

Investigating the Viscoelastic Properties and Mechanical Performance of Wood Modified by Biopolyester Treatments

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ABSTRACT: Oligomer systems based on poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(butylene succinate) (PBS) and poly(butylene adipate) (PBA) were impregnated in wood and polymerized *in situ* to improve the dimensional stability of the treated wood. Dynamic mechanical thermal analysis (DMTA) was used to characterize the impact on the treated wood properties. Cell wall bulking treatments (PLA and PGA oligomers: OLA and OGA) induced softening and plasticization of wood components. Lumen filling treatments (PBS and PBA oligomers: OBS and OBA) led to minor decreases in treated wood stiffness with any softening dependent on the polymer melt temperature. Overall, no oligomer treatment induced any significant wood reinforcement, but the T_g of wood components could be reduced significantly.

KEYWORDS: Wood modification, biopolyesters, *in situ* polymerization, plasticization

1 INTRODUCTION

Chemical modification of solid wood is one of the main approaches for improvement of wood durability, dimensional stability and mechanical properties. Primarily, this has been successfully achieved by substituting hydroxyl groups within wood by means of suitable chemicals such as isocyanates, aldehydes, acid or alkyl chlorides, anhydrides or methylation reactions [1–3]. Acetylation of wood is the most studied and advanced esterification reaction, consisting of the grafting of acetic anhydride to wood hydroxyls, releasing acetic acid as co-product. While not a systematic approach for substituting hydroxyl groups, the impregnation and *in situ* polymerization of monomers is another method for improving wood dimensional stability if the monomers diffuse into wood cell walls. Furfurylation is the most developed example of a successful *in situ* polymerization treatment [4,5]. The combination of these approaches for both chemical grafting to wood hydroxyls and *in situ* polymerization within the wood cell wall with lactic acid oligomers has been recently reported [6,7]. This treatment has

demonstrated a significant anti-swelling efficiency and improved biological resistance of the treated wood, together with greater surface hardness.

Chemical modification of wood can also induce property changes within the treated wood such as wood plasticization achieved upon benzylation [8] or acetylation [9]. Benzylation has also been shown to reduce the glass transition of components in wood fibers [8,10]. Furthermore, Backman and Lindberg [11] concluded that good adhesion of acrylate polymers within the cell wall also results in decreased T_g.

In the current study, chemical modification of wood with oligomer treatments was investigated for any impact on wood thermoplasticization. Oligomers of poly(lactic acid), poly(glycolic acid), poly(butylene succinate) and poly(butylene adipate) (PLA, PGA, PBS and PBA respectively) were used to treat and polymerize within the wood structure. While the main objective of these treatments was to improve the dimensional stability of wood [12,13], the viscoelastic and thermal properties of these treatments were also investigated. The results of this study further contribute to the fundamental understanding of the association and interactions between the *in situ* polymers and wood components of the treated wood.

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2 EXPERIMENTAL METHODS

2.1 Materials

Oven-dried beech wood samples (*Fagus sylvatica*) and radiata pine veneer samples (*Pinus radiata*) were used for impregnation and treatment. All chemicals were sourced from Sigma-Aldrich (Switzerland): L(+)-lactic acid solution ($\geq 85\%$), glycolic acid solution (70% in water, technical grade), 1,4-butanediol (99%), dimethyl succinate (98%), dimethyl adipate (98%) and titanium butoxide (97%).

2.2 Polyester Oligomers Synthesis

As described by Noël *et al.* [12,13], oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask (500 mL or 1 L) fitted with magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to observe the polymerization, condenser head and heater temperatures.

2.2.1 Lactic Acid and Glycolic Acid Oligomerizations

Lactic acid or glycolic acid (200–800 g as an aqueous solution) was poured into the flask. The solution was first heated at 70°C under reduced pressure (150 mbar) as an initial distillation step for 75 min. The initial oligomerization step involved gradually increasing the temperature to 100°C over 100 min, yielding the oligoester of lactic acid OLA1 (or glycolic acid OGA1). At the end of the oligomerization reaction, oligomers were poured into bottles, sealed and cooled to room temperature. OLA1 is liquid product at ambient temperature. Glycolic acid oligomers OGA1 tend to solidify, giving a wax-like solid product when cooled [12,13].

2.2.2 Butylene Succinate and Butylene Adipate Oligomerizations

Oligoesters were synthesized by melt polymerization of dimethyl succinate or dimethyl adipate and 1,4-butanediol, according to literature procedures [14]. This was achieved by adding a 25% stoichiometric excess of 1,4-butanediol in the presence of titanium(IV) butoxide as esterification catalyst (OBS2 and OBA2). A mixture of dimethylester, 1,4-butanediol and catalyst (200–800 g) was poured into the flask under a nitrogen purge. The mixture was gradually heated to 180°C over 130 min under reduced pressure (150 mbar). At the end of the oligomerization reaction, oligomers were poured into bottles, sealed and cooled. OBS2 and

OBA2 solidify as a white block when cooled. The melt temperatures of OBS2 and OBA2 were rheologically measured at ca. 75°C and 50°C, respectively [12,13].

2.3 Wood Treatment

Wood samples were placed in a container and immersed in liquid oligomer, either at room temperature (OLA1, OGA1) or at 90°C (OBS2, OBA2). Containers were then placed in a vacuum oven under reduced pressure (580 mmHg) for 1 to 2 hours, then at atmospheric pressure over 1 to 2 hours.

