Polyester Binders for Wood Containing Benzotriazole and HALS Light Stabilizers

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ABSTRACT: Three new polyester binders containing either benzotriazole-type or hindered amine light stabilizers (HALS)-type light stabilizers were synthesized. The binders were characterized by ^{13}C and ^{1}H NMR, FTIR, UV-VIS spectroscopy, and size exclusion chromatography. It was found that it was possible to bind a benzotriazole-type light stabilizer to the polymer backbone of the binder if a suitable group was present in the stabilizer. However, there was no proof that the HALS-type stabilizer was bound to the binder. The average penetration depth of the binders into the radial surface of pine wood was mainly below 480 μm into earlywood and below 2500 μm into latewood. The average penetration depth into the tangential surface was around 1000 μm in the earlywood and around 2500 μm in the latewood. Artificial weathering causes a binder-treated wood surface to darken independently of the binder used. The yellowness of the irradiated pine samples increased at the beginning of the exposure but decreased during longer exposure times. The benzotriazole stabilizer, Tinuvin 213, protected the surface of wood quite well; the other stabilizers were poor. The wood surface became rougher in appearance, cracks along the microfibril orientation became pronounced, and the bordered pits were degraded in the weathered samples. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1413–1421, 2004

Key words: polyester; light stabilizer; pine wood; penetration; light resistance

INTRODUCTION

Wood is a composite material consisting of polysaccharides—cellulose and hemicellulose—and polyphenolic lignin. Long cellulose chains form rigid, crystalline fibrils to which hemicellulose chains are attached. Amorphous lignin forms a matrix embedding the polysaccharides. The polysaccharides and lignin produce the physical and mechanical properties of wood.[1,2] Wood absorbs light[3] and most of the detrimental UV light is absorbed by lignin. Light induces radical reactions in the chemical components of wood. The reactions cause discoloration, weathering, and cracking of the surface of the wood. The color change takes place rather rapidly, but the erosion of the surface requires long exposure periods.[4,5] Protection methods have been developed to prevent the occurrence of degradation reactions. Paints and stains are traditional methods but the application of clear coatings has become increasingly popular.[6] The protection capability of the coatings has been improved by adding inorganic metal salts or photostabilizers, which can absorb UV light, scavenge free radicals, or quench excited molecules. The most common UV stabilizers used are 2(2′-hydroxyphenyl)-benzotriazoles and *o*-hydroxybenzophenones, which inhibit polymer degradation by absorbing ultraviolet light and dissipating the energy either by transferring it to surroundings or by re-emitting it through phosphorescence, fluorescence, or heat.[7–9] Hindered amine light stabilizers are widely used as radical scavengers.[10] However, the coating needs to be reapplied after some years in order to maintain the protection capability, especially if the wooden material is used in outdoor applications.[11,12]

The penetration pattern of different substances into wood has been a subject for several studies.[13–19] Wardrop and Davies[19] discovered that the initial penetration takes place through the cut ends of the tracheids and farther on to other tracheids through the pits in Radiata pine. They also postulated that the lateral penetration occurs through the ray cells, and from the ray cells the penetration into adjacent tracheids occurs via the pits. Resin canals also provide a path of penetration. The penetration is similar in both sapwood and heartwood but the penetration into the latewood is more pronounced than in the earlywood due to lesser extent of aspiration. Overall the penetration into wood is fairly ununiform. Usually the cells just beneath the surface are filled with the binder and deeper penetration consists of a binder which absorbed to the cell walls. More pronounced penetration into the latewood than into the earlywood was recorded in several studies. There are inconclusive results as to whether the tangential penetration is more pronounced than the radial.[15,16,20–22]

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Both natural and artificial weathering induce a rapid change in the color of wood. Generally, the color turns into yellow and brown and, under prolonged exposure, to gray. The conversion of the color is a complex process of photo-oxidative and photodegradative reactions.[23] The brown color is due to the degradation products of lignin and extractives. As rain, or artificially induced rain, dissolves the brown decomposition products, a gray layer of fibers of loose and disordered arrangement, develop over the brown layer. The gray layer consists mainly of the more leach-resistant parts of the partially degraded wood cellulose. However, the change of color is also dependent on the wood species in question and its original color.[2,24–26]

