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Mechanical behaviour of acetylated rubber wood subjected to artificial weathering

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Abstract: Rubber wood utilization in Nigeria has become a viable alternative because of over-exploitation of more durable species. The use of rubber wood in its native form has some disadvantages including dimensional instability, low durability and susceptibility to weathering in outdoor uses. However, it may be improved through chemical modification such as acetylation. In this study, we revealed the effectiveness of acetylation on the protection of rubber wood against weathering in terms of weight loss (WL), colour change, lignin degradation, and mechanical properties. Acetylation was carried out using two different reaction times to achieve weight percent gains (WPG) of around 7% and 10%. Understanding of the effect of acetylation and subsequent weathering on mechanical properties was enabled by analysing wood chemistry with Fourier transform infrared (FTIR) analysis and Raman spectroscopy. The mechanical tests of weathered unmodified and acetylated rubber wood revealed a decrease of tensile stiffness of the unmodified samples as a function of weathering time, while stiffness was retained for the acetylated samples. Weathered unmodified samples showed a bi-phasic stress-strain pattern with a high strain at breakage indicating a slippage of fibres under stress due to degradation of the middle lamella. This was hardly visible for acetylated samples. Thus, acetylation was shown to be effective for protecting rubber wood used in outdoor conditions.

Keywords: accelerated weathering, acetylation, infrared spectroscopy, mechanics, Raman microscopy, rubber wood

Introduction

Wood has been considered as one of the most valuable and useful natural resources for construction throughout history due to its physical and mechanical properties as well as its relative abundance. One of the disadvantages of wood is its vulnerability to insects and fungi (Freeman et al. 2003). Next to this, abiotic factors including ultra-violet radiation (sun light) and moisture lead to weathering and surface degradation that reduces aesthetics and can also influence the mechanical properties of wood (Winandy and Rowell 1984). Chemical modification is one way to slow down wood degradation caused by weathering or fungi. Modification ensures long service life and prevents untimely failure of wood structures, which reduces maintenance costs. Among several chemical wood modification techniques, acetylation has proven to be effective for improving dimensional stability and decay resistance (Wang et al. 2002; Hill et al. 2006; Rafidah et al. 2006; Mohebbi and Militz 2010; Gascón-Garrido et al. 2013; Rowell and Dickerson 2014). Acetylated wood is not toxic to humans and has a low environmental impact compared to biocide treatments (Gérardin 2016). Acetylation is already commercialised, which makes it relatively easy to be adopted in developing countries. The process involves the reaction of hydroxyl groups of wood cell wall (cw) polymers (in particular the free hydroxyl groups in the lignin-hemicellulose matrix) with acetic anhydride to form acetyl groups. This treatment results in a lower moisture uptake below the fibre saturation point compared to unmodified wood, which improves dimensional stability (Militz, 1991; Papadopoulos and Hill, 2003). Next to this, acetylation may also be relevant in terms of the weathering of wood, which is the exposure to a combination of rain, UV radiation, temperature changes and wind in outdoor usage. Exposure to UV radiation leads to colour changes caused by lignin degradation. This is followed by an increase of surface roughness and loss of fibres in

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the case of rain, because of leaching of degraded lignin (Rowell and Dickerson 2014). Acetylation is known to enhance lignin stability against degradation by UV radiation (Feist et al. 1991).

The mechanical behaviour of weathered wood is yet to be studied in detail. In an earlier work, Evans et al. (2000) studied the tensile strength of very thin veneers of Scots pine subsequent to acetylation with four different WPGs and weathering. It was reported that loss in tensile strength due to weathering depends on the level of WPG. At low WPGs, losses in tensile strength were higher compared to samples with higher WPGs.

