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International Wood Products Journal

DOI:

[10.1080/20426445.2016.1160559](https://doi.org/10.1080/20426445.2016.1160559)

Published: 01/06/2016

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

Noel, M., Grigsby, W. J., Ormondroyd, G., & Spear, M. (2016). Influence of water and humidity on chemically modifying wood with polybutylene succinate bio-polyester. *International Wood Products Journal*, 7(2), 80-88. <https://doi.org/10.1080/20426445.2016.1160559>

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--Manuscript Draft--

Manuscript Number:	IWP239R1	
Full Title:	Influence of water and humidity on chemically modifying wood with polybutylene succinate bio-polyester	
Article Type:	Special Issue Article	
Keywords:	bio-polymer, dimensional stabilisation, poly(butylene succinate), poly(lactic acid), wood modification	
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Funding Information:	European Cooperation in Science and Technology (STSM-FP1303-100515-060044)	Dr. Marion Noël

Influence of water and humidity on chemically modifying wood with polybutylene succinate bio-polyester

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1. Abstract

This paper reports attempts to optimise the chemical modification of wood impregnated with polybutylene succinate oligomers (OBS). OBS impregnation at temperature and subsequent heating to induce *in-situ* polymerisation led to high OBS uptake, but limited dimensional stability. However, subsequent water soaking followed by drying enhances wood dimensional stability in both high humidity environments and in liquid water. To enhance OBS treatment and performance, it was found that OBS impregnation followed by wet heat or water soaking and a second heating step, promoted oligomer migration into wood cell walls. These combined treatments provided modified wood with anti-swelling efficiency at 95% relative humidity ($ASE^*_{95\%RH}$) values of 55 to 70 %.

Keywords: bio-polymers, dimensional stabilisation, poly(butylene succinate), poly(lactic acid), wood modification

2. Introduction

Enhancing the properties and performance of wood has been extensively studied over many decades. During this time, a range of wood treatments have been developed and commercialised to improve the strength, hardness and durability of treated woods (Hill 2006; Rowell 2005; Lande *et al.* 2004; Chang and Chang 2002; Ibach 2005; Xie *et al.* 2005; Belgacem and Gandini 2008; Choura *et al.* 1997). With an increasing awareness of sustainability and the emergence of bio-derived materials, there is also a similar need to consider more environmentally benign options for treating wood. Recently a promising wood modification using biopolymers based on glycolic and lactic acids and polybutylene succinate and polybutylene adipate esters was reported. Wood was treated with these polyesters in their oligomeric forms *via* a bulk impregnation and then polymerised *in-situ* within the wood to variously enhance wood properties such as dimensional stability (Noël *et al.* 2015a, 2015b, 2015c; Vitkeviciute, 2015). However, across these biopolyester treatments, differing degrees of impregnation and cell wall infiltration were observed, with corresponding variations in the *in-situ* polymerisation and wood properties (Figure 1). This was most contrasted by the polylactic acid (PLA) oligomer (OLA) and polybutylene succinate (PBS) oligomer (OBS) ester treatments.

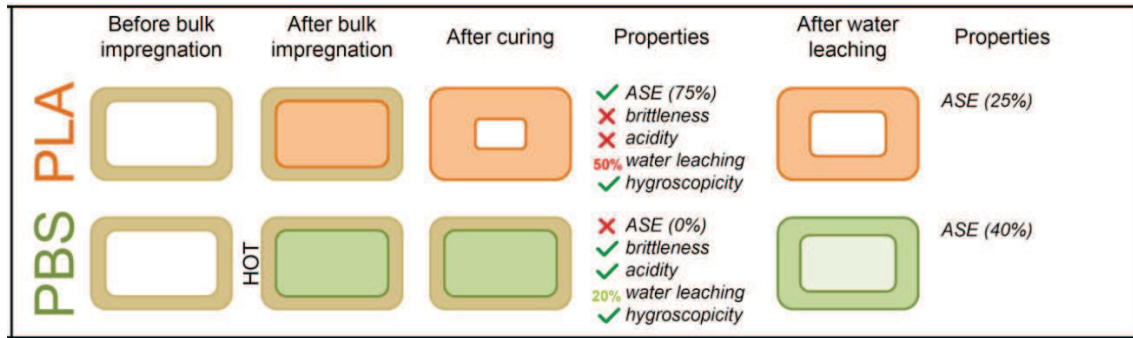


Figure 1: Comparison of PLA and PBS oligomers efficiency for wood modification in relation to the cell wall modification

On impregnating oligomeric esters into wood, OLA-based treatments were revealed to be cell wall bulking, whereas OBS treatment remained lumen-filling only (Figure 1) (Noël *et al.* 2015a). This manifested in wood properties where OLA esters led to very good dimensional stabilisation (up to 75% ASE), but increased brittleness of the treated wood (unpublished results). In contrast, OBS esters (70% of polymers weight uptake in wood) decreased the wood hygroscopicity, but were found to provide only limited dimensional stabilisation (Noël *et al.* 2015a), most likely because of a highly hindered capillary conduction. In comparison to untreated wood exposed at high humidity, a lower equilibrium moisture content of OBS treated wood with identical resulting swelling can be explained by the partial OBS solubility. OBS oligomers are partially solubilized and transported to the cell wall. The swelling observed during high humidity exposure is thus due to water and oligomers diffusion and explains the decreased EMC. The OBS ester treatment did not influence the mechanical properties of the treated wood. Furthermore, as part of ASE evaluations, treated wood was observed to variously leach polyester materials when initially in contact with water on testing. While the leaching was considered relatively high for OLA treatments, the OBS oligomers appeared retained within the wood structure on water leaching, with only 20% of polymer loss (Noël *et al.* 2015a).

An aspect of OBS polyester treatment and testing was an unexpected improvement in ASE cyclic humidity testing performance after initial water soaking. Original, unleached OBS treated samples show no ASE*_{95%RH} as the cell walls were not impregnated (Figure 1). However, OBS treated samples initially exposed to water as part of leaching resistance testing were subsequently observed to have substantially improved properties as evidenced by high ASE*_{95%RH} values and no detrimental impact to mechanical performance (Noël *et al.*, 2015a). This unanticipated finding has prompted a further evaluation of biopolyester treatments using OBS oligomers together with attempts to optimise the processing of treated wood. This has included an evaluation of temperature and *in-situ* polymerisation times together with water treatment conditions to enhance OBS penetration into wood cell wall and wood property enhancement. Ultimately, the goal of this study is a range of tailored biopolyester treatments for the enhancement of wood stability and performance.

3. Experimental methods

3.1. Synthesis of the PBS oligomers (OBS)

Oligomeric polyesters were synthesised by their direct polymerisation under vacuum, using a four-necked flask fitted with a magnetic stirrer and reflux condenser linked to an

1 inline cold trap and vacuum pump. Thermometers were used to observe the
2 polymerisation, condenser head, and heater temperatures.

3 Oligoesters (OBS) were synthesised by melt polymerisation of dimethyl succinate and
4 1,4-butanediol. This was achieved by adding a 25% stoichiometric excess of 1,4-
5 butanediol in the presence of titanium (IV) butoxide as esterification catalyst. A mixture
6 of dimethylester, 1,4-butanediol, and catalyst was poured into the flask under a nitrogen
7 purge. The mixture was gradually heated to 180°C over 130 min under reduced pressure
8 (150 mbar). At the end of the reaction, oligomers were poured into bottles, sealed and
9 cooled. OBS esters solidify as a white block on cooling. The melt temperature of the
10 resulting oligomeric OBS material was rheologically measured at *ca.* 75°C.

11 3.2. Wood treatment

12 Wood OBS oligomer treatments followed a published processing procedure (Noël *et al.*
13 2015a). Wood samples were immersed in liquid oligomers at 90°C as an initial
14 impregnation step. Containers were then placed in a vacuum oven under reduced
15 pressure (580 mmHg) for 40 min, then atmospheric pressure over 40 min. Impregnated
16 samples were then wiped and set on aluminium foil in a ventilated oven under
17 controlled temperature and duration (Table 1). Anhydrous sample weight was measured
18 before impregnation, after impregnation and then after heat treatment. Weight uptake
19 has been calculated according to Eqn. 1.

$$20 \quad WU_{i/t} (\%) = \frac{w_{i/t} - w_0}{w_0} \times 100 \quad (1)$$

21 where w_i stands for the impregnated sample weight, w_t for the sample weight after
22 complete treatment, and w_0 the oven dried sample weight before treatment.