When a wooden surface is exposed to weathering the radical reactions induced by the energy of light cause degradation of the wood structure. The degradation is not uniform; there are differences between the deterioration of softwood and hardwood species, between the tangential, radial, and transverse sections, and localized areas of resistance are possible. The rate of degradation is mainly dependent on the density of the wood and thus on the cell wall thickness. The chemical reactions, and therefore the degradation of the cell wall structure, are rather fast phenomena. However, degradation, to such an extent that severe cracking of wood surface and deterioration of mechanical strength of wood occurs, requires a long time of exposure.[5,26–30] Softwoods contain more lignin than hardwoods[24] and are therefore more susceptible to degradation by UV light. The thin-walled earlywood cells degrade more easily than the thick-walled latewood cells in softwoods.[29] The first indication of deterioration are voids in the lignin-rich cell corners of the transverse section that extend to the compound middle lamella. As the exposure time increases, the cell walls are separated, the secondary wall is destroyed, and the bordered pits between the tracheids are gradually degraded. In the cell wall, cracks and voids are generated, causing the wall to become fragile, which can be seen especially in the radial cell wall. The most severe cracks may spread over the tracheid wall.[25,27] The most prominent signs of photodegradation in the tangential section are microchecks that run along the microfibril angle in the cell wall S_2 layer and may pass through the bordered pits. The checks are narrower in the earlywood than in the latewood.[2,25]

The aim of the present study was to synthesize and characterize wood-protecting binders that contain benzotriazole and hindered amine types of light stabilizers. The penetration of the binders into the radial and tangential surface of wood was determined by a coloring method in combination with fluorescence microscopy. The protection capability of the binders on pine wood under irradiation to UV light, and the evaluation of the results are reported.

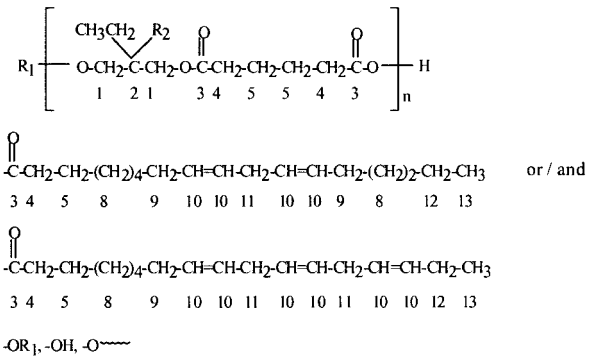

Figure 1 A possible structure of the synthesized binder without the light stabilizers.

EXPERIMENTAL

Materials, synthesis, and sample preparation

Trimethylol propane was obtained from Neste Chemicals, adipic acid from Merck, tall oil fatty acid from Ekopine, and xylene from Suomen Plastkem. The light stabilizers Tinuvin 213, Tinuvin 320, and Tinuvin 622 LD were obtained from Ciba–Geigy. Safranine T was a product of Fluka. All the chemicals were of synthesis grade and were used without further purification.

The polyester for the binders was synthesized from trimethylol propane (0.250 mol), adipic acid (0.250 mol), and tall oil fatty acid (0.214 mol) and is referred to as TAT. The synthesis was by bulk polymerization and the reaction was carried out in a temperature range starting from 140°C increasing to 200°C after 6 hours. Seven wt. % of xylene was used as an azeotropic cosolvent in order to ease the removal of the water formed in the reaction. The water was collected in a Dean–Stark trap. The reaction was carried out until the acid number was approximately 60. After synthesis the polyesters were vacuum distilled so that all possible traces of water and xylene were removed. The products were dried in a vacuum desiccator overnight. A possible structure of the binder is described in Figure 1.

Three different stabilizers were tested in the study (Fig. 2) and a concentration of 1% of stabilizer by weight was used in the binders. Tinuvin 320 was mixed with TAT after the polyester synthesis at 160°C because there is no reactive group that could be linked with the polyester chain. The product is referred to as PSE5. Tinuvin 213 and Tinuvin 622 LD were added to the reaction system in the beginning of the synthesis in order to bind the stabilizer to the polymer backbone. The products are referred to as PSE1 and PSE7, with Tinuvin 213 and Tinuvin 622 LD, respectively.

Scots pine (*Pinus sylvestris*) was used for the penetration experiments. All the samples were stored in the dark at ambient temperature before use. Pieces 1 cm $\times$ 1 cm $\times$ 1 cm in size were treated with the binders

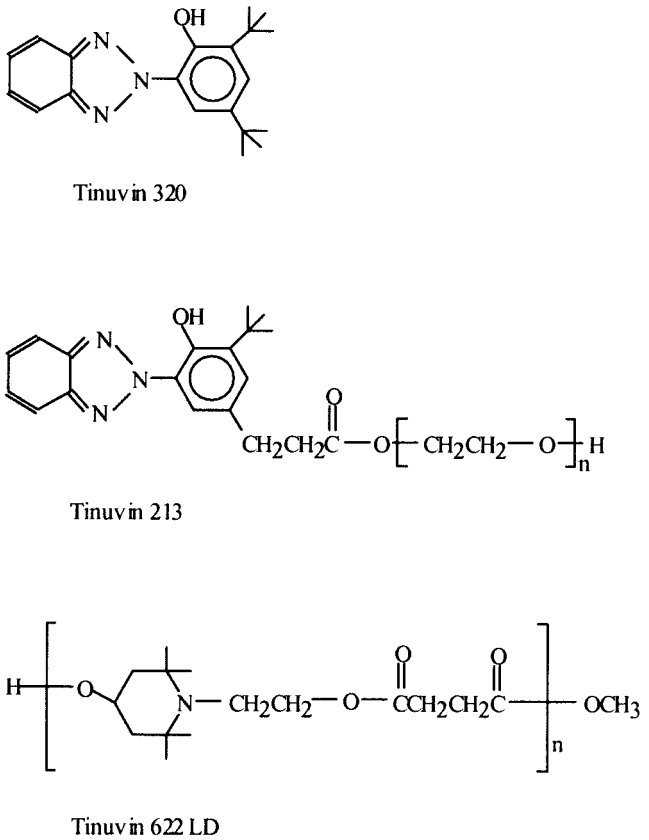

Figure 2 The applied light stabilizers.