Impregnated samples were then wiped and set on aluminum foil in a ventilated oven at either 103°C for 26 hours (low temperature procedure, LT) or 120°C for 6 hours (high temperature procedure, HT). Anhydrous sample weight was measured before impregnation, after impregnation and after heat treatment. Weight uptakes have been calculated according to Equations 1 and 2:

$$WU_i (\%) = \frac{w_i - w_0}{w_0} \times 100 \quad (1)$$

$$WU_t (\%) = \frac{w_t - w_0}{w_0} \times 100 \quad (2)$$

where w_i stands for the impregnated sample weight, w_t for the sample weight after complete treatment, and w_0 the oven-dried sample weight before treatment [12,13].

Impregnated samples are referred to as OLA1IW, OGA1IW, OBS2IW and OBA2IW. Treated samples, following LT or HT procedures, are referred to as OLA1 IWL/HT, OGA1 IWL/HT, OBS2 IWL/HT and OBS2 IWL/HT.

To assist with GPC analysis, pure oligomers (OLA1, OGA1, OBS2 and OBA2) were also poured into containers and set in a ventilated oven at either 103°C for 26 hours or 120°C for 6 hours. These samples are referred to as OLA1LT/HT, OGA1LT/HT, OBS2LT/HT and OBA2LT/HT.

2.4 Extractions

Water leaching consisted of soaking treated samples in distilled water at 20°C for 7 days. After leaching, samples were oven dried at 103°C until constant weight. Weight loss due to water leaching and weight loss of the polymer were calculated as follows:

$$WLP_{wl} (\%) = \frac{w_t - w_{we}}{WU_t \times w_0} \times 100 \quad (3)$$

where w_t stands for sample weight after complete treatment, and w_{we} for treated sample weight after water leaching.

Soxhlet extraction was carried out on small chips cut out of sample specimens in chloroform at 60°C for 48 hours. After extraction, samples were oven dried at 103°C until constant weight. Weight loss due to solvent extraction has been calculated as:

$$WLP_{se} = \frac{w_t - w_{se}}{WU_t \times w_0} \times 100 \quad (4)$$

where w_t stands for sample weight after complete treatment, and w_{se} for treated sample weight after solvent extraction [12,13].

2.5 Bending Resistance

Beech samples of dimensions 140 x 12 x 7 mm (L x T x R) have been tested according to four-point bending equipment using a Zwick universal testing machine (2.5 kN) and associated software. Samples were charged with linear force application in the elastic zone. Young's modulus was obtained from the stress-strain curve [13].

2.6 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was undertaken on a Polymer Labs GPC system using a mixed-C column (Polymer Labs) and chloroform as eluent. All samples were dissolved in GPC solvent (40 mg/mL) and run on the GPC, employing both refractive index (RI) and UV detectors. Polystyrene calibration standards were used to calculate molecular weight profiles [12,13].

2.7 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical analysis (DMA) was performed in three-point 40 mm flexural mode using a Thermal Analysis Instruments G2RSA DMTA IV. Viscoelastic properties of samples were measured at a frequency of 1 Hz, strain rate of 0.05% and a heating rate of 3°C/min over a temperature ranging from 25°C to 200°C.

2.8 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instruments Q1000 Differential Scanning Calorimeter. Samples (5–10 mg)

were loaded into standard aluminum pans and were run using a heat/cool/heat cycle with a heating rate of 10°C/min and cooling rate of 5°C/min under a nitrogen atmosphere. The cooling and second heating cycles were reported, with the first heating cycle given in Supporting Material (Figure A – Supplementary Materials).

2.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) measurements were performed using a Thermal Analysis Instruments Q500 Thermogravimetric Analyzer. Samples (8–14 mg) were weighed out on platinum pans and heated to 600°C at 10°C/min under a nitrogen atmosphere. All thermal analysis employed duplicate runs for each sample [12].

2.10 Sample Preparation of Semithin Micro Slices

Wood cubes (3 x 3 x 5 mm) at ambient moisture content were first dried using aqueous isopropanol with increasing concentrations: 50%, 70% and 100%. Samples were then infiltrated with embedding solution in isopropanol (1:1), then finally placed in pure embedding solution. After embedding, samples were heated in an oven (60°C) for 24 h. After trimming to obtain a cutting surface, microsections were taken using a diamond blade or steel blade (profile C). To stain microsections, they were first hydrated using aqueous isopropanol solutions of 100%, 70%, 50%, 30% and then pure water before dipping into a solution of Safranin and Acriflanin for 6 hours. Sections were briefly dried (60°C for 15 min) before being placed in Xylol and finally on glass slides with Malinol resin [15].

3 RESULTS AND DISCUSSION

3.1 Polymer Characterization

The polymer systems prepared for impregnation into wood structure show significantly different properties. As evidenced in As evidenced in Figure 1a and Figure 1b the OLA1 and OGA1 DSC thermograms do not exhibit the polymeric properties for PLA and PGA, respectively [16–18]. There was no definitive glass transition (T_g) nor melt feature, only an exotherm at high temperature, which is suggestive of material degradation [12] (Figure B – Supplementary Materials). For the OBS2 and OBA2 thermograms, typical polymer thermal transitions were observed for these materials. A broad melting peak was observed for both systems,