23 3.3. Anti-swelling efficiency (ASE)

24 All treated samples (15 x 15 x 10 mm, T x R x L) were placed in 95% relative humidity
25 (RH). Sample dimensions were measured before exposure in dry state (due to treatment
26 process) and after weight stabilisation. Regular weight measurements were made in
27 order to determine the equilibrium moisture content of samples with time and
28 conditioning.

29 As some treatments show a strong bulking effect in the cell wall while others only
30 penetrate wood lumens (Figure 1), the ASE calculation was based on the corrected
31 swelling calculation of treated samples (S_t) as defined in Eqn. 2 (Thybring, 2013):

$$32 \quad S_t^* (\%) = \frac{V_{95\%st} - V_t}{V_0} \times 100 \quad (2)$$

$$33 \quad ASE^* (\%) = \frac{S_{nt} - S_t^*}{S_{nt}} \times 100 \quad (3)$$

34 where $V_{95\%st}$ stands for the treated sample volume after stabilisation at 95%RH, V_t for
35 the treated sample volume before stabilisation at 95% RH, V_0 the oven dried sample
36 volume before treatment and S_{nt} the reference untreated sample swelling:

$$S_{nt} (\%) = \frac{V_{95\%st} - V_{nt}}{V_{nt0}} \times 100 \quad (4)$$

where $V_{95\%st}$ stands for the reference untreated sample volume after stabilisation at 95%RH and V_{nt} for the oven dried reference untreated sample volume.

For treated samples, the reduced equilibrium moisture content EMC_{Rt} has been calculated as defined in Eqn. 5:

$$EMC_{Rt} (\%) = \frac{w_{95\%st} - w_t}{w_0} \times 100 \quad (5)$$

where $w_{95\%st}$ stands for the treated sample weight after stabilisation at 95%RH, w_t for the dry treated sample weight before stabilisation at 95%RH, and w_0 the oven dried sample weight before treatment.

The reduced EMC, or EMC_{Rt} , allows comparison of the different treatments by relating the water uptake to the dry wood weight, not taking in consideration the weight of polymer into wood structure which may differ between treatments.

Swelling and anti-swelling efficiency of samples soaked into liquid water were calculated as well according to formulae (2), (3) and (4) where “95%” can be replaced by “lw” standing for liquid water.

3.4. Leaching

The treatment resistance to water leaching was measured in terms of weight loss of polymeric material (WPL) resulting from the ASE test in liquid water. The samples were soaked in water at 23°C for 7 days. At the end of the test, the samples were air dried at 23°C / 56%RH for 24h and subsequently oven dried until constant weight. The WPL was calculated as defined in Eqn. 6:

$$WPL (\%) = \frac{w_{t10} - w_t}{w_t - w_0} \times 100 \quad (6)$$

where w_{t10} stands for the treated sample weight after leaching and oven drying, w_t for the treated sample weight (necessarily oven dried) and w_0 the oven dried sample weight before any treatment.

3.5. Dynamic Mechanical Analysis

The DMTA analysis has been carried out on a Triton TTDMA equipped with a humidity generator set up to allow a temperature ramp and the RH in the chamber for samples of dimensions 50 x 10 x 4 mm, L x RT x TR. The temperature changes were manually performed when the conditions in the chamber were stable. Once the temperature and RH were stable, the average of five values of the stabilised storage modulus, taken at 3 min intervals, was calculated with this average storage modulus value reported in Figure 5. Only thermal scans carried out at 1 Hz are reported in this paper.

Sample swelling was measured as the ratio between the sample volume after DMTA run and on further oven drying (at 103°C for 24h) and comparing with the initial dry sample volume immediately after the hot oligomer impregnation.

3.6. Durability assessment and natural weathering

1 A preliminary determination of the potential conferred durability has been carried out
2 according to a modified EN 113 standard, with the following variation: 11 week-
3 exposure to *Coriolus versicolor*, samples dimensions of 50 x 15 x 12.5 mm³. Virulence
4 controls showed a 14.5% weight loss, and did not reach the 25% threshold of the
5 standard. Samples treated with OBS (160°C / 2 days) and leached (according to the EN
6 84 standard, with following deviations: water boxes not placed in controlled conditions
7 of humidity and temperature, oven drying of samples after leaching instead of
8 stabilisation at 65%/20°C) have been tested, as well as untreated samples heated at
9 160°C for 2 days for evaluation of the thermal treatment influence.

10 Natural, outdoor weathering has been conducted in Biel (Switzerland) at 45° from the
11 ground with the sample wood grain direction exposed horizontally. The assessment was
12 conducted according to a modified EN 927-3 standard, with the following variation:
13 samples dimensions of 150 x 72 x 12 mm³ (L x R x T), no protection of the end-grain
14 and edges. Along the exposure, the following evaluations have been made: deformation,
15 cracking, colour homogeneity, mould attack, colour change.

18 4. Results and discussion

19 4.1. *Relation of OBS treatment with water and wood*

22 Even if no direct correlation can be drawn between the behaviour of pure chemicals and
23 the behaviour of these chemicals in wood, the polyester was prepared in pure form so to
24 assess any responsiveness of OBS polyesters to exposure to varying humidity, and to a
25 near saturated environment (*ca.* 95% RH). This revealed that the sensitivity of OBS to
26 water sorption was relatively limited, and in accordance with literature (Phua *et al.*
27 2011; Tserki *et al.* 2006; Frollini *et al.* 2013). After 10 weeks exposure, weight
28 increases of less than 0.5% were observed with no distinctions between OBS polyesters
29 prepared at 140°C or 160°C. In contrast, polymerised OLA oligomers heated at 120°C
30 can absorb up to 28% moisture content at 95% RH (Vitkeviciute 2015). Furthermore,
31 water absorption profiles reveal OBS to rapidly achieve equilibration, whereas moisture
32 sorption by OLA polymer increases with time (Figure 2). It is also possible that the
33 polyester undergoes hydrolysis which may increase hydrophilicity, according to the
34 following process: the polymer degradation through ester bond hydrolysis leads to an
35 increased amount of carboxylic end groups, which are known to autocatalyse the ester
36 hydrolysis, and to an increase in acidity due to soluble oligomers leaching resulting in
37 accelerated degradation (Proikakis *et al.* 2006; Edlung and Albertsson 2003; Madhavan
38 Nampoothiri *et al.* 2010; Cho *et al.* 2001).