from either tangential or radial surfaces. samples of Scots pine 12 cm × 10 cm × 2 cm in size were brush applied with the binders over the 12 cm × 10 cm area surface and left to dry. The samples were stored in the dark at ambient temperature and, after drying, exposed to UV light.

Analytical methods

Both ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were determined with a Varian Gemini 2000 spectrometer operating at 200 MHz. Solutions were made either in deuterated chloroform or in deuterated acetone. Tetramethylsilane was the internal standard. The chemical shifts have been assigned and calculated by using values obtained from the literature.[31–34] The results are collected in Table I.

Infrared (IR) spectra were determined using a Nicolet 205 spectrometer. Potassium bromide pellets were prepared of the solid samples and a Horizontal Attenuated Total Reflectance crystal was used for the liquid samples. The IR absorptions of the binders are collected in Table II.

The ultraviolet (UV) spectra of the samples were determined using a Shimadzu UV-2101PC UV-VIS Scanning Spectrophotometer apparatus in the wavelength range 900 to 200 nm. The solutions were made in AaS grade ethanol.

Determination of the molecular mass was done by size exclusion chromatography (SEC). The equipment consisted of PLgel 10-μm columns from Polymer Laboratories (pore sizes: 10^5 Å, 10^4 Å, and 500 Å), a Millipore Waters 500 HPLC pump, and an ERC-7515B refractive index detector by Erma Cr. Inc.. The samples were dissolved in tetrahydrofuran, and polystyrene of different molar masses was used for the calibration. The number and weight average molecular masses and the polydispersity M_w/M_n of the binders are collected in Table III.

The efficiency of the protecting polymers was tested in a Q-Panel Lab Products' QUV/Spray chamber equipped with UVA 340 lamps. The cycle for the

TABLE I
Chemical Shifts of the Binder[a]

Atom number[a]	δ (ppm)	
	^{13}C-NMR	^{1}H-NMR
1	62–66	3.41–4.19
2	40–43	—
3	173–175	—
4	33–35	2.27–2.37
5	24–25	1.64–1.66
6	7	0.85–0.92
7	22–24	1.26–1.50
8	29–32	1.26–1.50
9	26–28	1.96–2.10
10	127–131	5.26–5.42
11	24–26	2.77
12	22–23	1.26–1.50
13	14	0.85–0.92

[a] Atom numbers refer to the carbon atoms or hydrogen atoms attached to them in Figure 1.

TABLE II
FTIR Absorptions of the Binders

Binder	Band cm^{-1}	Assignment
TAT	2926	CH_2 stretching
	2855	CH_3 stretching
	1735	C═O stretching
	1462	CH_2 bending
	1416–1357	CH_2 vibrations
	1238–1141	C—O stretching
	1057	C—O vibration of alcohol
PSE1	3500	OH stretching of Tinuvin 213
	1539	C—N vibrations of Tinuvin 213
	871	Aromatic vibrations of Tinuvin 213
	749	Aromatic vibrations of Tinuvin 213
PSE5	1560	C—N vibrations of Tinuvin 320
	871	Aromatic vibrations of Tinuvin 320
	749	Aromatic vibrations of Tinuvin 320
PSE7	1560	C—N vibrations of Tinuvin 622 LD
	878	CH_2 vibrations of Tinuvin 622 LD

TABLE III
Molecular Masses of the Binders

Binder	M_w (g/mol)	M_n (g/mol)	M_w/M_n
TAT	8549	2661	3.21
PSE1	3628	1305	2.78
PSE5	4086	1426	2.87
PSE7	4330	1483	2.92

irradiation was: exposure to the UV light for 4 hours at 50°C and dark treatment for 2 hours at 40°C, repeatedly. The total exposure times were 3, 7, 14, 21, and 28 days. There was moisture present in the chamber but the pine surfaces were not directly exposed to liquid water.