In the present study, we have widened the scope of mechanical analysis of small samples of weathered wood. We describe the stress-strain behaviour, including stiffness, strength and strain at failure for further insight in the mechanical behaviour of acetylated and weathered rubber wood (*Hevea brasiliensis* Muell Arg.) Rubber trees originate from Brazil and have been planted as an agricultural crop for latex production in many countries including Nigeria as far back as 1895. Tapping of latex from rubber wood starts about 7 years after planting and lasts until a tree age of 25–30 years after which the latex production declines. Following this decline, rubber trees are felled and either burned on site, used as fuel wood (Severo et al. 2016) or furniture (Teoh et al. 2011). Its use as timber material in Nigeria today is motivated by the decline in supply of naturally durable hardwood species due to over-exploitation and deforestation by illegal means. Shortcomings of rubber wood are its poor dimensional stability, and its low durability (Rafidah et al. 2006; Teoh et al. 2011). For an efficient use of rubber wood as construction material, especially in exterior conditions, treatments that improve its dimensional stability and durability are of high importance. For rubber wood, the occurrence of tension wood is a common phenomenon (Lim et al. 2002; Nobuchi and Daneetha 2011). It is not known, if the presence of tension wood alters the influence of acetylation and weathering on the mechanical properties of rubber wood. Rubber wood has previously been acetylated with different WPGs, depending on treatment temperature and reaction times (Chauhan et al. 2001; Pandey and Pitman 2002; Pandey and Srinivas 2015; Rafidah et al. 2006). Many of these studies report on using high temperature and long treatment times to achieve high WPGs. It was shown that acetylation improves the dimensional stability of rubber wood.

Here, we acetylated rubber wood using milder processing parameters, for example, lower temperature, compared to the above mentioned studies. By varying treatment time, two different WPGs were achieved. We

characterised the stress-strain behaviour, tensile strength and Young's modulus of unmodified and acetylated samples. In all cases, the average proportion of tension wood was estimated. Fourier transform infrared (FTIR) and Raman spectroscopy were used to characterise the unweathered and weathered acetylated rubber wood for understanding the effect of acetylation and weathering on mechanical properties. Additionally, we report the effect of acetylation and weathering on colour change, weight loss (WL), and sorption of rubber wood.

Materials and methods

Wood procurement and conditioning: Rubber wood (*H. brasiliensis* Muell Arg.) was obtained from a private plantation at Legbogbo village, Ode-Irele Ondo State Nigeria (Lat. 06.59308°N, Long. 004.89078°E). By the time of the visit (April 2017), the trees of the plantation were well over 30 years old and latex production had ceased. One tree was felled at a height of 0.5 m. Two boles were cut from the lower part of the trunk, which included the region at breast height, for preparing all samples. Density and mechanical properties are usually highest from this point downwards to the basal part of the tree stem (Weber and Montes 2005; Zhou et al. 2012). The selected boles were sawn into planks with the dimension 550 mm × 120 mm × 40 mm, pre-dried in a solar kiln for 5 days at the Central Laboratory, Federal University of Technology, Akure, Nigeria, and shipped to ETH Zurich, Switzerland. On arrival, the planks were immediately stored for conditioning at 65% relative humidity (RH), and 20°C for 6 months before starting the experiments.

Sample preparation and categorisation: One hundred and eighty samples of 50 mm × 15 mm × 1 mm size (L × T × R) were prepared and divided into three equal groups (reference, 8 h acetylation and 48 h acetylation) consisting of 60 samples. Each group was subdivided into four batches of 15 samples, out of which three batches were subjected to accelerated weathering of 2, 3, and 4 weeks, respectively (see section Accelerated weathering). The first batch was left unexposed. All batches were mechanically tested (see section Tensile test).

Acetylation of rubber wood: Rubber wood was dried at 65°C for 48 h and placed in a flask with dimethylformamide (DMF) and acetic anhydride (50 v/v %). Impregnation was done under vacuum for 18 h to ensure sufficient and homogeneous penetration. Subsequently, the mixture was heated to 70°C under reflux and the reaction was conducted for either 8 h or 48. The acetylated samples were washed in acetone for 5 days to remove the excess acetic acid. The washing solution was changed twice a day throughout the washing period. Samples were oven-dried at 65°C for 48 h until a constant weight was reached. The weight percent gain (WPG) was calculated as:

$$\text{WPG}(\%) = \left(\frac{W_t - W_o}{W_o} \right) \times 100 \quad (1)$$

with W_t = dry weight after acetylation, W_o = dry weight before acetylation. The moisture content of all samples was calculated from their conditioned weight at 65% RH and their dry weight.