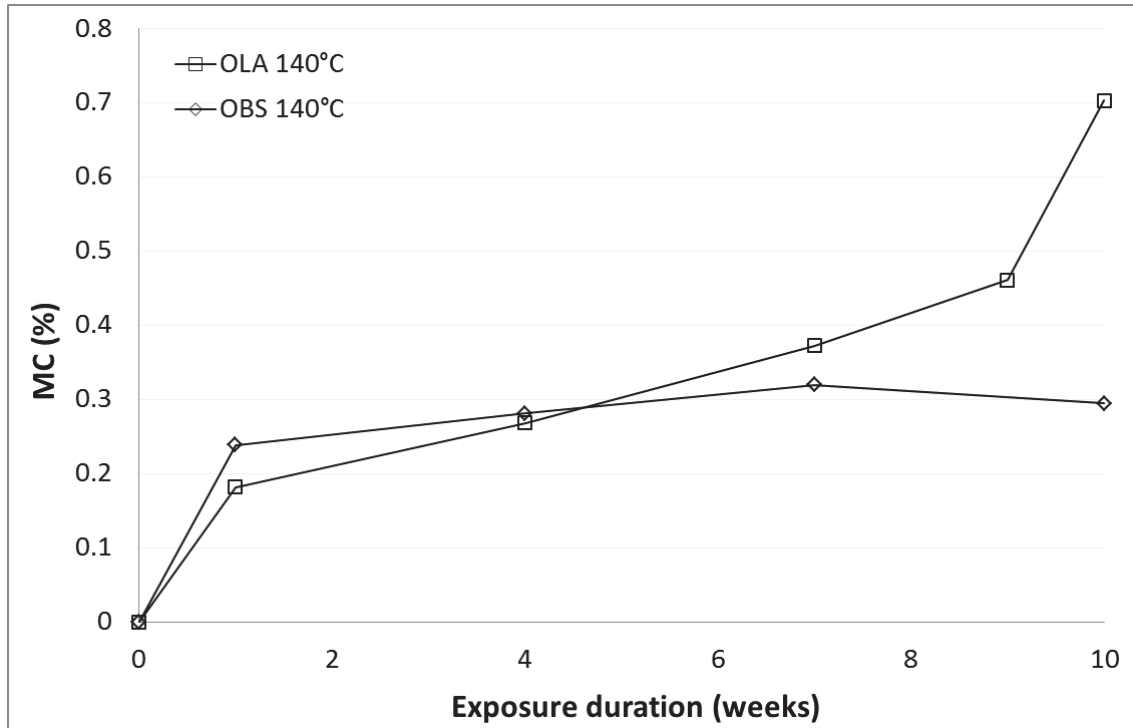


Figure 2: Moisture content of OLA and OBS oligomers, preliminary heated for 2 days at 140 °C, then exposed at 96%RH at room temperature [Vitkeviciute, 2015]

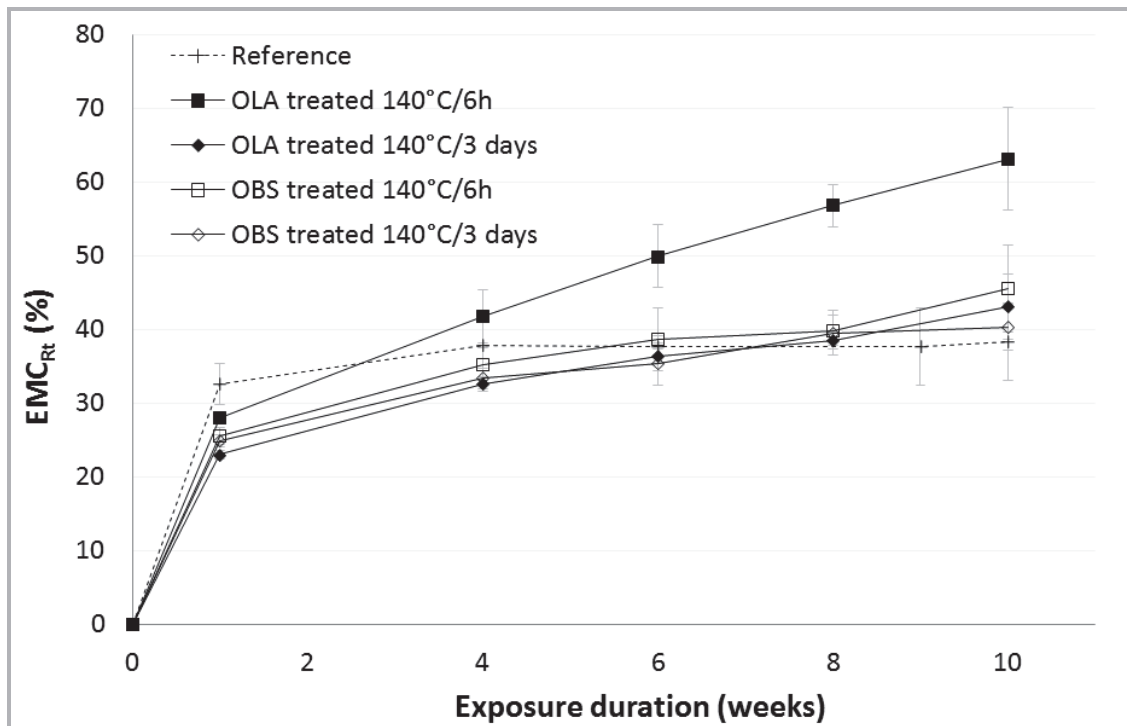


Figure 3: EMC_{Rt} of wood samples treated with OLA or OBS oligomers heated at 140°C for 6h or 3 days, then exposed to 96%RH at room temperature [Vitkeviciute, 2015]

An evaluation of moisture uptake at high humidity revealed wood samples treated with OLA show an increasing EMC_{Rt} over time, and this occurred at a greater rate when thermal treatment and *in-situ* polymerisation was short (6h, Figure 3). Similarly, samples treated with OBS also have greater moisture sorption when polymerised with a shorter thermal treatment. However, with these OBS samples the EMC_{Rt} profile

appeared stabilised (*ca.* 40%) after 6 weeks of exposure with the EMC_{Rt} comparable to the reference, untreated sample (Figure 3). This comparable EMC_{Rt} was consistent with the pure OBS polyester moisture uptake exhibited in Figure 2, but also suggests the impregnation treatment was insufficient to significantly decrease the EMC_{Rt} .

An evaluation of OBS treated samples which underwent the water soak leaching step revealed comparatively lower EMC_{Rt} profiles than unleached samples (95%RH at 23°C, Figure 4). Firstly, samples prepared with extended cure heating (160°C, 9 days) exhibited distinctly lower EMC_{Rt} profiles than moderately cured OBS samples (160°C, 2 days) (Figure 4). The influence of treatment duration and water leaching was shown with significantly lower EMC_{Rt} values after 240 days at 95%RH/23°C. Moreover, the trends in EMC_{Rt} values for leached OBS treated sample also manifested in the 95%RH/23°C ASE evaluations of these samples. In this case, the treated samples displayed greater dimensional stability ($ASE^*_{95\%RH}$ of *ca.* 40%) after the water leaching with up to 55% $ASE^*_{95\%RH}$ for the extended cure treatment (9 days at 160°C). Given these samples swell after leaching and drying, this suggests partial penetration of the OBS oligomers into wood cell walls, and may provide an insight to the observed ASE values.

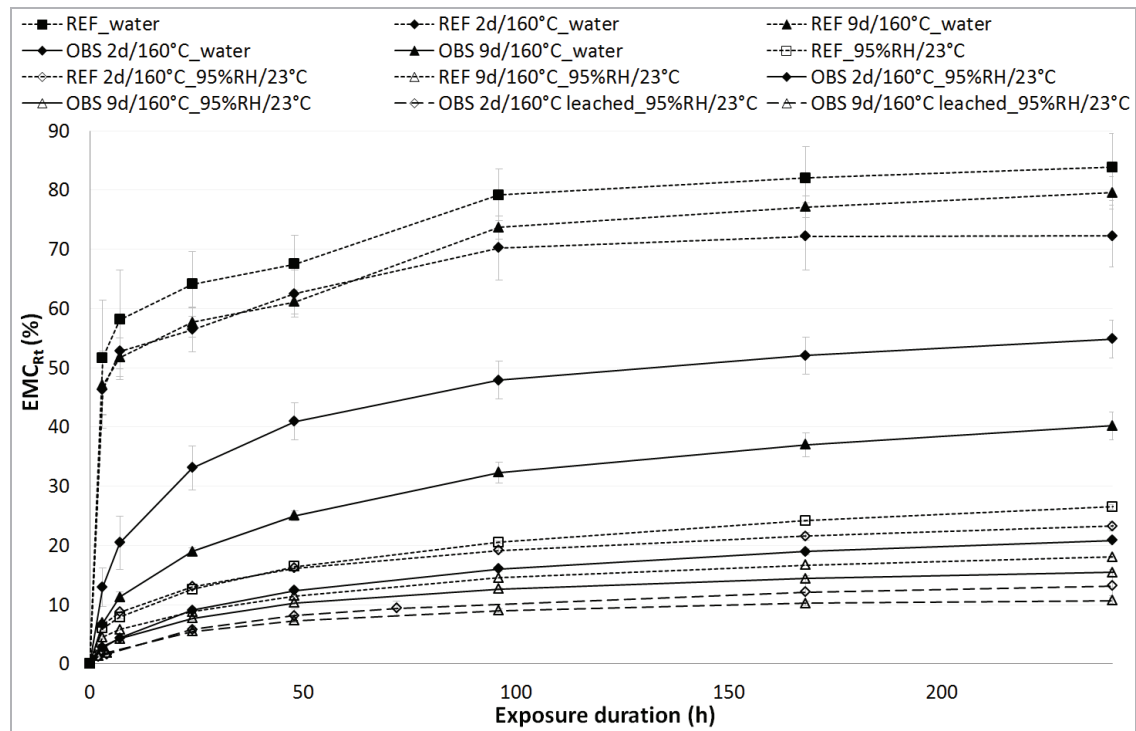


Figure 4: EMC_{Rt} of OBS treated samples (160°C/2days and 9 days) and reference samples not heated, or heated (160°C/2 days and 9 days) along exposure time to 95%RH at 23°C (_95%RH/23°C), or to water soaking (_water)