The penetration of the binders into the wood surface was studied with a coloring method described previously.[35] The fluorescence microscopy examination was carried out using an Olympus Vanox S microscope equipped with an AH2-RFL-T 36428 lamp system and an AH-2 control box and Olympus RH-RFCA microscope system. The color of the wood surfaces was measured with a Minolta Spectrophotometer CM-508i at wavelengths from 400 to 700 nm and the results were obtained as described by the CIE L*a*b* method.[36,37] The spectrophotometer was calibrated by measuring a white reference sample included in the kit. The scanning electron microscopy (SEM) examination was carried out using a JEOL JSM-820 microscope. The samples were set on a small metal disk and the edges were treated with conductive graphite adhesive to obtain sufficient conductivity in the sample. The samples were sputter coated with platinum for 20 seconds before the examination. The accelerating voltage used was 5 kV.

RESULTS AND DISCUSSION

Nuclear magnetic resonance spectroscopy

In the ^{13}C-NMR spectrum of TAT the methyl groups of trimethylolpropane (TMP) and the fatty acid portion appear at about 7 ppm and 14 ppm, respectively. The different methylene groups in TMP and the acids show peaks in the 22–32 ppm area. The methylene groups next to carbonyl functionalities generate a peak at 33–35 ppm and those with an oxygen linkage appear at 62–66 ppm. The quaternary carbon in the TMP gives a peak at 40–43 ppm. The carbons in the fatty acids, with a double bond connection to another carbon atom, are shown at 127–131 ppm. The carbons with a carbonyl group in the acids are noted at 173–175 ppm.

It has been suggested that the NMR spectra in structural analysis of polyesterification of trimethylolpropane and *o*-pthalic anhydride can be divided into five different zones of the spectral field, and that the progress of the reaction can be evaluated by the position of the peaks.[34] The methylic region at 7 ppm showed a shift to the upper field as the number of ester groups was increased whereas, in the methylenic region at about 21–22 ppm, no pronounced shift, or a shift to the lower field, was noticed in chloroform or in dimethylsulfoxide, respectively. The quaternary nucleus at 40–43 ppm caused an upfield shift when the substitution of the hydroxylic groups by ester groups was increased. In the oxymethylenic zone at 61–65 ppm, the esterification of the alcoholic hydroxyl group produced an upfield shift and, as the reaction continued, a downfield shift was produced but a new peak also was formed. For the carboxylic group at 170 ppm the esterification caused the peak to appear at lower ppm values.

By using these statements the esterification of TAT can be inferred. The ^{13}C-NMR spectrum of TMP shows a methylic peak at 7.83 ppm and in the TAT spectrum there are two peaks at 7.31 and 7.39, which can be considered as a sign of esterification taking place. At the methylenic region TMP has a peak at 22.70 ppm and for TAT there are four peaks in the region 22.23–23.01 ppm. These values are close to each other but, since the solvent was chloroform, no noticeable difference can be expected by the statements of Callejo Cudero et al. The quaternary carbon in TMP appeared at 44.06 ppm and for TAT two peaks in the area 40.70–42.51 ppm were visible; thus the upfield shift is an indication of esterification. In the oxymethylenic region TMP has a peak at 65.12 ppm. In TAT this region shows four peaks at 62.40–65.68 ppm. The shift of the peaks suggests that the hydroxyl groups are replaced by the acid groups and thus the reaction is taking place. By considering these results it can be concluded that the esterification was successfully accomplished.

In the ^{1}H-NMR spectrum of TAT the peak at 0.85–0.92 can be attributed to the methyl group of both TMP and the fatty acids. The methylene groups next to other methylene groups resonate within 1.26–1.66 ppm. The methylene groups in the fatty acids that are next to a carbon with a double bond show peaks at 1.96–2.10 ppm and the methylene hydrogens in a carbon between two double bonds containing carbons resonate at 2.77 ppm. The methylene groups in a carbon, next to a carbonyl functionality, appear at 2.27–2.37 ppm and, in the alcohol part, the methylene groups that are linked with an oxygen have peaks at 3.41–4.19 ppm. In the double bonded carbons the hydrogens show peaks at 5.26–5.42 ppm.

The esterification can be followed by determining the oxymethylenic region peaks of the TMP ^{1}H-NMR spectrum.[34] The chemical shifts of the hydrogens attached to the carbon in the —CH_2OH group move to smaller ppm values when esterification takes place. In

addition, the chemical shifts of the methylene groups in the esterified part (—CH_2O—) appear at larger values. In TMP the oxymethylenic zone shows two peaks at 3.53 and 3.56 ppm. In TAT there are small peaks at 3.43 and 3.57 ppm and a more intense one at 4.02 ppm. A very small peak was noted at 4.19 ppm. These values can be considered as a verification of the esterification reaction.

The identification of the stabilizers in the ^{13}C- and the ^{1}H-NMR spectra of the synthesized binders is considered to be impossible because of the small amount of the stabilizer in the binder. Very small aromatic region peaks can be noted in the ^{1}H-NMR spectra of PSE1 but no conclusions can be drawn about the binding of the stabilizer molecules to the polyester backbone. There are no other characteristic stabilizer peaks visible in the spectra; therefore other spectroscopic methods were used to confirm the presence of the stabilizers.