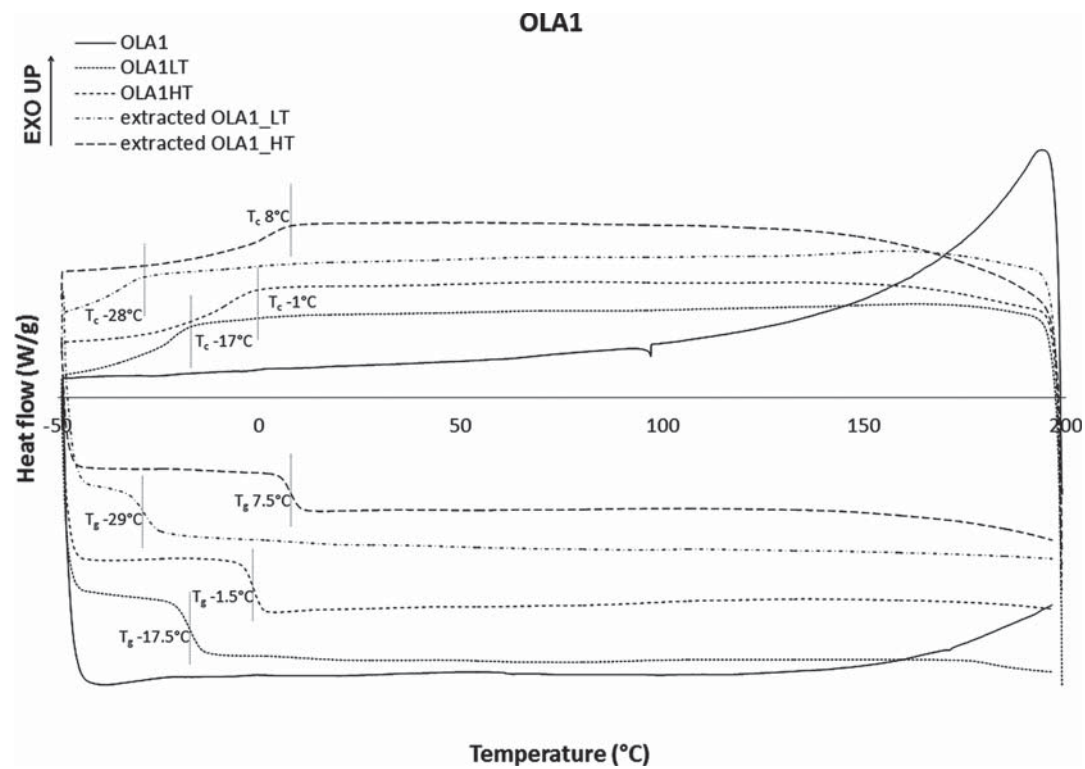


Figure 1a DSC thermograms of pure OLA1, after heating step at 103°C/26h (OLA1LT) and 120°C/6h (OLA1HT), and extracted after impregnation and heating in wood (Beech) structure (extracted OLA1_LT and_HT).

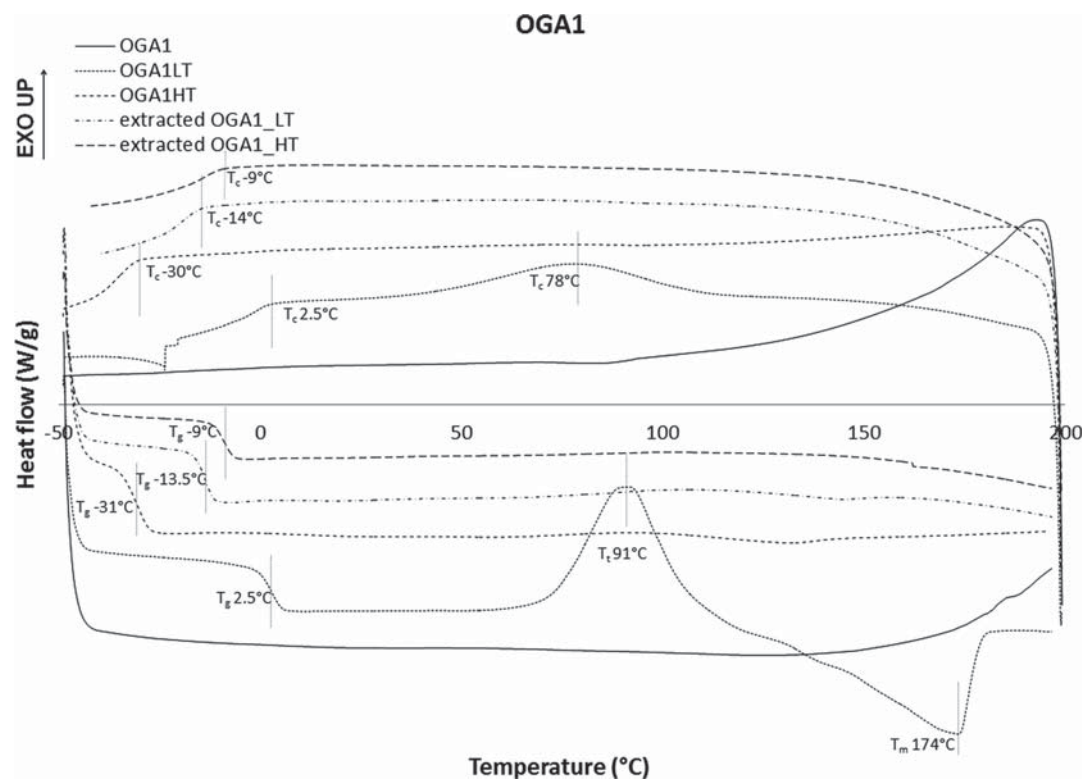


Figure 1b DSC thermograms of pure OGA1, after heating step at 103°C/26h (OGA1LT) and 120°C/6h (OGA1HT), and extracted after impregnation and heating in wood (Beech) structure (extracted OGA1_LT and_HT).