To provide further understanding of the partial OBS oligomer penetration achieved on leaching, dynamic mechanical analysis (DMA) under fixed humidity (35%RH, 57%RH and 86%RH) was performed on treated and leached samples (Figure 5). The objective was to link the differing physico-mechanical properties of the wood with relative humidity and temperature using sample stiffness (storage modulus, E'). For the OBS treated sample at 35%RH, the E' decrease was relatively consistent from 20 to 40°C, decreasing by 0.4 GPa at 40°C. At 57%RH, the sample behaviour was relative similar,

also decreasing by 0.4 GPa. Moreover, the DMA heating induced swelling of the OBS sample by 5.6% and 7.4% at 35%RH and 57%RH, respectively (swelling measured at dry state after and before the test). At 85%RH, the E' loss of the OBS sample was higher (>0.8 GPa) and at a greater rate, resulting in 17.6% sample swelling. The analysis of volume gain indicates that with higher RH, each heating run allowed OBS material to penetrate into the cell wall contributing to greater swelling, and further confirmed by the observation that untreated samples do not swell. This initial relationship between the E' change and polymer cell wall penetration will require further study to better understand the mobility and interaction between OBS and wood components.

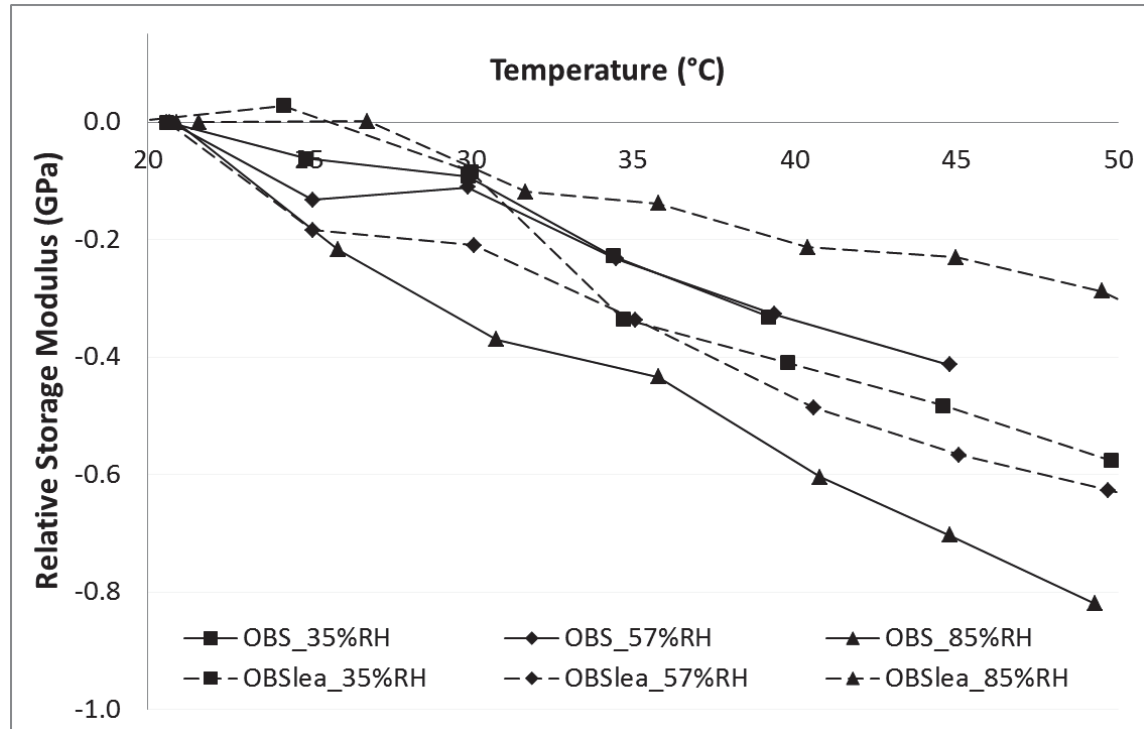


Figure 5: Relative storage modulus of samples impregnated (solid line), impregnated and leached (dotted line); at 35%RH, 57%RH and 85%RH along temperature increase from 20 to 50°C

For OBS impregnated and leached samples (where the polymer had been observed to penetrate cell walls), DMA revealed differing E' behaviours. At 35%RH, the E' loss of the leached sample was relatively similar to that for the impregnated sample and associated with swelling of 2.4%. At 57%RH, the E' curve was comparable to the impregnated sample, but with a greater decrease in E' value. However, sample swelling was only 1.7%. At 85%RH, the leached sample had a differing E' profile with only a moderate loss in E' , similar to the untreated reference sample (not presented). The additional swelling of this sample was 3.7%, being significantly lower than the unleached sample. This suggests the heating of leached samples with increased humidity does not promote any significant additional cell wall penetration as observed with the impregnated-only samples.

4.2. Aging of OBS treated wood

OBS treated samples (160°C / 2 days) were exposed to outdoor weathering. After 12 months, the surface quality of treated samples was assessed as being better (no cracking and no mould attack) than the reference on which many wide and deep cracks were visible, as well as a darker coloration (Supplementary Material 1).

According to the preliminary durability assessment, OBS treated samples (160°C / 2 days) showed a weight loss of only 3.7% (17% for control samples), whereas untreated samples heated according to the same thermal treatment (160°C / 2 days) showed 12.2% weight loss (15.4% for control samples). Furthermore, there appeared a substantial fungicidal effect conferred by the OBS treatment which cannot be attributed to only the thermal treatment (Hakkou *et al.* 2006; Kamdem *et al.* 2002). Presently, further investigation is pending to determine if OBS treatment is fungicidal or if the decreased EMC conferred by this treatment contributes the improved durability.

4.3. Applications potential

Given the promising properties of the OBS treatment above and the previously reported results (Noël *et al.* 2015a), further samples were produced to determine OBS treatment efficiency (Table 1). A range of processing and cure temperatures (120°C and 140°C) were used, being intermediate temperatures relative to the previous sample treatments. This showed that treatment at differing temperature did not induce any swelling on impregnation (S_i), despite a high weight uptake (WU_i , *ca.* 65%) of most samples. Only for treatment of fresh, green wood (98% mc) was there no weight uptake nor swelling observed, likely a result of adsorbed water being replaced by the oligomer material which was associated with intense foaming from the sample during impregnation. The analysis of volume gain indicates that with higher RH, each heating run allowed OBS material to penetrate into the cell wall contributing to the observed greater sample swelling. In contrast, untreated samples do not swell under these conditions. The wet treatment followed by dry heating variously led to sample swelling (S_t) which was *ca.* 7% for high temperature drying samples (samples 3 and 5) and *ca.* 13% for wet step samples (samples 2, 7-16). Furthermore, wet heating for 30 min (samples 7, 9, 10) led to higher oligomer cell wall penetration than water leaching at room temperature (7 days, sample 2). A longer wet heating did not lead to higher swelling (samples 11-16). Comparing samples 9-16, it was observed that a longer heating step at higher temperature generally led to greater swelling (samples 10, 12, 14 and 16 in comparison to samples 9, 11, 13 and 15). A comparison of samples 7 and 9 shows that longer heat treatment at 103°C led to higher swelling, whereas the comparison of samples 7 and 10 shows that for a four-day heating step, a higher heating temperature did not lead to greater swelling. For samples 2 and 7-16 their wet treatment may have led to partial oligomer hydrolysis (Cho *et al.* 2001) promoting oligomer mobility into the cell wall together with leaching of oligomers from the wood.