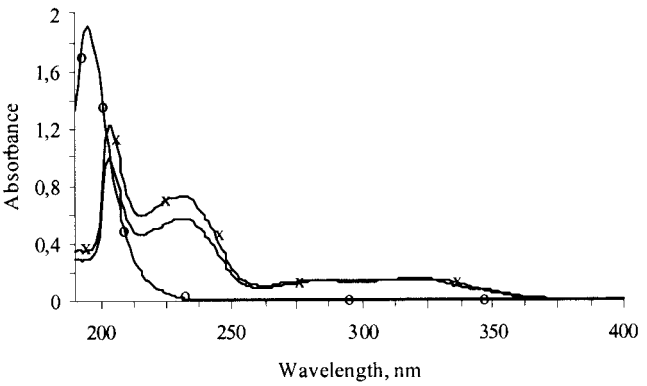

Figure 3 UV spectra of PSE1 (—), washed PSE1 (—x—), and the water phase of washing (—o—).

Infrared spectroscopy

The strong absorption at 2926 cm^{-1} and the sharp band at 2855 cm^{-1} are due to CH_2 stretching and CH_3 stretching, respectively. The very intense band at 1735 cm^{-1} results in the absorption of carbonyl functionalities of ester groups within the binder. The area from 1462 to 1357 cm^{-1} shows different vibrations of CH_2 groups, including CH_2 bending. The C—O functionalities in the binder backbone, and in possible free alcoholic groups, induce medium absorptions at 1238–1057 cm^{-1}.

The amount of stabilizer in the binder is very small, and therefore most of the absorption bands are overlaid by the bands of the binder. Weak bands or only shoulders within a binder band can be noted. In the PSE1 binder the stabilizer compound is Tinuvin 213, which has a benzotriazole structure. The Tinuvin 213 molecule and the polyethylene glycol contain unbound hydroxyl groups whose stretching vibration is visible at 3500 cm^{-1}. The carbon to nitrogen bond (C—N) shows absorption at 1539 cm^{-1}. The aromatic character of benzotriazole induces absorptions that are visible as shoulders at 871 cm^{-1} and 749 cm^{-1}.

The binder PSE5 contains benzotriazole-type stabilizer Tinuvin 320. A similar kind of band at 3500 cm^{-1} to that for the other benzotriazole, including binder PSE1, is not noted. Therefore it can be concluded that, in PSE1, the hydroxyl absorption is mainly due to the polyethylene glycol proportion of the stabilizer structure. C—N absorption on the other hand is noted at 1560 cm^{-1} and aromatic ring vibrations as shoulders at 871 cm^{-1} and 751 cm^{-1}. The Tinuvin 662 LD stabilizer in the PSE7 binder is of a hindered amine type and does not have an aromatic character. The characteristic absorption of the C—N vibration and CH_2 vibrations are noted at 1560 cm^{-1} and at 878 cm^{-1}, respectively.

Ultraviolet spectroscopy

The presence of the stabilizers in the synthesized binders was detected by ultraviolet spectroscopy. The binders to which stabilizer had been added were washed with hot distilled water in order to separate the part of stabilizer that had not been bonded to the polymer backbone. In the absorption spectra of Tinuvin 213 there are two absorption maxima at 340 nm and 303 nm, due to the benzene ring absorptions, and the absorptions at 284 nm and 202 nm are due to the aliphatic polyethylene glycol part in the stabilizer. PSE1, washed PSE1, and the water phase from the PSE1 washing in Figure 3 show that the water phase does not have any absorptions typical for Tinuvin 213, and it can thus be concluded that Tinuvin 213 has bound to the polymer.

The Tinuvin 622 LD shows one maximum at 201 nm. In the PSE7 spectrum there is little indication of Tinuvin 622 LD binding to the polymer. The amount of the stabilizer is rather small and its molecular weight is high, so it may be possible that the binding cannot be detected. The water phase from washing reveals mainly a Tinuvin 622 LD kind of absorption and therefore the Tinuvin 622 LD may not be bound to the polymer.

Size exclusion chromatography

The weight average molar masses vary between 3628 g/mol for PSE1 and 8549 g/mol for TAT and the number average molecular masses between 1305 g/mol for PSE1 and 2661 g/mol for TAT. The polydispersity M_w/M_n varies from 2.78 for PSE1 to 3.21 for TAT. From the results it can be concluded that the TAT based binders have rather low molecular masses and hence they are oligomeric.