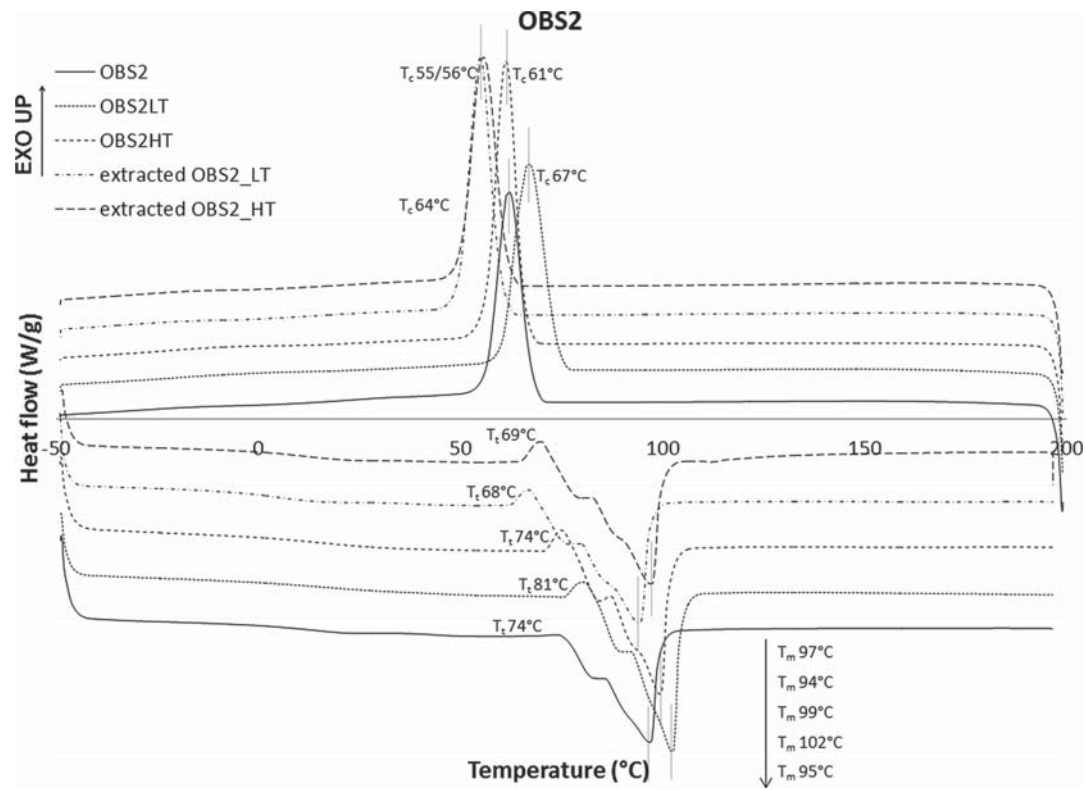


Figure 1c DSC thermograms of pure OBS2, after heating step at 103°C/26h (OBS2LT) and 120°C/6h (OBS2HT), and extracter after impregnation and heating in wood (Beech) structure (extracted OBS2_LT and_HT).

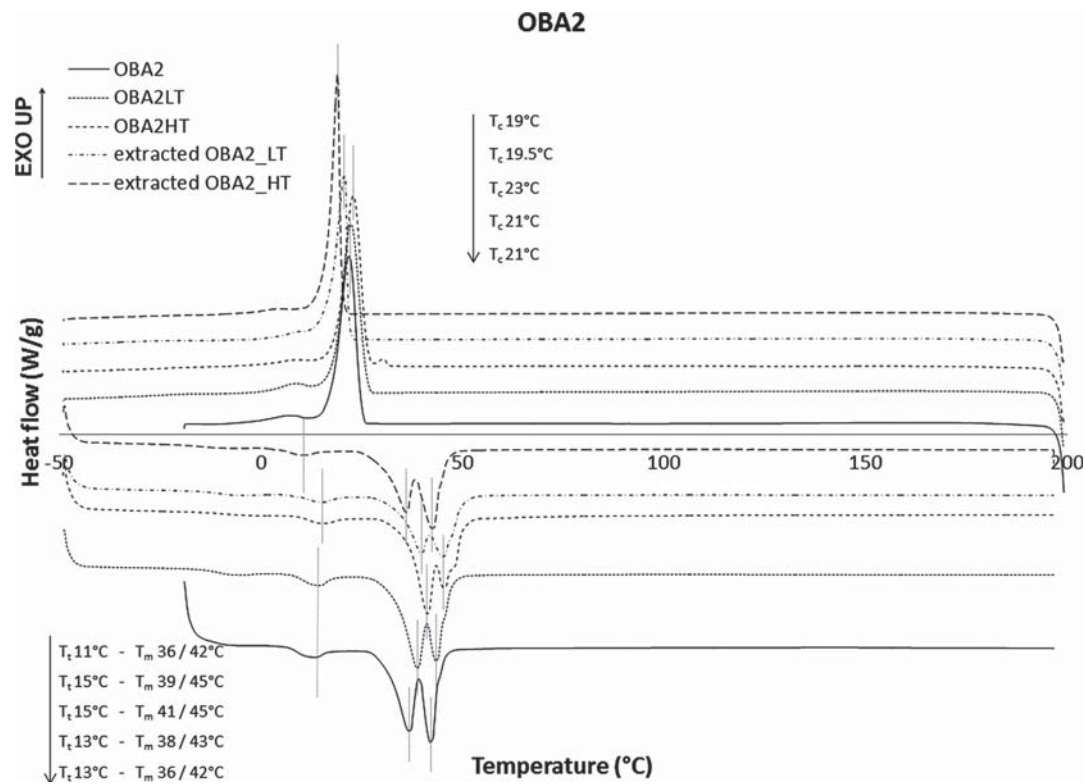


Figure 1d DSC thermograms of pure OBA2, after heating step at 103°C/26h (OBA2LT) and 120°C/6h (OBA2HT), and extracter after impregnation and heating in wood (Beech) structure (extracted OBA2_LT and_HT).

consistent with the Mw profile of each sample (Figure C – Supplementary Materials). Crystallization peaks were evident at 64°C and 21°C, for OBS2 and OBA2 respectively, suggesting their preparation led to a semicrystalline material. Sub-ambient Tg values were observed between 4°C and 18°C for OBS2 and –15°C and –7°C for OBA2.