Table 1: Treatment parameters evaluated

Ref.	EMC ^a [%]	Impregnation temperature [°C]	Wet step	Dry step
1	0	90	-	Oven heating, 103°C/12h
2	0	90	Water leaching, 23°C/7d	Oven heating, 103°C/2.5d
3	0	90	-	Oven heating, 140°C/12h
4	0	130	-	Oven heating, 103°C/12h
5	0	130	-	Oven heating, 140°C/12h
6	0	90	Wet heating, 100°C/100%RH/30min	-
7	0	90	Wet heating, 100°C/100%RH/30min	Oven heating, 103°C/4d
8	98 ^b	90	-	Oven heating, 103°C/4d
9	0	90	Wet heating, 100°C/100%RH/30min	Oven heating, 103°C/2.5d
10	0	90	Wet heating, 100°C/100%RH/30min	Oven heating, 120°C/4d
11	0	90	Wet heating, 100°C/100%RH/2h	Oven heating, 103°C/2.5d
12	0	90	Wet heating, 100°C/100%RH/2h	Oven heating, 120°C/4d
13	0	90	Wet heating, 100°C/100%RH/5h	Oven heating, 103°C/2.5d

14	0	90	Wet heating, 100°C/100%RH/5h	Oven heating, 120°C/4d
15	0	90	Wet heating, 100°C/100%RH/10h	Oven heating, 103°C/2.5d
16	0	90	Wet heating, 100°C/100%RH/10h	Oven heating, 120°C/4d

^aWood EMC before impregnation, ^bNon dried wood, freshly cut

Table 2: Treatments description and efficiency

Ref.	S _i [%]	WU _i [%]	S _t ^a [%]	WU _t ^a [%]	ASE* _{lw} ^b [%]	EMC _{Rt} ^b [%]	WLP [%]	S _{lw} ^c [%]	ASE* _{95%} ^d [%]	EMC _{Rt} ^{95%} ^d [%]
1	0.2 ± 0.4	66.6 ± 2.1	0.9 ± 0.3	64.6 ± 2.2	-1.4 ± 6.5	52.6 ± 0.8	-23.6 ± 0.4	5.6 ± 0.4	30.3 ± 5.8	31.4 ± 0.8
2	0.3 ± 0.1	65.3 ± 5.4	11.6 ± 0.7	49.6 ± 4.2	42.8 ± 4.4	56.9 ± 1.9	-5.2 ± 0.3	2.1 ± 0.3	55.2 ± 5.1	30.5 ± 0.5
3	-0.1 ± 0.3	63.8 ± 7.5	7.8 ± 0.3	55.2 ± 6.6	37.1 ± 3.2	53.8 ± 1.3	-7.3 ± 0.7	-2.1 ± 0.8	37.3 ± 6.3	28.0 ± 0.5
4	0.5 ± 0.4	62.6 ± 9.5	0.8 ± 0.1	60.8 ± 9.3	1.9 ± 11.9	55.6 ± 2.0	-21.2 ± 0.6	5.1 ± 0.7	33.2 ± 11.9	30.4 ± 1.0
5	0.8 ± 0.6	68.2 ± 5.5	6.7 ± 1.1	63.0 ± 5.1	29.3 ± 9.7	55.6 ± 3.1	-11.7 ± 1.0	0.5 ± 1.5	40.1 ± 9.8	30.5 ± 1.3
6	0.5 ± 0.2	64.2 ± 5.5	- ^e	- ^e	- ^e	- ^e	- ^e	- ^e	18.3 ± 7.6	31.8 ± 1.7
7	0.7 ± 0.4	65.2 ± 7.4	14.9 ± 1.0	51.9 ± 7.2	53.8 ± 3.8	61.0 ± 0.6	-16.4 ± 1.0	-1.9 ± 0.8	47.8 ± 7.2	30.5 ± 1.0
8	-2.4 ± 1.4	-1.8 ± 0.9	12.0 ± 1.2	57.4 ± 5.5	56.9 ± 4.3	48.0 ± 3.4	-19.5 ± 0.9	-0.8 ± 0.8	55.1 ± 4.9	29.4 ± 2.1
9	0.7 ± 0.4	74.4 ± 3.8	8.8 ± 0.4	70.5 ± 3.2	36.8 ± 6.5	53.7 ± 1.9	-18.0 ± 0.5	-3.8 ± 0.8	64.0 ± 5.8	24.5 ± 0.6
10	0.9 ± 0.4	75.3 ± 7.4	12.3 ± 0.8	69.8 ± 7.4	43.6 ± 4.7	50.4 ± 1.4	-14.1 ± 0.5	-4.1 ± 0.9	70.8 ± 3.5	23.9 ± 1.0
11	0.5 ± 0.1	67.2 ± 7.5	14.5 ± 1.3	63.6 ± 7.2	50.6 ± 6.7	55.8 ± 4.1	-17.0 ± 0.9	-1.1 ± 0.8	52.8 ± 8.3	25.6 ± 0.9
12	0.5 ± 0.2	67.4 ± 7.2	16.0 ± 0.6	61.6 ± 8.2	61.9 ± 2.7	57.4 ± 2.2	-14.0 ± 0.3	-1.4 ± 0.6	68.7 ± 1.4	25.1 ± 1.0
13	0.3 ± 0.2	60.8 ± 5.8	15.0 ± 1.1	58.1 ± 7.3	51.1 ± 8.4	53.5 ± 1.7	-15.2 ± 0.7	-0.5 ± 0.6	54.7 ± 2.3	25.4 ± 0.5
14	0.3 ± 0.2	65.0 ± 3.3	17.1 ± 0.4	60.1 ± 4.0	62.9 ± 3.3	53.9 ± 1.4	-12.3 ± 0.8	-2.6 ± 0.2	71.1 ± 1.6	25.0 ± 0.4
15	0.6 ± 0.4	69.0 ± 4.1	13.6 ± 2.1	55.8 ± 8.0	42.1 ± 10.6	59.8 ± 3.0	-16.1 ± 0.8	0.1 ± 1.2	46.0 ± 7.1	25.1 ± 0.3
16	0.1 ± 0.2	68.6 ± 4.0	17.1 ± 0.7	59.0 ± 5.9	60.8 ± 2.4	59.7 ± 1.0	-12.5 ± 0.7	-1.8 ± 0.8	66.5 ± 1.6	25.1 ± 0.3

^aTreatments are defined in Table 1. They consist in the wet and dry step. ^bASE* and EMC_{Rt} in liquid water. ^cSwelling measured after the water leaching and oven drying. ^dASE* and EMC_{Rt} at 95%RH. ^eThis data could not be calculated because the ASE_{lw} step directly followed the wet step. An intermediate drying would have been necessary for the calculation.

To further characterise the treatment effectiveness, ASE values were determined in both liquid water (23°C/7d, measured as ASE*_{lw}), and then after oven drying (103°C) subjection to 95%RH/23°C conditioning (ASE_{95%}, Table 2). For samples immersed in water, the EMC_{Rt} values were found to be *ca.* 55%, but the ASE* were highly dependent on the treatment process. Samples 7, 8, 12, 14 and 16 attained the highest ASE*_{lw} values (*ca.* 55-60%) with the high initial sample EMC and the wet heating followed by long heating at high temperature, suggestive of efficient processing compared to water soaking prior to heating (sample 2, 43% ASE). With slightly lower swelling (S_t), samples 9 and 10 led to lower ASE_{lw}. High temperature drying with no wet step (140°C, samples 3 and 5) lead to ASE*_{lw} values of *ca.* 30%. This result suggests a high *impregnation* temperature does not improve the stability properties which was also observed with samples 1 and 4 which had no ASE and used the lower (103°C) heating temperature.