Accelerated weathering: Reference and acetylated rubber wood samples were exposed to accelerated weathering in the QUV Accelerated Weathering Tester (Q-Lab, Miami, FL, USA). The tester is equipped with a heating compartment, UV-A lamps with maximum emission at 340 nm and water spray. Only one side of the samples was exposed. The three sample batches were weathered for 2, 3 and 4 weeks, respectively. Standardised exposure procedure is described in the EN 927-6 (2006). A single test cycle consists of alternating 30 min water spray, 2 h, 30 min of UV exposure with an irradiance of 0.89 W/m², and a panel temperature of 60°C.

Colour measurement: Prior to and after weathering, colour measurements were carried out with a Chroma Meter CR-200 (Minolta, Miami Lakes, FL, USA) on all samples. The determination of colour change was done according to the $L^*a^*b^*$ colour space (CIE standard). The total colour change (ΔE) was calculated as:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (2)$$

with L representing the lightness in the range of 0–100 (black to white); $+a^*$ is red and $+b^*$ is yellow; $-a^*$ is green and $-b^*$ is blue.

Tensile test: For mechanically testing, the rectangular samples were re-shaped with a cutting template to the dimension shown in Figure 1. Tensile tests were conducted on a universal testing machine (Zwick/Roell, Ulm, Germany), using a 10 kN load cell at a test speed of 1 mm/min until failure of the samples. Video extensometry was employed to measure strain by attaching contrasting paper strips on the sample. Young's modulus was calculated within 10–40% of the maximum stress. Tensile strength was calculated by taking into account only those samples, which ruptured outside the grip

Figure 1: Dimensions of the samples for tensile test (units in mm).

positions. At least seven successful tests were conducted per configuration to derive the elastic modulus. Tensile strength was determined for at least five samples per configuration.

Chemical and structural analysis: *FTIR:* All samples were analysed with FTIR spectroscopy using a TENSOR 27 FTIR spectrometer (Bruker, Karlsruhe, Germany) in attenuated total reflection (ATR) mode. Each sample was measured once on both surfaces. An average of 128 scans was obtained for each spectrum within the spectral range of 4000 cm⁻¹ to 350 cm⁻¹ at a resolution of 4 cm⁻¹. All 15 spectra of each treatment batch and sample side were then averaged. Baseline correction of the averaged spectra was done, using the rubber band method (Bruker, OPUS, Karlsruhe, Germany). Normalisation of spectra was performed by taking the maximum intensity within 980–1100 cm⁻¹ corresponding to C-O stretching of cellulose (Colom et al. 2003). This peak range was chosen as it is least affected by chemical modification and weathering. For unmodified rubber wood, IR absorbance peaks in the fingerprint region between 800 and 1800 cm⁻¹ were assigned to functional groups from wood biopolymers according to literature (Harrington et al. 1964; Hon 1989; Pandey 1999; Pandey and Pitman 2002; Gierlinger et al. 2008; Le Troedec et al. 2008; Nazarpour et al. 2013).

Raman microscopy: For confocal Raman spectroscopy measurements, cross-sections of 20 µm thickness were prepared from unweathered and 2-weeks weathered reference and 8-h acetylated samples and sealed in deionised water between a glass slide and a cover slip. Raman spectra were then recorded as two-dimensional mappings with an inVia Raman microscope (Renishaw, Wotton-under-Edge, Gloucestershire, UK) equipped with a motorised stage. A linearly polarised Nd:YAG laser ($\lambda = 532$ nm) and a 100× oil-immersion lens with a numerical aperture of 1.3 were used. The Raman signal was detected by an air-cooled charge coupled device (CCD) camera behind a spectrometer with a spectral resolution of approximately 1 cm⁻¹. The individual spectra were recorded with a laser power of about 25 mW in the spectral region between 300 and 1800 cm⁻¹ and a lateral step size of 300 nm. Cosmic ray removal and baseline correction were performed in the software Wire 4.1 (Renishaw, Gloucestershire, UK). The data were further processed with the Matlab based software Cytospec (version 2.00.01). Average spectra of defined areas were extracted from the secondary cw and the cell corners (cc) from regions of interest of two to five mappings per cross-section and three cross-section per configuration. Spectra were normalised (min/max) for better comparison.