The ability of all oligomers to increase their degree of polymerization with further heating was evidenced in analysis of the pure polymers. Heating oligomers OLA1 and OGA1 at 103°C (OLA1LT, OGA1LT) and 120°C (OLA1HT, OGA1HT) gave materials which exhibited Tg and crystallization temperatures of higher molecular weight polyesters, but these were at lower temperatures than typical commercial PLA and PGA polymers [16,17]. Both OLA1LT/HT and OGA1LT/HT have similar Tg and Tc values consistent with their relatively low molecular weight (Figure D – Supplementary Materials).

3.2 Mechanical Performance with Temperature

Analysis of *in situ* polymerization of the oligomer treatments within wood is difficult. However, the degree of polymerization has been assessed previously by polymer extraction and molecular weight analysis by GPC and indirectly by means of thermogravimetric analysis profiles of treated wood [12,13]. Dynamic mechanical thermal analysis (DMTA) offers corroborating analysis to determine the extent of polymerization as well as any wood matrix reinforcement provided by the polymer. DMTA was initially applied to determine the onset of *in situ* polymerization within treated samples at 80°C, 100°C and 120°C (Figure 2a-d). Across all samples, there was an initial decrease in storage modulus (E') likely due to softening and plasticization of wood components upon heating. Generally, with time and water loss the isothermal treatments result in recovery of E' values, but the extent of E' values was dependent on oligomer treatment and temperature. For OLA1-impregnated samples (OLA1IW), isothermal heating at 80°C for 2 hours led to a gradual increase in E' to the initial value for this sample. This was likely due to water loss and reduced plasticization, but potentially to the polymerization of the OLA component. This was also the case for OLA1IW at 120°C, whereas isothermal heating this sample at 100°C gave a lower E' value after 2 hours. The distinction in E' values after heating may reflect sample reinforcement achieved due to *in situ* polymerization compared with wood component softening. However, this observation may be further complicated by oligomer penetration into wood cell wall (Table 1).

For the isothermal heating of the OBA2 and OBS2 treatments, after an initial E' loss, samples similarly showed the effect of reduced plasticization as water was lost on heating. Any effect of increasing polymerization due to temperature was not readily distinguished in these samples. Isothermal heating of the OGA1 treated sample showed no significant increase in E' values at 80–120°C. This was particularly evident at 120°C, with the sample having a relatively lower E' value than at 80 or 100°C. Overall, across the four oligomer treatments, the above results suggest that the heat treatments at 103°C for 26 hours and 120°C for 6 hours were likely to achieve sufficient *in situ* polymerization within samples. However, these isothermal heating experiments using DMTA did not distinguish any impact of resulting polymer properties to observed E' values, particularly those for OLA1 and OGA1 (Figure 2a and Figure 2b).

3.3 Polymer Association with Wood Cell Wall and Thermal Properties

Oligomer impregnation and polymerization in the wood cell wall were suggested by swelling measurements (Table 1 [13]). For example, ca. 25% swelling of OLA1 and OGA1 treated samples was observed upon oligomer impregnation and heating (LT/HT). OGA1 oligomer impregnation induces at least 10% swelling even at room temperature. However, for OBS2 and OBA2 treated samples, neither treatment led to any significant wood swelling ($\leq 2\%$), indicating both OBS2 and OBA2 treatments provide limited penetration of the cell wall.

In addition to the isothermal experiments above, DMTA temperature sweeps (Figure 3a-d) showed the relative sample stiffness with temperature for impregnated (IW) and heat-treated samples (IWLT and IWHT). This revealed that the influence of OLA1 and OGA1 treatments differed from OBS2 and OBA2. Impregnation with OLA1 and OGA1 induced significant material softening evidenced by E' decreases as observed in Figure 2a and Figure 2b. For OLA1IW this was most apparent between 70°C and 120°C compared to untreated wood and may explain the varying response of this sample at each isothermal temperature with respect to time. The heated OLA1 (LT/HT) samples show a relatively gradual decrease in E', with this sample having greater softening than exhibited by untreated wood. This observation appeared independent of heat treatment temperature. A greater E' decrease than in untreated wood was perhaps consistent with softening induced by the polymeric component in the cell wall, as reported by Jebrane *et al.* [9] for acetylated wood blocks. For the OGA1-impregnated sample in which