1 Typically, conditioning in high humidity revealed most samples to have high EMC_{Rt}
2 values (*ca.* 25-30%) with samples distinguished by differing ASE*_{95%} values. Samples 2
3 and 8 have the similar ASE*_{95%} (55%) demonstrating that either water leaching at room
4 temperature or oligomer impregnation of wet wood led to similar treatment efficiency.
5 High temperature heating conferred an ASE*_{95%} value of *ca.* 40%, showing that the
6 temperature was not the most significant parameter in this treatment. Samples 1 and 4
7 which do not have a wet step and use the lower temperature heating step gave ASE*_{95%},
8 values of 30%. In the case of sample 6 which had the lowest ASE*_{95%} value of 18%
9 suggests the wet step needs to be followed by a dry heating step to confer dimensional
10 stability. Samples 12, 14 and 16 which have the greatest ASE*_{95%}, confirm this
11 observation.
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14 The influence of temperature and humidity on the treatment efficiency was confirmed
15 with these results. A high wood EMC before impregnation or a wet heating step after
16 impregnation led to better performance than a room temperature water soaking before
17 dry heating. Increasing the dry heating temperature also led to better performance than a
18 higher impregnation temperature. It is hypothesised that the wood cell wall swelling
19 induced either by the high wood EMC before impregnation, or by a wet heating step,
20 contributed to the partial dissolution of OBS oligomers during this process and allowed
21 higher oligomer diffusion into the wood structure. Higher temperatures are likely to
22 decrease OBS oligomer viscosity, also contributing to the partial product diffusion into
23 the cell wall, but to a lesser extent than where wood is swollen by water or humidity.
24 Moreover, contact of wood and polymer at high temperature must be sufficient to
25 observe this effect and may explain why an 80 min impregnation step gave lower treated
26 wood performance compared to 12h, 2.5d or 4d heating steps.
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31 5. Conclusions

32 A comprehensive evaluation of OBS biopolyester impregnation followed by moisture
33 exposure and a second heating step has confirmed this treatment process confers
34 dimensional stability to the treated wood. Results indicate the OBS oligomers can be
35 impregnated in wood over a range of temperatures (90-130°C). While this treatment
36 alone is predominantly lumen filling, a subsequent water soak step then drying step can
37 enhance wood dimensional stability in both liquid water and high humidity. This was
38 likely through partially hydrolyzed OBS oligomer diffusion to the cell wall contributing
39 the dimensional stability and performance improvements in weathering and durability
40 evaluations.
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45 Attempts to define the water exposure and dry heating steps to optimise OBS oligomer
46 treatment revealed impregnation can be undertaken over a range of temperatures from
47 90 to 130°C. Samples can then be processed in a wet state either by water soaking or
48 wet heat (100°C) to promote oligomer hydrolysis and migration into wood cell walls.
49 The temperature of the final dry heating step contributes to treatment efficacy where a
50 higher temperature was associated with greater dimensional stability. Further
51 understanding of the degree of hydrolysis and polymerisation rate required within these
52 treatment steps will further aid optimisation and enhancement of this promising wood
53 treatment.
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56 6. Acknowledgements

57 The authors would like to acknowledge Christian Brönnimann, Aurèle Bourquin and
58 Charlotte Grosse for laboratory work, together with Patrick Kaiser and María-Inés
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1 Placencia Peña. Thanks is also extended to the COST Organisation, through COST
2 Action FP1303 for financial support to conduct a short term scientific mission (Grant
3 letter STSM-FP1303-100515-060044) at the BioComposites Centre laboratories in
4 Bangor (Wales) where TTDMA work was undertaken. This paper is part of a special
5 issue of the 8th European Conference on Wood Modification.
6

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41 **8. Figure captions**

42 Figure 1: Comparison of PLA and PBS oligomers efficiency for wood modification in
43 relation to the cell wall modification
44

45 Figure 2: Moisture content of OLA and OBS oligomers, preliminary heated for 2 days at
46 140 °C, then exposed at 96%RH at room temperature [Vitkeviciute, 2015]
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48 Figure 3: EMC_{Rt} of wood samples treated with OLA or OBS oligomers heated at 140°C
49 for 6h or 3 days, then exposed to 96%RH at room temperature [Vitkeviciute, 2015]
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1 Figure 4: EMC_{Rt} of OBS treated samples (160°C/2days and 9 days) and reference
2 samples not heated, or heated (160°C/2 days and 9 days) along exposure time to
3 95%RH at 23°C (_95%RH/23°C), or to water soaking (_water)

4 Figure 5: Relative storage modulus of samples impregnated (solid line), impregnated
5 and leached (dotted line); at 35%RH, 57%RH and 85%RH along temperature increase
6 from 20 to 50°C
7

8 Figure S1: Wood samples exposed for one year outdoors. (A) OBS-treated samples
9 (160°C / 2 days) (B) untreated reference (pictures have been slightly and equivalently
10 lightened to make the cracks more visible)
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12 **9. Table captions**

13
14 Table 1: Treatment parameters evaluated

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16 Table 2: Treatments description and efficiency
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Figure 1