X-ray diffraction (XRD): Cellulose microfibril orientation of mechanically tested wood strips was measured by wide-angle X-ray diffraction (WAXD) using a Nanostar (Bruker AXS, Karlsruhe, Germany) and CuK α radiation with a wavelength of 1.54 Å. The X-ray beam diameter was ~300 µm and the sample-detector distance was set to 9.1 cm. From the edges of all mechanically tested samples, microtome sections of 100-µm thickness were cut, which resulted in 1-mm wide samples (representing the thickness of the mechanically tested samples). For each sample, one diffraction image was taken with 10-min exposure time. For cellulose orientation analysis, azimuthal intensity profiles of the (200)-Bragg peak of cellulose were generated from the diffraction images by radial integration according to Rüggeberg et al. (2013). The azimuthal profiles were then used to calculate the microfibril orientation distribution for each measuring spot.

Data analysis: Statistical analysis was performed by one-way analysis of variance (ANOVA) with the statistical package for social scientists (IBM SPSS, version 22). Results are shown as mean and standard deviation of the different treatments.

Results and discussion

Weight gain of acetylated rubber wood

Acetylation of rubber wood for 8 h and 48 h resulted in an average WPG of around 7% and 10%. The WPG obtained in this study is at the lower limit of what has been reported in previous studies (Pandey and Pitman 2002, Pandey and Srinivas 2015; Rafidah et al. 2006). In those studies temperatures of 100°C and above were used, whereas modification was performed at 70°C in the present study. This comparatively low temperature was chosen, as treatment at high temperatures may have some implications on mechanical properties (Xie et al. 2013). Utilising DMF during the acetylation process enhanced the swelling of wood and eased penetration of acetic anhydride into the cw (Ashton 1973; Mantanis et al. 1994). While such solvent treatment is straightforward at laboratory scale, its application at industrial scale is challenging from an economic and ecological point of view.

Chemistry of acetylated rubber wood

The WPG could be explained by the acetylation of OH-groups, which was confirmed by FTIR and Raman spectroscopy. After acetylation, we observed an increase in the IR absorbance peak at 1735 cm⁻¹ (Figure 2), which corresponds to C=O stretching vibrations of acetyl groups. The increase at 1369 cm⁻¹ is attributed to C-H bending vibrations of the CH₃ group from acetyl groups. An increase in absorbance was also observed at 1236 cm⁻¹. However, assigning this peak to a particular cw polymer or functional group is difficult as absorbance by newly formed ester bonds by acetylation (C-O-C asymmetric stretching) and C=O stretching of lignin overlap in this range (Gierlinger et al. 2008). In the Raman spectra (Figure 3a), the increased intensity at 1732 cm⁻¹ corresponds to an increased acetyl content. This was visible for both cc and cw. Taken together, IR and Raman spectra confirmed that acetylation has taken place in cw and in cc.

Sorption behaviour of acetylated rubber wood

DVS measurements revealed that sorption was lowered due to acetylation compared to unmodified rubber wood (Figure 4). Part of the hydroxyl groups, which represent the sorption sites, are blocked by the acetyl groups. The EMC for unmodified rubber wood at 65% RH was 10% in adsorption and 13% in desorption, whereas for acetylated

Figure 2: FTIR spectra of reference and acetylated samples in unweathered state and after 2 weeks (exposed side and unexposed side) and 4 weeks of weathering (unexposed side).

rubber wood, values were lower at 6% (sorption) and 8% (desorption). Similar sorption pattern and values for acetylated wood have previously been reported for other species such as Scots pine (*Pinus sylvestris* L.), and Norway spruce (*Picea abies* (L.) H. Karst.) (Chauhan et al. 2001; Tserki et al. 2005; Thygesen et al. 2010).

Weathering of rubber wood: shape distortions and colour changes

During the weathering process, shape distortions such as twisting and cupping, and cracks were observed in

Figure 3: Raman mapping images and averaged spectra for samples in (a) unweathered condition (reference, 8-h and 48-h acetylation) and (b) 2-week weathered condition (reference and 8-h acetylation).