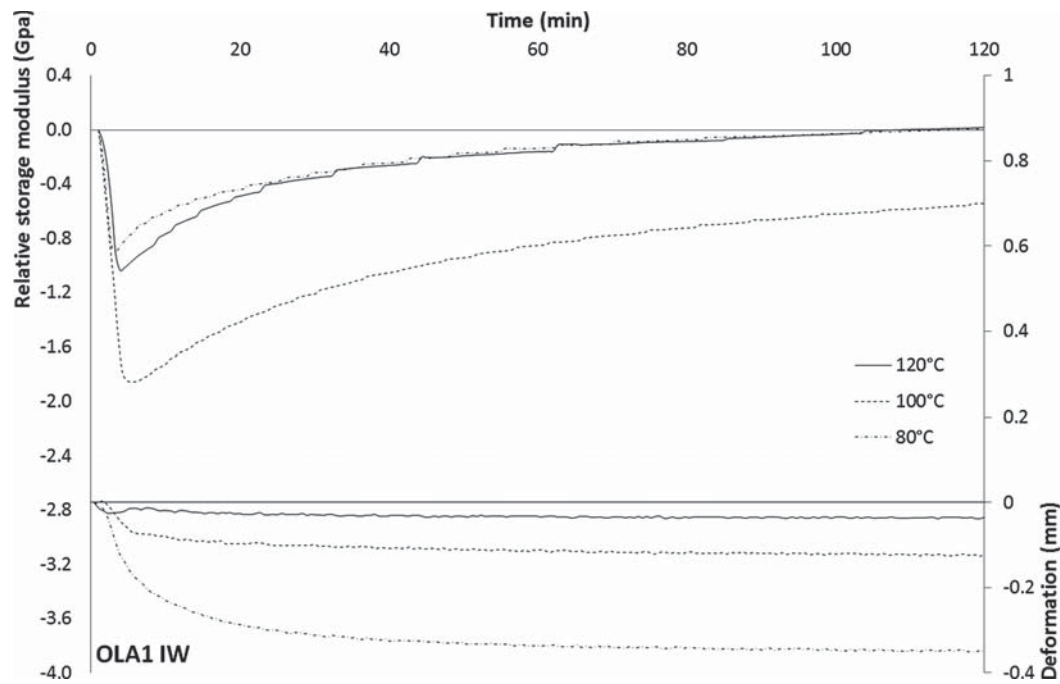


Figure 2a Relative storage modulus E' and deformation under isothermal conditions of wood (Radiata pine) impregnated with OLA1 at 80°C, 100°C and 120°C.

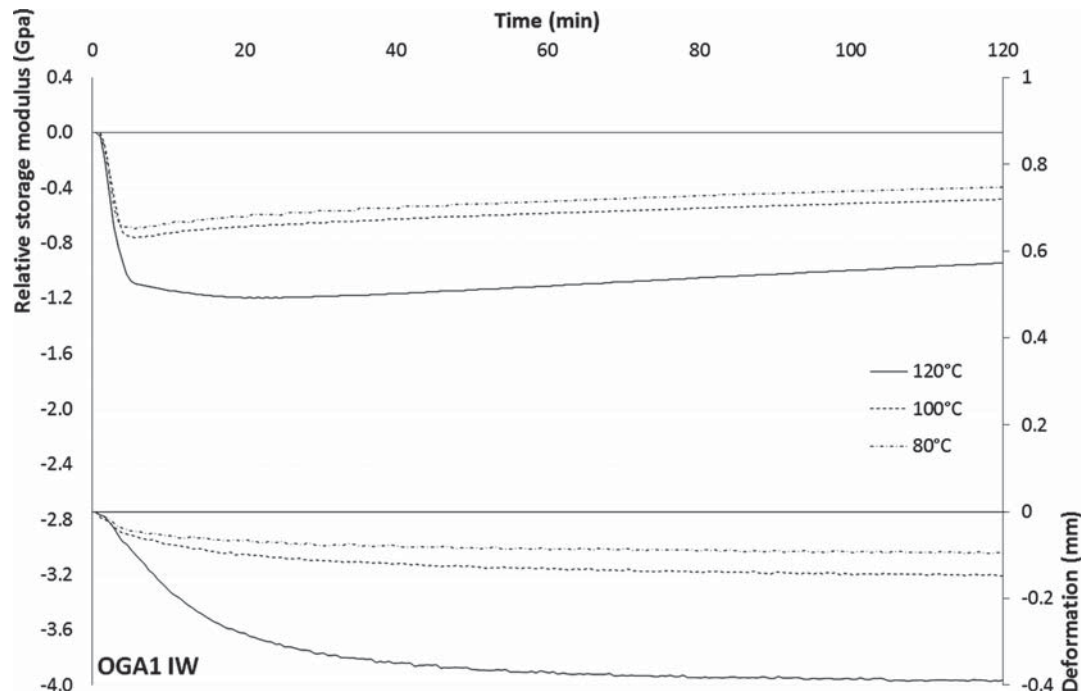


Figure 2b Relative storage modulus E' and deformation under isothermal conditions of wood (Radiata pine) impregnated with OGA1 at 80°C, 100°C and 120°C.

oligomers partially penetrate wood cell walls (Table 1) the E' decreases were similar to OLA1, however above 120°C the sample further softens, with all specimens observed to break at > 150°C. This result was likely due to the heating rate exceeding any *in situ* polymerization

achieved within the sample during this experiment. However, heat treatment of OGA1-impregnated samples (OGA1 IWL/HT) gave similar E' profiles, which were intermediate to the OGA1 IW and OLA1 LT/HT samples.