HOT

Figure 1



HOT

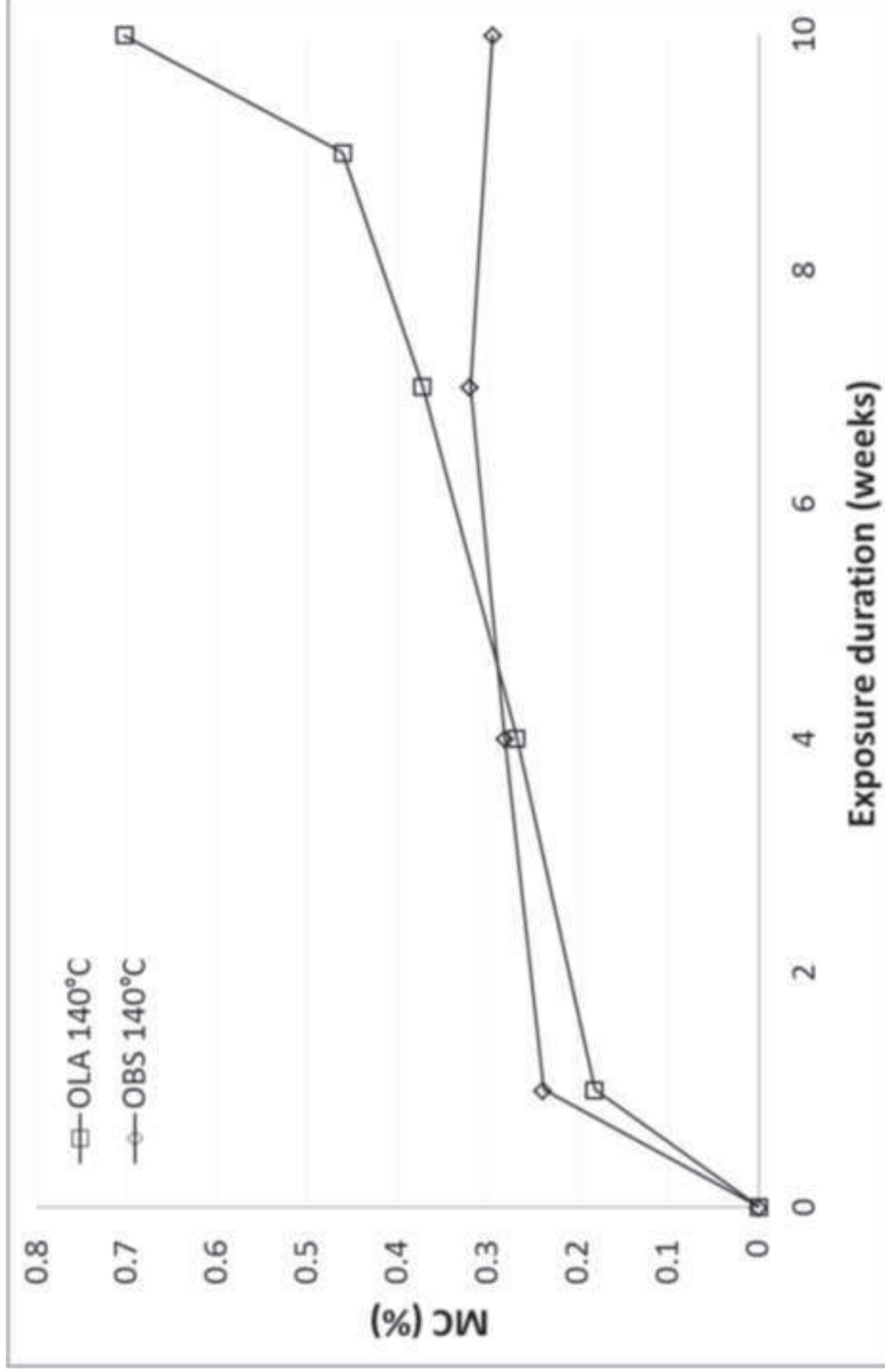


Figure 2

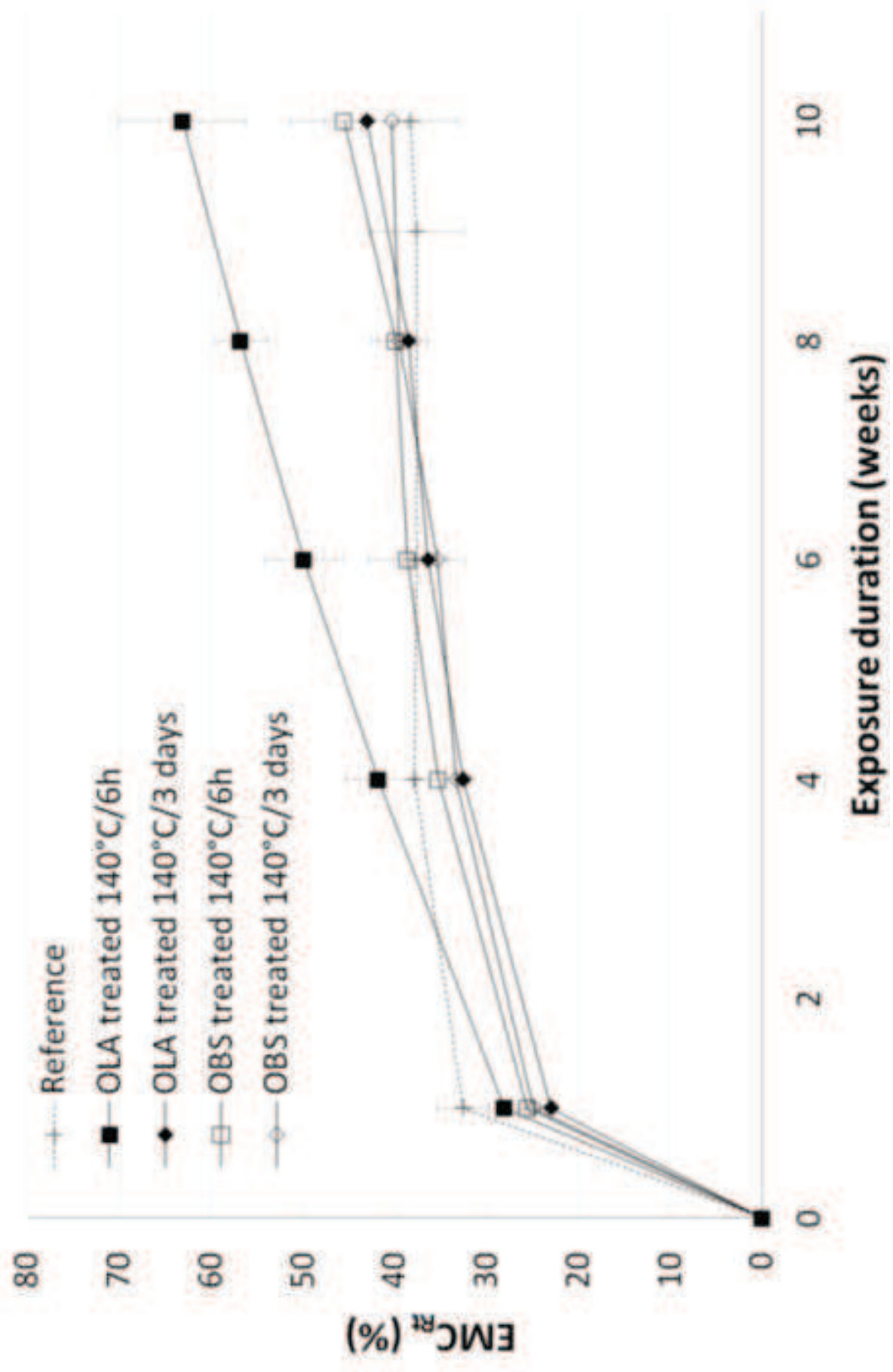


Figure 3

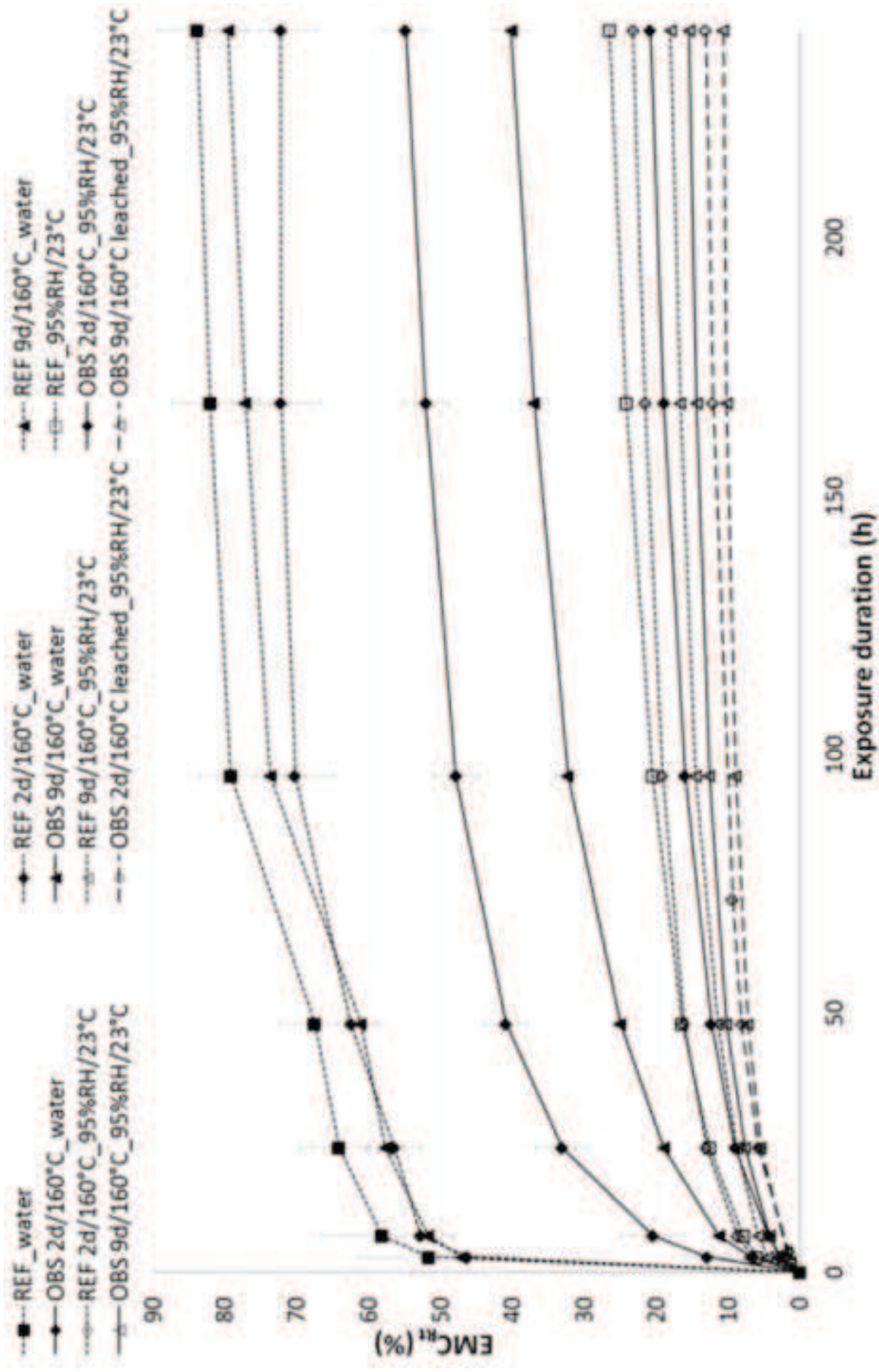


Figure 4

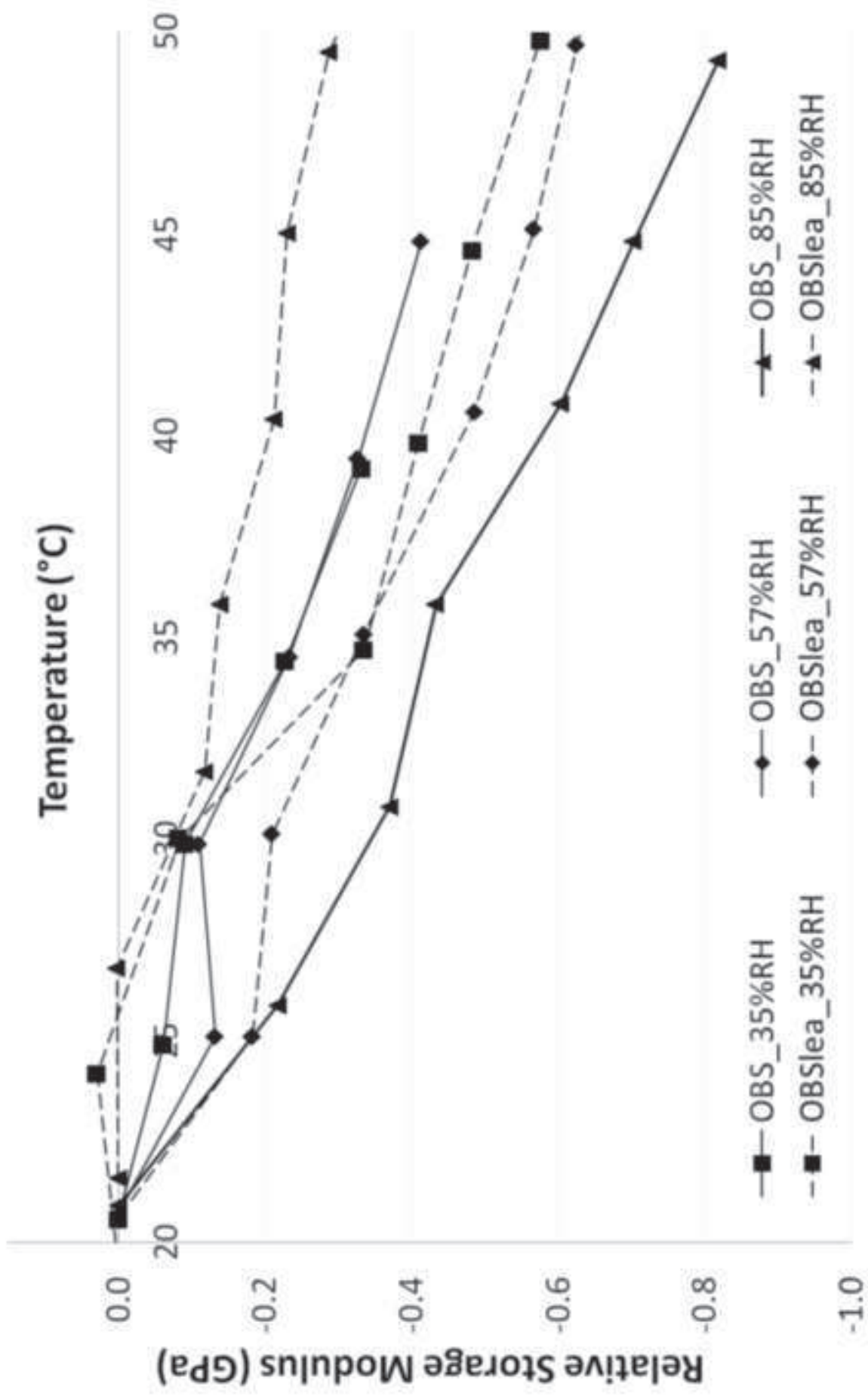
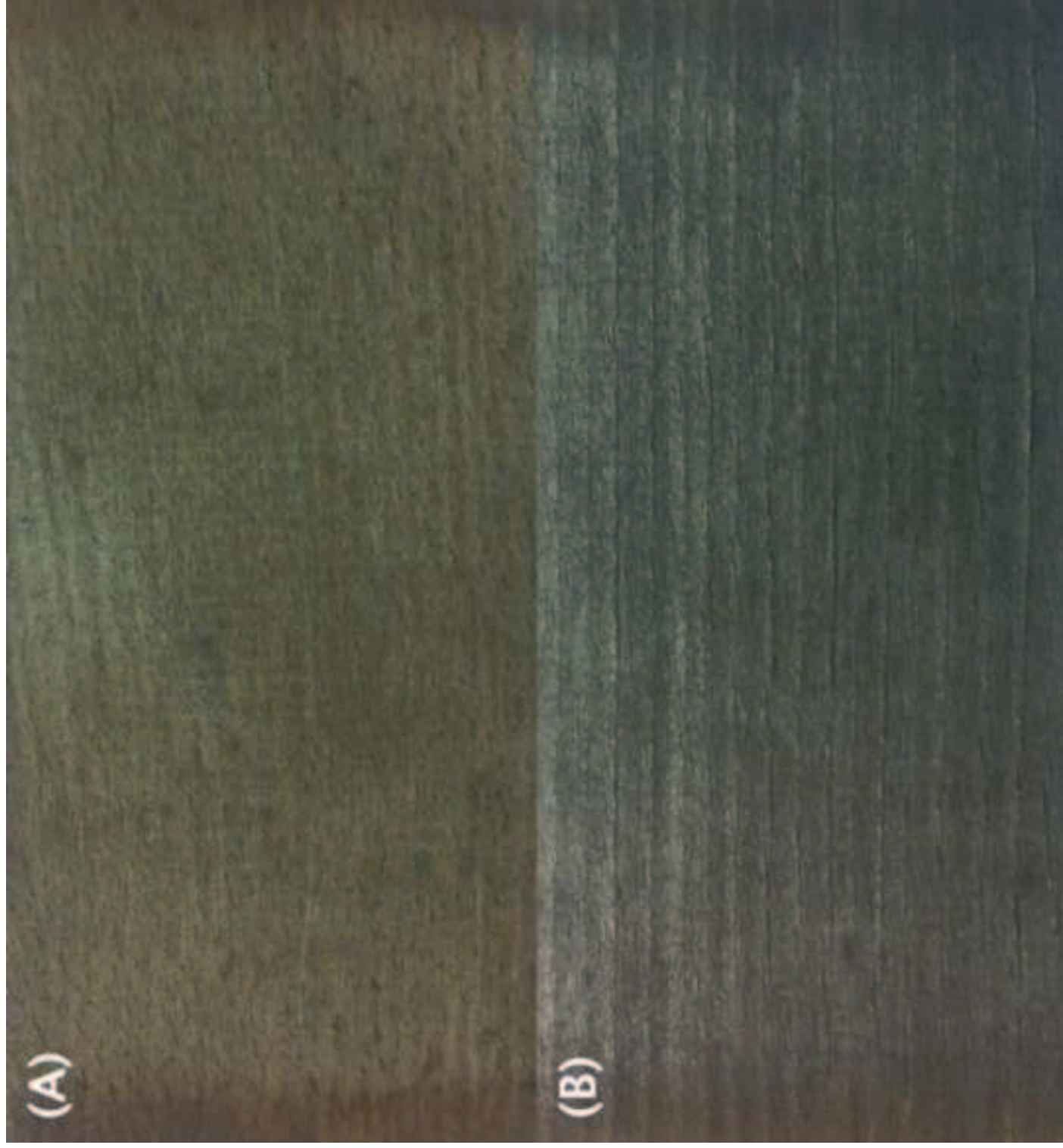


Figure 5



Supplementary materials list

Figure S1 is an illustration of the weathering of untreated and treated wood outdoors, where many deep cracks and a dark grey colour are observable on the untreated wood, whereas the OBS-treated wood remains brown and shows an undegraded surface after one year of exposure.

Caption of Figure S1:

Figure S1: Wood samples exposed for one year outdoors. (A) OBS-treated samples (160°C / 2 days) (B) untreated reference (pictures have been slightly and equivalently lightened to make the cracks more visible)