Mapping show integrated intensity of the 1600 cm⁻¹ peak scaled to different (indicated) intensities. Marked areas indicate regions taken for generating averaged spectra (white: cw, blue: cc).

the reference samples, but not in the acetylated samples (Figure 5a). Shape changes and cracks in wood exposed to weathering are usually the result of internal stresses generated by moisture changes during wetting and drying. Visible cracks that appear at the wood surface during accelerated weathering primarily originate from micro-cracks in the cw (Sandberg and Söderström 2006). In acetylated samples, moisture uptake was reduced. Consequently, internal stresses due to alternate wetting and drying were lower compared to unmodified samples,

which diminished the appearance of distortions and cracks.

As shown in the supplementary information (Figure 5a, Supplementary information SI-1), colour changes were observed during weathering. The acetylated samples were lighter after the UV exposure and water spray compared to the reference samples, which were turning grey. The more persistent lightness in acetylated samples has been attributed to photo-bleaching of modified wood surfaces (Salla et al. 2012). Such colour changes

Figure 4: DVS measurement of reference and acetylated rubber wood showing sorption and desorption curves.

were also reported for weathered rubber wood esterified with fatty acid chlorides and for acetylated weathered Norway spruce (Mitsui and Tolvaj 2005; Mitsui 2010).

WL and degradation of lignin due to weathering

As shown in Figure 5b, there was a persistent WL as a result of weathering in the reference and acetylated samples (Figure 5b). WL was higher for the reference samples (up to 9.6% after 4 weeks) compared to the acetylated samples (7.6% for 8 h acetylation and 5.3% for 48 h acetylation). This WL was most likely due to the well-documented degradation of lignin and the subsequent leaching of lignin fragments from wood surfaces during exposure to UV-radiation and rain (Feist and Hon 1984; Feist et al. 1991; Evans et al. 2000). This degradation and leaching of lignin could be detected by FTIR and Raman analysis. FTIR spectra of the exposed and non-exposed side of 2 weeks weathered samples and of the unexposed side of 4 weeks weathering are shown in Figure 2. The other spectra are shown in the supplementary information (Supplementary information SI-2). After 2 weeks of weathering, the IR spectra show complete disappearance of the aromatic lignin band at 1504 cm^{-1} and the $\text{C}=\text{O}$ aromatic skeletal vibrations at 1597 cm^{-1} (Schwanninger et al. 2004) for the exposed side of unmodified and acetylated samples (Figure 4). For the unexposed side of the unmodified wood, the absorbance of these two peaks was slightly reduced after 2 weeks of weathering. Reduction of absorbance became more significant after 3 and 4 weeks of weathering. For the unexposed side of acetylated

Figure 5: (a) Visual appearance of the rubber wood samples after 4 weeks of weathering, (b) weight loss of the weathered reference and acetylated samples.

Asterisks (*) are used to show that the treatment effects are significant at $P \leq 0.05$. Box plots features: centre dot and line: mean and median; upper and lower lines: 75th and 25th percentile; whiskers: 95th and 5th percentile, dots outside whiskers: max and min values.

samples, the absorbance of the two lignin peaks was hardly affected by weathering.

Raman measurements were conducted on reference and 8-h acetylated samples after 2 weeks of weathering. Sample preparation proved to be difficult for longer exposure to weathering. Raman images based on the integration of the lignin marker band at 1600 cm^{-1} (Larsen and Barsberg 2010) showed that the middle lamellae and cc of the exposed side of reference samples were heavily degraded (Figure 3b). The peak at 1658 cm^{-1} , which is assigned to aldehyde side groups within lignin, was very

much reduced, indicating structural changes and partial degradation of lignin due to weathering of the cw. For the exposed sides of acetylated samples, middle lamellae and cc are still visible and changes in the cw are less pronounced. The differences between FTIR and Raman spectra concerning reduction of lignin content may be attributed to the different depths at which the measurements have been conducted. The IR spectra were taken at the surface, which experienced direct exposure and strongest weathering. In contrast, the Raman spectra were taken from cross-sections and, thus, below the surface, which led to less pronounced weathering. For the unexposed sides of reference and acetylated samples, Raman spectra do not show any significant change in the spectra, which confirms the findings of the FTIR measurements.