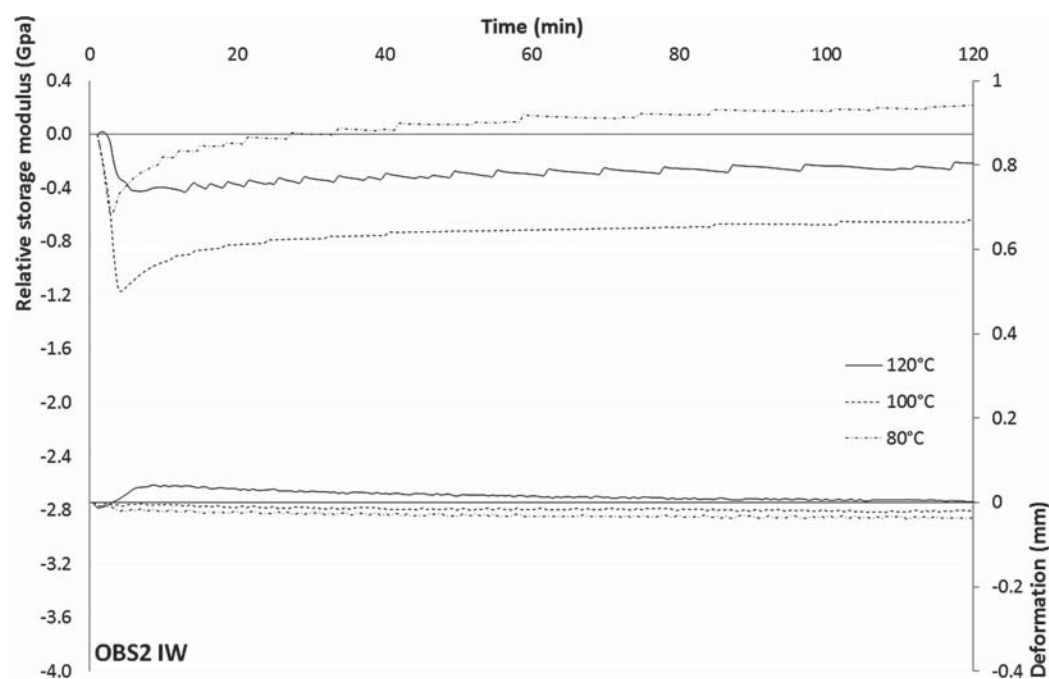


Figure 2c Relative storage modulus E' and deformation under isothermal conditions of wood (Radiata pine) impregnated with OBS2 at 80°C, 100°C and 120°C.

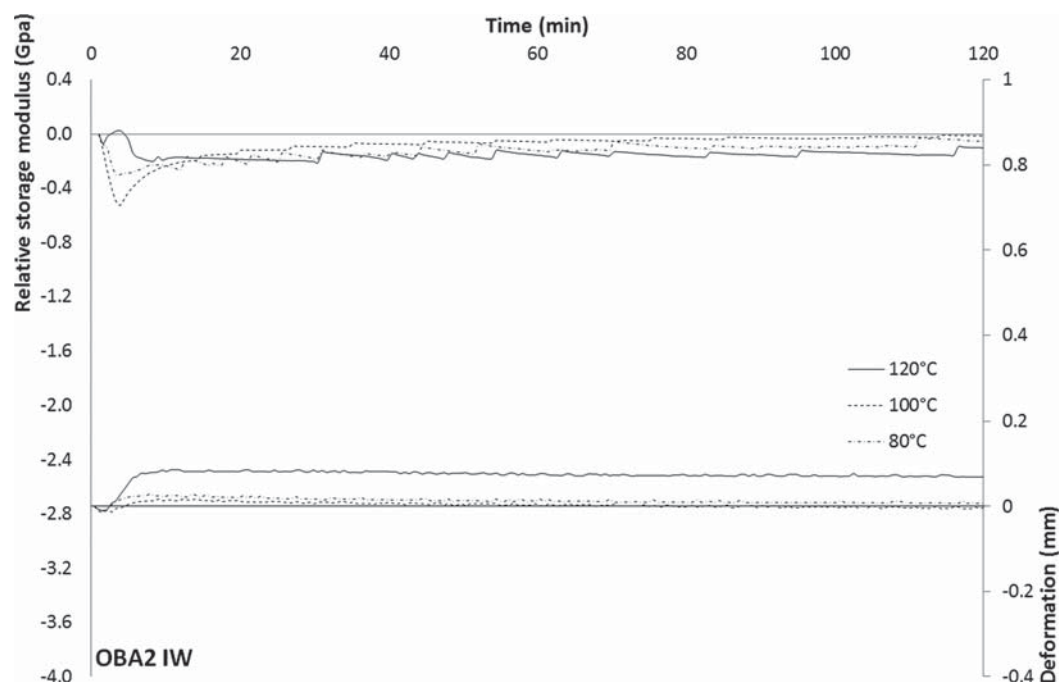


Figure 2d Relative storage modulus E' and deformation under isothermal conditions of wood (Radiata pine) impregnated with OBA2 at 80°C, 100°C and 120°C.

The relatively low penetration of OBS2/OBA2 oligomers into wood cell walls (Table 1) was reflected in DMTA for both impregnated and heat-treated samples (Figure 3c and Figure 3d). Sample stiffness

decreased slowly upon heating, but at ca. 95°C and 50°C, the E' of samples decreased, perhaps reflective of the melting of OBS2/OBA2 polymers, respectively (Figure 1c; Figure 1d; Figure B - Supplementary

Table 1 physical properties of impregnated and treated wood samples according to weight uptake with impregnation and treatment, weight loss with water leaching or solvent extraction, and volume swelling due to impregnation and treatment.

Ref.	Weight uptake		Weight loss		Volume swelling	
	WU _i (%)	WU _t (%)	WLP _{wl} (%)	WLP _{se} (%)	S _i (%)	S _t (%)
OLA1LT	76	54	31	37	3	23
OLA1HT	81	56	29	39	0.9	24
OGA1LT	118	84	15	11	24	28
OGA1HT	150	92	19	14	9	26
OBS2LT	68	65	7	37	2	1.0
OBS2HT	64	64	13	51	0.6	1.7
OBA2LT	64	61	5	51	1.2	0.3
OBA2HT	68	67	10	56	0.1	1.3