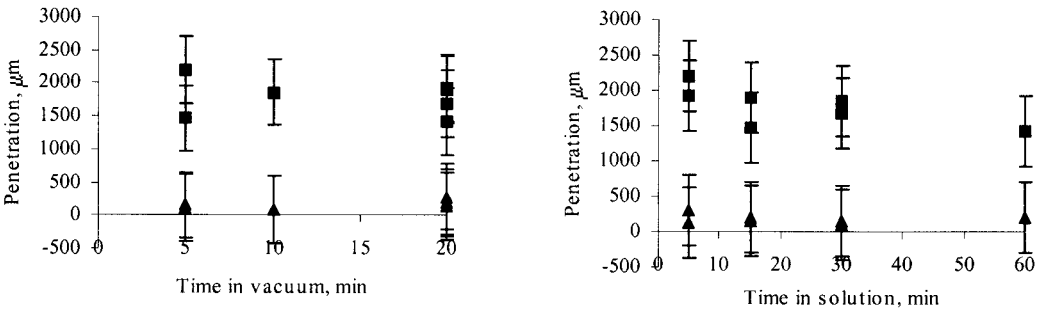

Figure 4 Penetration of PSE1 into radial pine surface as a function of the time in vacuum or the time in the solution: earlywood (▲); latewood (■).

Penetration of polymer into wood surface

The penetration of the binders varies depending on the surface on which the binder was applied and on the part of the annual ring. The average penetration depth into the radial surface is between 170 and 480 μm into earlywood and between 1300 and 2320 μm into latewood. However, there are exceptions and the penetration can be deeper than the average values. Penetrations as deep as 810 μm were measured for earlywood and 2890 μm for latewood.

The penetration into the tangential surface is more pronounced than into the radial surface but there is also more variation in the depths, except for PSE7. The average penetration in the earlywood was between 330 and 1290 μm but the scale includes many values starting from 125 to almost 3000 μm. In the latewood the average penetration depth was between 1730 and 2560 μm. However, in the latewood, there was also variation but it was not as pronounced as in earlywood. The penetration into the latewood may exceed 3000 μm.

The penetration depths of PSE1 into the radial surface are presented as a function of the time in vacuum, or the time in the dye solution, in Figure 4. In these graphs the pronounced penetration into the latewood is the predominant feature. There is some variation in the penetration depths but the values for the earlywood and the latewood fit well within the standard error limits. Since the penetration depths are mostly within the error limits it can be concluded that neither the time in vacuum nor the time in dye solution affect the penetration of the binder into wood, either on the radial or on the tangential surface.

De Meijer et al.[16] measured penetration for different binders into both pine and spruce. Pigmented alkyd emulsion penetrated to about 40 μm into spruce and 150 μm into pine surface. Pigmented high-solid alkyd and solvent-borne alkyd filled the three first cell layers in pine but the penetration can be as deep as 1000 μm along the parenchyma cells. Unpigmented binders had the same basic penetration pattern as the pigmented ones but the actual penetration was deeper. The water-borne alkyd emulsion penetrated pine ray parenchyma to 150 μm and even up to 500 μm. The high-solids alkyd filled the outer 1–3 tracheids and 1–6 tracheids in earlywood and latewood, respectively. The rays were penetrated up to 2 mm and, for diluted binder, even up to 6 mm. The unpigmented solvent-borne alkyd filled the outer cells, but the penetration in parenchyma cells can be 2 mm in pine. An uneven and partially deep penetration of linseed oil into white spruce was discovered by Schneider.[15] Linseed oil was discovered even 4 cm below the treatment surface. Deep penetrations can be achieved depending on the nature of the binder. Alkyd-type systems can easily penetrate, at least partially, up to several millimeters of depth. Thus the results obtained for the synthesized binders are not surprising, and the penetration seems to be sufficient for protection of the wood surface.

The pronounced penetration into the latewood can be explained by capillary effects and pit aspiration. The smaller diameter lumen of the latewood has more effective capillarity than the earlywood, which has a larger lumen. Thus the small molecular size TAT-based binders will diffuse deeper into the thick-walled cells and the smaller sized lumina of the latewood than in the cells of the earlywood, which have thinner walls and larger lumina. The torus is able to block the bordered pit between two tracheids by pressing against the other side of the pit. The pit becomes aspirated and no flow can occur through it. More pit aspiration occurs in the earlywood than in the latewood; therefore the path of the binders to penetrate is less restricted in the latewood than in the earlywood.[19,20] The binders fill some of the cell lumina, mostly in the latewood but also in the earlywood. The penetration probably takes place through the pits in the cell walls. Some binder passes from the latewood side to the earlywood side through the pits and via the rays. In the samples treated on the tangential surface the binder may penetrate along the latewood even though there would not be any binder visible above it in the earlywood part.

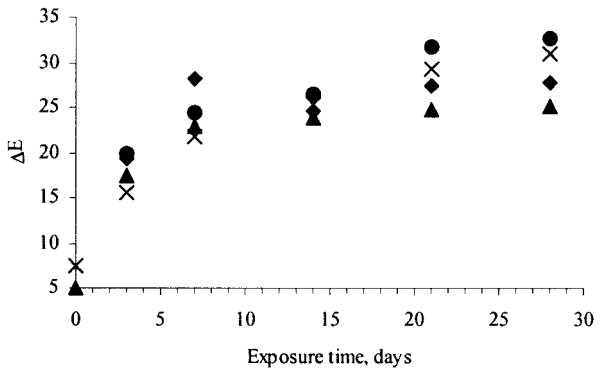

Figure 5 Total color change (ΔE) as a function of exposure time: TAT (▲), PSE1 (◆), PSE5 (×), PSE7 (●).