The vanishing of the lignin peak in the FTIR spectra of the exposed side correlates with the weight loss of weathered samples (Figure 5b), as mainly lignin was degraded and leached out (Feist and Hon 1984; Evans et al. 2000). The WL was higher for unmodified samples than for modified samples, and the extent of WL of the weathered samples correlates with the extent of reduction in lignin absorbance with the losses being more pronounced for reference samples than for acetylated samples. The more pronounced WL of the unmodified samples could be also due to the removal of extractives by weathering, whereas for acetylated samples, extractives could have been removed during acetylation already. Extractives of rubber wood are predominantly hydrophilic sugars and starch, contributing up to 10% in weight of freshly felled wood, while it is 3–4% for oven-dried wood (Azizol and Rahim 1989; Simatupang et al. 1994). As the starch granules were still visible in both reference and acetylated samples after weathering (Figure Supplementary information SI-5), we conclude that increased degradation and leaching contributed most to the higher WL in the reference samples compared to the acetylated samples. Thus, weathering with leaching of degraded lignin fragments progressed faster and more deeply into the reference samples than into the acetylated samples. The resistance of acetylated wood to UV degradation has been reported before (Feist et al. 1991). It is thought that acetylation contributes to the retardation of free radical production, which causes degradation of cw components, especially lignin (Feist and Hon 1984).

The FTIR spectra (Figure 2) also reveal a slight decrease of the acetyl content for the exposed surface of the weathered samples, as absorbance at 1734 cm^{-1} decreased as a function of weathering time. This decrease may be explained by the leaching of degraded, acetylated

fragments of hemicelluloses and lignin. Absorbance stayed almost constant for the unexposed surface. For the Raman measurements, intensity at 1732 cm^{-1} remained almost constant for the exposed and unexposed side, which may be attributed to the measurement location as mentioned above.

Furthermore, changes of cellulose related absorbance peaks at 1030 cm^{-1} , 1103 cm^{-1} , 1151 cm^{-1} , and 1325 cm^{-1} are visible for the IR spectra of weathered samples. The width at 1103 cm^{-1} and 1151 cm^{-1} decreased, while the single broad peaks at 1030 cm^{-1} and at 1325 cm^{-1} appeared as double peaks in the spectra of weathered samples. Changes were more pronounced for reference samples than for acetylated samples and for the exposed sides than for the unexposed sides. It can be speculated that parts of the hemicelluloses and amorphous cellulose were leached out, which would have led to a relative increase in the content of crystalline cellulose and, thus, to sharper peaks (Lionetto et al. 2012).

Sorption behaviour of weathered unmodified and acetylated rubber wood

Weathering of unmodified rubber wood resulted in a lower equilibrium moisture content (EMCs). This may be explained by the removal of sorption sites resulting from the degradation and leaching of amorphous biopolymers. For acetylated wood, weathered samples showed an increase of EMC of about 1% compared to unweathered samples. The decrease in the absorbance peak of C=O stretching of the acetyl group at 1734 cm^{-1} in the FTIR spectra of the acetylated weathered samples indicates that acetylated polymers were leached during the weathering process. This leaching may have led to a relatively increased concentration of OH-groups available for sorption compared to that of the non-weathered acetylated samples and, thus, to a slight increase in EMC of the acetylated weathered samples.

Density, microfibril orientation and the presence of tension wood

For revealing the influence of acetylation and subsequent weathering on mechanical properties, any influence of other parameters, such as density, orientation of cellulose microfibrils (microfibril angle) or tension wood (Winandy and Rowell 1984) need to be considered. The mechanically tested samples were checked for variations of these factors. Neither density nor microfibril angle showed

any significant differences between the different sample batches (Supplementary information SI-3 and Supplementary information SI-4). However, large proportions of tension wood were detected by the presence of G-layers in cross-sections, despite the straightness of the harvested stem (Supplementary information SI-5). The extent of tension wood spanned a range of 46–68% (Figure 6a) measured as area proportion in cross-sections. This ubiquitous presence of tension wood confirms previous observations on rubber wood (Lim et al. 2002; Nobuchi and Daneetha 2011). Rather than trying to avoid tension wood, we considered it as a characteristic feature of this species. As the proportion of tension wood present in each treatment batch was similar on average, it is assumed that it has not affected the main outcome of the mechanical study. Therefore, the changes observed in mechanical behaviour of acetylated and weathered samples could be linked to the respective treatments.

