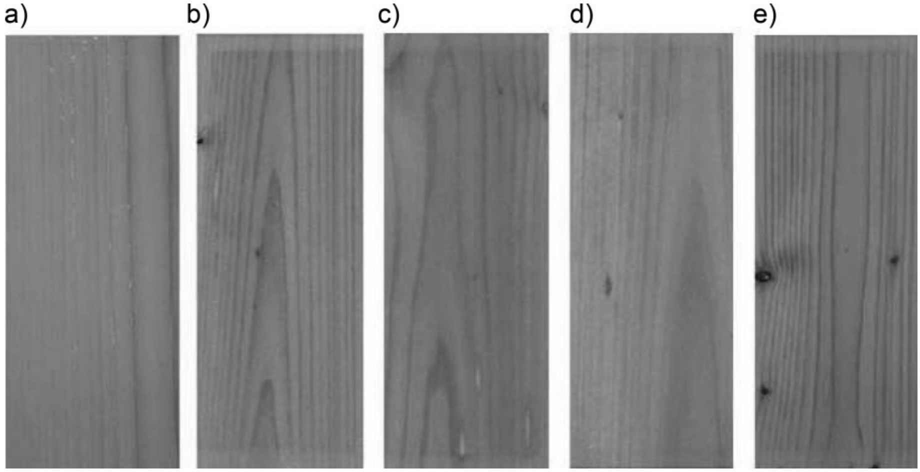

Figure 5.
Images of spruce wood samples coated with UV-nanocomposites based on different nano-sized ZnO species after 1500 hours of artificial weathering. The wood samples were primarily treated with a lignin protecting impregnation. A: non-weathered, B: **ZnO-1**, C: **ZnO-2**, D: **ZnO-3** and E: **ZnO-4**.

and 3.1, respectively), meaning that the yellowing could be reduced using ZnO. Larger color shifts were observed for samples **ZnO-2** ($\Delta b^* = 4.8$) and **ZnO-4** ($\Delta b^* = 5.8$). Similar results were obtained for the brightness changes. While coatings with **ZnO-1** and **ZnO-3** showed a higher brightness stability ($\Delta L^* = -3.4$ and -3.6, respectively), the coatings with **ZnO-2** and **ZnO-4** revealed an increased loss of brightness ($\Delta L^* = -6.6$ and -9.8, respectively) as compared to a coating without any ZnO ($\Delta L^* = -6.5$).

The images of the coatings on wood after 1500 hours of artificial weathering are presented in Figure 5. A **ZnO-3**-based coating applied on wood showed the highest UV-protection effect as becomes evident by comparing the color differences between the irradiated samples with those of the non-irradiated one. This is in agreement with the results obtained from color and brightness change measurements above. All other wood samples showed slightly stonger discoloration, which was, however, still acceptable. In general, the weathered coatings were still transparent, did not delaminate and showed only a small number of cracks.

Conclusion

Wood species for the use in outdoor applications were efficiently protected from yellowing using nanocomposite lacquers based on nano-sized ZnO. The investigated coatings showed high transparency. The best results with regard to color and brightness changes were obtained when the wood surface was additionally treated with a water-based wood impregnation containing a special lignin protector combination before application of the ZnO-based coating. Compared to conventional available UV-protective agents, the investigated commercial and self-prepared laboratory-scale ZnO species showed significantly higher stabilizing efficiency. Furthermore, the delamination between wood surface and coating layer caused by UV-irradiation and moisture could be avoided using ZnO.

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