Artificial weathering

The change of color of the exposed pine surfaces toward brown is clearly visible by the naked eye. Color had already changed more yellow after 3 days of exposure and continued to darken as the exposure time increased. The changes of total color difference ΔE, as a function of the exposure time, are shown in Figure 5. The overall trend is that ΔE increases as the exposure time increases, and thus the pine surface becomes darker. In the beginning of the exposure the ΔE value increases rather rapidly and continues to increase at a slower rate until a point is reached, which can be defined as the point where leveling off begins.

In the beginning of the exposure the reference sample, without any protection, darkened slightly more than the pine samples protected by the binder. When the exposure time was increased, the ΔE values of the reference sample and the treated samples became closer to each other. After approximately 10 days, the samples treated with the PSE7 showed higher ΔE value than the reference sample and, after about 14 days, the samples treated with the PSE5 binders had higher ΔE values than the reference. Both PSE5 and PSE7 show higher ΔE values than the reference sample after 28 days of exposure. This is rather surprising since it gives the impression that the binders with stabilizers do not protect wood from photodegradation. However, the situation is not simple. It has to be kept in mind that there are differences between the original colors of the pine samples due to the different shades of earlywood and latewood. The color of different wood samples varies, depending on the amount of the lighter earlywood and the darker latewood in the sample. In fact, when comparing the brightness values (L) of the unexposed reference, PSE5 and PSE7, the reference appears to be the brightest in color.

The yellowness values (b*) of the exposed samples, as a function of the exposure time, are presented in Figure 6. It seems that, in the beginning of the irradiation, the yellowness increases but decreases slightly at the end of the exposure. There were only small differences in the b* values between the different treatments but the results show that the reference sample, without any binder, was less yellow than the samples treated with the binder. This is due to the slightly yellow color of the binders applied, which increases the yellowness of the wood. After 28 days of irradiation the PSE7-treated pine had the greatest yellowness value. It was not the most yellow sample in the beginning of the exposure; therefore the strongest yellowness is caused by the formation of chromophores during irradiation to UV light. The PSE1-treated sample gave the smallest yellowness value after 28 days of irradiation. The brightness of the samples decreased during irradiation and the a* values became greater, indicating a shift to darker and more red than green shades with increasing exposure time.

The benzotriazole stabilizer, Tinuvin 213, protected the surface of wood quite well. The benzotriazole Tinuvin 320 does not function as well in the binder. This can be due to easier leaching out of Tinuvin 320. It is possible that the binder does not form a network structure that would hold the stabilizer in the polymer. The hindered amine light stabilizer, Tinuvin 622 LD, was the poorest stabilizer: the high ΔE value of PSE7 is an indication of this. Hence it can be concluded that the benzotriazole-type stabilizers are the most suitable for these binders and the HALS is the least appropriate.

The ΔE values after 28 days of irradiation were between 25 and 33. In the literature it was reported that Tinuvin 622 LD treatment results in a ΔE value of about 15 and Tinuvin 213 treatment in a value of about 14 in artificially weathered (for 50 hours) maritime pine.[38] After 200 hours the ΔE for unprotected Scots pine was measured to be 19.[39] Fifty hours corresponds to about 2 days of exposure and 200 hours to about 8 days. After 2 days all the tested binders show approximate ΔE values under 15, but after 8 days the reference seems to be darker than reported by Tolvaj and coworkers.[39] Grelier et al.[40] found that, after 8 hours of

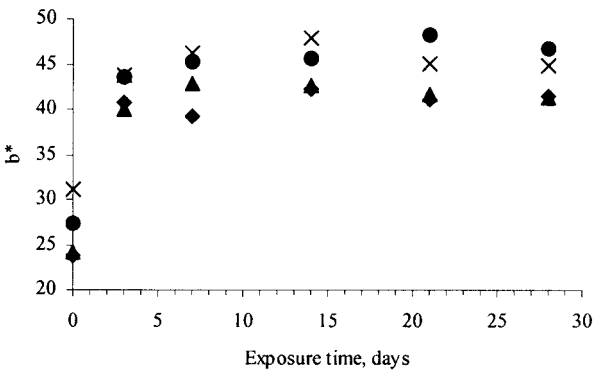

Figure 6 Yellowness value (b*) as a function of exposure time: TAT (▲), PSE1 (◆), PSE5 (×), PSE7 (●).

exposure, samples treated with hindered amine light stabilizers (HALS) and a benzotriazole had ΔE values close to 8 and 5, respectively. Synergism was noted and the ΔE was a little over 2 after 8 hours of exposure when HALS and benzotriazole were mixed. Eight hours is a rather short time in predicting weathering resistance, but it is nevertheless interesting to notice the point of synergism.