Impact of acetylation on mechanical properties

Unweathered reference samples showed a mean tensile stiffness of 19.0 ± 4.5 GPa (Figure 6a), whereas stiffness was significantly reduced to 13.7 ± 3.1 GPa for 8-h acetylation and 16.2 ± 2.6 GPa for 48-h treatment. The stiffness of rubber wood in this study was higher than values reported in previous studies, which are in the range of 3.5 GPa to 16 GPa (Gnanaharan and Dhamodaran 1993; Devi et al. 2003; Teoh et al. 2011; Naji et al. 2014). The comparatively high stiffness in the present study was mainly attributed to the presence of tension wood (Coutand et al. 2004). A decrease in stiffness was obtained after acetylation of rubber wood despite the low treatment temperature used. This decrease in stiffness is in line with the results of previous studies, which link the observed decrease in stiffness to the presence of acetic acid in wood as by-product of acetylation. The acid could induce hydrolysis of carbohydrate polymers during and after treatment (Dreher 1964; Chai et al. 2016). Possible hydrolysis of cellulose may lead to a decrease in stiffness as cellulose represents the main stress-bearing polymer of the cw due to its very high stiffness compared to the cw matrix (Winandy and Rowell 1984). Next to this, the swelling of wood due to the use of solvent and the subsequent bulking by acetylation may also explain the decrease, as forces were converted to stresses taking an increased cross-section. However, other studies report that acetylation had no influence on stiffness (Larsson and Simonson 1994; Papadopoulos 2008). The impact of hydrolysis and high temperature treatment may also be species dependent. Tensile strength of acetylated

Figure 6: Mechanical properties of acetylated rubber wood showing (a) elastic modulus, with average tension wood percentage in each treatment batch in parenthesis (b) tensile strength, and (c) maximum strain.

The description of box plots is given in Figure 5. Asterisks (*) indicate significant treatment effects at $P \leq 0.05$.

samples (8 h: 68.3 ± 20.9 MPa; 48 h: 71.0 ± 14.9 MPa) was lower compared to reference samples (82.5 ± 10.4 MPa), but this decrease was not significant (Figure 6). Strain at failure

was in the range of 0.5%–0.7% for reference and acetylated samples without any significant difference.

Impact of weathering on mechanical properties

Elastic modulus of the reference samples decreased as a function of weathering time to 10.3 ± 4.7 GPa after 4-weeks of weathering (Figure 6a). Tensile strength was reduced by 47% subsequent to 2 weeks of weathering for unmodified samples (Figure 6b). No further decrease was found after 3 and 4 weeks. Weathered reference samples showed an increasingly pronounced bi-phasic behaviour as a function of weathering time (Figure 7). Hereby, the first phase, which describes the elastic behaviour, was very short and already at low stresses, the second phase, which is usually assigned to plastic deformation, is visible in the case of weathered reference samples. This change of behaviour with the induction of plastic flow as a function of weathering time was also reflected in the differences between

the sample batches concerning strain at failure. Values increased from 0.6% to 1.4% as a function of weathering time in the reference samples. Occurrence of bi-phasic behaviour has previously been reported in the tensile tests of other plant and wood tissues (Köhler 2000; Köhler and Spatz 2002; Gindl and Keckes 2004). In these studies, bi-phasic behaviour was attributed to slippage of microfibrils at high microfibril angles resulting in a large plastic deformation before failure, because the yield stress of the matrix had been exceeded in the test.

In the present study, however, the change in mechanical behaviour could not be attributed to a change in microfibril angle, as similar microfibril angles in the range of $13\text{--}18^\circ$ were detected for the different batches (Supplementary information SI-4). Thus, the bi-phasic behaviour is more likely the result of the impact of weathering. Raman analysis of the exposed side of the reference samples and previous studies (Evans et al. 2000) have revealed that weathering leads to the degradation of the middle lamella (Figure 5b). Degradation of the middle lamella may result in a low yield stress and

Figure 7: Weathered reference samples showed an increasingly pronounced bi-phasic behaviour as a function of weathering time. Stress-strain characteristics of (a) reference (unmodified), (b) acetylated rubber wood with a treatment time of 8 h, and (c) acetylated rubber wood with a treatment time of 48 h, in non-weathered state and after 2–4 weeks of weathering.

in a slippage of the fibres. This would explain the short first phase in the stress-strain curves with yield stresses of 5–20 MPa and the pronounced ductility (plastic flow) visible for the reference samples. The creation of a weak link between the fibre cells likely lowers the maximum stress wood can bear in tensile loading. This would lead to the observed reduction in strength and stiffness. In contrast, acetylated samples retained their tensile stiffness throughout the weathering process (Figure 6a). For tensile strength, a decrease of 37% for the 8 h acetylated samples and of 33% for the 48 h treated samples was visible after 2 weeks of weathering (Figure 6b). For longer weathering times, no further decrease in tensile strength was visible in the acetylated samples. Next to the differences in stiffness and strength, the stress-strain curves revealed that in the acetylated samples, bi-phasic behaviour is visible to a lower extent only. Strain at failure was slightly reduced for weathered samples compared to the non-weathered samples. This reduction in strain at failure is significant for the 8 h acetylated samples, but not for the 48 h samples. Sliding of fibres due to degradation of middle lamella is not evident for the acetylated samples as the middle lamella is still present as shown by Raman analysis (Figure 5). The absorbance at 1732 cm^{-1} , which is an indicator for acetyl content shown by Raman spectra, is still high in the cw after weathering of the acetylated samples. Hence, there is a possibility that acetylation protects the matrix of the cw and especially lignin (Winandy and Rowell 1984; Köhler and Spatz 2002), which may have prevented a severe degradation of the middle lamella.

Lower strain at failure and decrease in tensile strength may be an indication that acetylated samples show a more brittle failure compared to the ductile failure described for the weathered reference samples. It is known that weathering leads to degradation and leaching of hemicelluloses as described by Evans et al. (Evans et al. 1992). The continuous decrease in the absorbance at 1734 cm^{-1} of the FTIR spectra (Figure 4 and Supplementary information SI-2) also show that hemicelluloses may have partly got degraded leading eventually to leaching of the degraded parts during weathering process. A similar effect on stiffness and strength has been reported by Köhler and Spatz (2002). In their study, the chemical extraction of hemicelluloses from plant tissues led to a decrease in tensile strength and failure strain. Thus, degradation of middle lamella was likely the cause of ductile behaviour with a reduction in strength and stiffness, while the brittle behaviour of the weathered acetylated samples can be attributed to leaching of degraded parts of the hemicelluloses.

Conclusion

Acetylation of rubber wood at low temperature (70°C) resulted in a WPC of up to 10%. Acetylation largely prevented colour change and cracking of 1-mm thick samples during accelerated weathering. This may be attributed to the reduced EMC and increased dimensional stability (less swelling and shrinking) of acetylated wood compared to unmodified wood. Acetylated samples also showed reduced degradation and leaching of lignin. Although FTIR results showed a complete removal of lignin from the surface of acetylated weathered wood, the modification seems to slow down further degradation within the sample. Indeed, high-resolution Raman analysis revealed that the middle lamellae in acetylated weathered wood was preserved, whereas degradation and leaching of middle lamellae were observed in untreated weathered samples. The stiffness of rubber wood was reduced due to acetylation, but the treatment paid off during weathering. Stiffness of acetylated rubber wood was retained during weathering, while it continuously decreased for unmodified samples. In conclusion, acetylation was effective in protecting rubber wood in outdoor uses. Dimensional stability was increased and surface degradation by weathering was slowed down, which is beneficial for the mechanical properties and most likely the durability of rubber wood when used in outdoor conditions.

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