The irradiation of pine samples induces an increase in the amount of carbonyl groups and degradation of the lignin chemical structure. There is an increase in the intensity of the carbonyl stretching band at 1735 cm^{-1}. This is due the formation of new carbonyl groups and is hence a sign of reactions taking place during exposure to UV light. The absorption bands caused by lignin aromatic vibrations decrease during irradiation. Bands in the area of 1658–1602 cm^{-1} decrease, and there is a considerable decrease in the intensity of the benzene ring stretching band at 1510 cm^{-1} and, to a lesser extent, at the lignin carbonyl stretching band at 1271–1222 cm^{-1}. There is an overall decrease in the intensities of the band at the area 1300–1000 cm^{-1}, which is a sign of demethylation and/or demethoxylation taking place. It can be concluded that the lignin portion of the pine surface degrades when exposed to UV irradiation and, moreover, it degrades more than cellulose. These results are congruent with the findings reported in the literature.[41] The deterioration of the chemical structure of wood is already visible after 3 days of exposure and becomes more distinct when the irradiation time is increased. The lignin absorption bands do not disappear totally, which indicates only a partial degradation of the structure.

The wood samples that were exposed to UV light, including the samples that had not been irradiated, were examined by scanning electron microscopy to determine the degradation of the wood surface. The surfaces of the samples were slightly broken from the earlywood part due to the preparation—sawing and planing—of the wood pieces. The appearance of the earlywood part is more uneven than the latewood part because the thicker walled latewood is more resistant to mechanical treatment.

No signs of degradation were visible after 3 days of exposure in any of the samples. The surface was smooth and no cracks caused by the effect of light were present. Some separation of tracheids took place after 7 days of irradiation and the surface became rougher. After 14 days of exposure the separation of the tracheids was more pronounced and the surface appearance was more rugged than in the samples that had been irradiated for 7 days. Only a few cracks were visible in the samples that had been exposed for 3, 7, and 14 days. For samples exposed for 3 and 7 days these may be due to the mechanical abrasion of the preparation of the wood samples, but some in the samples irradiated for 14 days are due to the degradation reactions caused by light. The surfaces are most damaged in the samples exposed for 21 and 28 days. The surface became rougher and cracks along the microfibril orientation became pronounced. The bordered pits were degraded during the exposure to light. The pits can be partially filled with the binder but, under exposure, severe degradation takes place in the form of cracks leading to total destruction.

CONCLUSIONS

The object of this research study was to synthesize and characterize wood binders, which could protect wood against the action of light. The synthesis method proved to be successful and oligomeric: easily penetratable polymers were produced. Nuclear magnetic resonance spectroscopy proved to be a good method in evaluating the progress of the reaction. The small amount of light stabilizers in the binder made it difficult to prove whether the stabilizer was bound to the polymer backbone of the binder. With NMR and FTIR this was not possible, but ultraviolet spectroscopy gave some proof that the Tinuvin 213 was bound while the Tinuvin 622 LD was not.

The penetration of the binders was detected by a method consisting of dyeing the wood sample and examination by fluorescence microscopy. The binder is not affected by the dye and thus the penetration capability of the binders is not changed. The dyeing time did not have an effect on the penetration depths of the binders. The penetration was deeper into the latewood than into the earlywood and the overall penetration pattern was uneven. The average penetration depth into the radial surface was mainly below 480 μm in the earlywood and below 2320 μm in the latewood but much deeper penetrations were also measured. The average penetration depths in the tangential direction were approximately 1000 μm for the earlywood and below 2500 μm for the latewood. The depths of the binders thus should be suitable for decent protection. The pronounced penetration into the latewood is due to the more effective capillarity in the small lumina of the latewood than in the larger lumina of the earlywood. Pit aspiration has been proved to take place less in the latewood than in the earlywood.[19,20] This phenomenon also affects the greater penetration into the latewood. The penetration was found to be more pronounced into the tangential surface than into the radial surface; the main transfer mechanism from cell to cell is most probably through the pits. Some binder passes from the latewood part to the earlywood side through the pits and the rays.

Pine samples treated with the binders darkened during irradiation with UV light. The total color change was up to 33. The surfaces became more yellow but the yellowness decreased after certain time of

irradiation. Of the applied stabilizers the benzotriazole Tinuvin 213 performed the best while the HALS-type stabilizer Tinuvin 622 LD performed the poorest. FTIR showed degradation of the lignin chemical structure on the wood surface and SEM indicated degradation and cracking of cell structure already after 14 days of irradiation. Separation of the cells occurred and cracks along the microfibril orientation were visible. The pits were degraded as well. The deterioration was most severe after 21 and 28 days of irradiation.

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