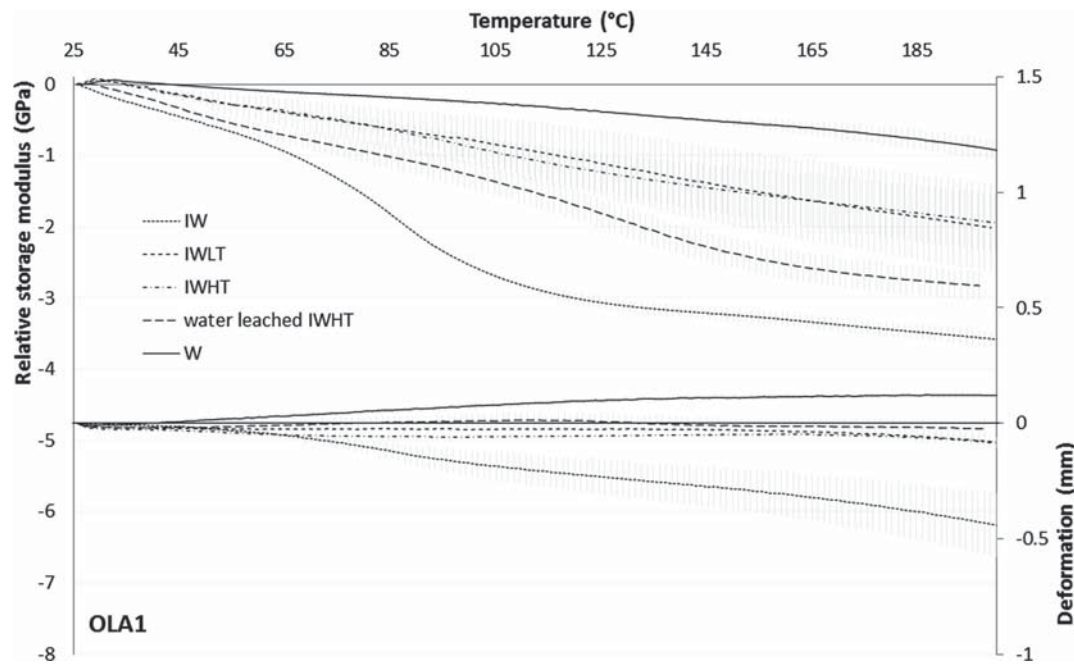


Figure 3a Relative storage modulus E' and deformation along temperature ramp of wood (Radiata pine) impregnated with OLA1 (IW), impregnated and heated (IWLT, IWHT) and impregnated, heated and water leached (water leached IWHT), in comparison to untreated wood (W).

Materials). However, above 150°C there were no differences in E' values across the heat-treated samples and untreated wood. The relatively lower melting temperature of OBA2 oligomer (50°C) confirmed the effect exhibited in DMTA profiles, with treated samples initially softening at this temperature. This feature appeared independent of any heat treatment temperature. Given that both OBS2 and OBA2 treatments were likely lumen-filling only, sample softening upon melting contrasts the gradual softening and plasticization of wood cell wall components exhibited by the OLA1 and OGA1 treated samples.

Treatment impact on resulting cell wall properties was further evident in Figure 4B and 4C, where thickening of the cell wall, cracks, lumen shape and irregular dye absorption were observed with OBA2 IWHT (Figure 4B) and OLA1 IWHT (Figure 4C) samples. Transverse sections of an untreated sample (Figure 4A) show regular lumen and pits with homogeneous cell wall dyeing. However, with the OBA2 IWHT sample (Figure 4B) the cell walls appear with two colors and multiple cracks. With the OLA1 IWHT treated sample (Figure 4C) the cell wall coloration was more heterogeneous with partial delamination of cell wall layers. The

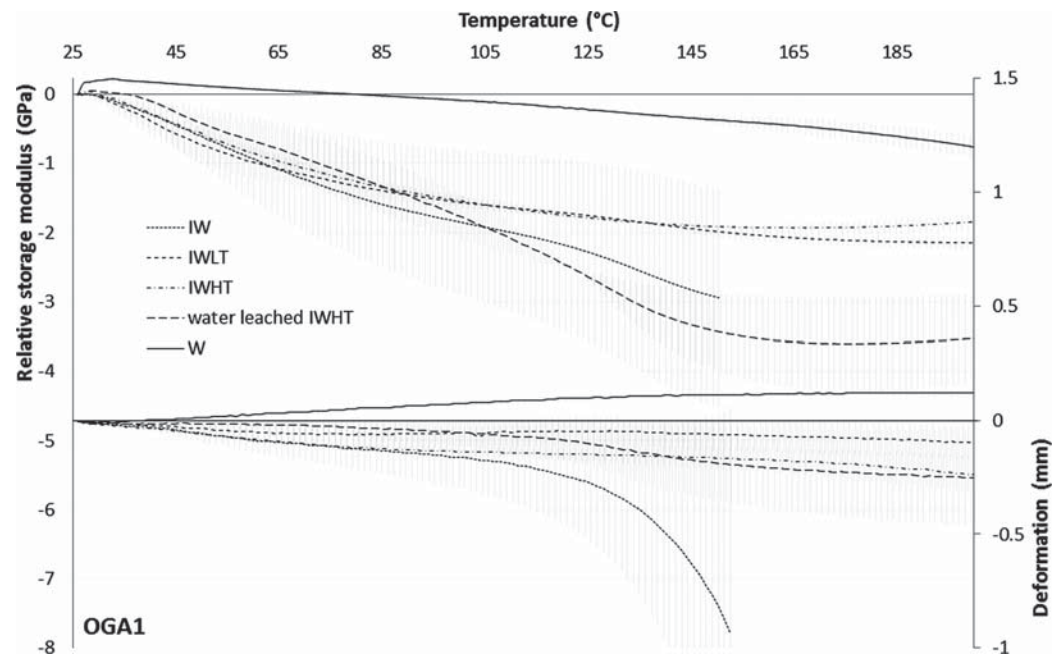


Figure 3b Relative storage modulus E' and deformation along temperature ramp of wood (Radiata pine) impregnated with OGA1 (IW), impregnated and heated (IWLT, IWHT) and impregnated, heated and water leached (water leached IWHT), in comparison to untreated wood (W).

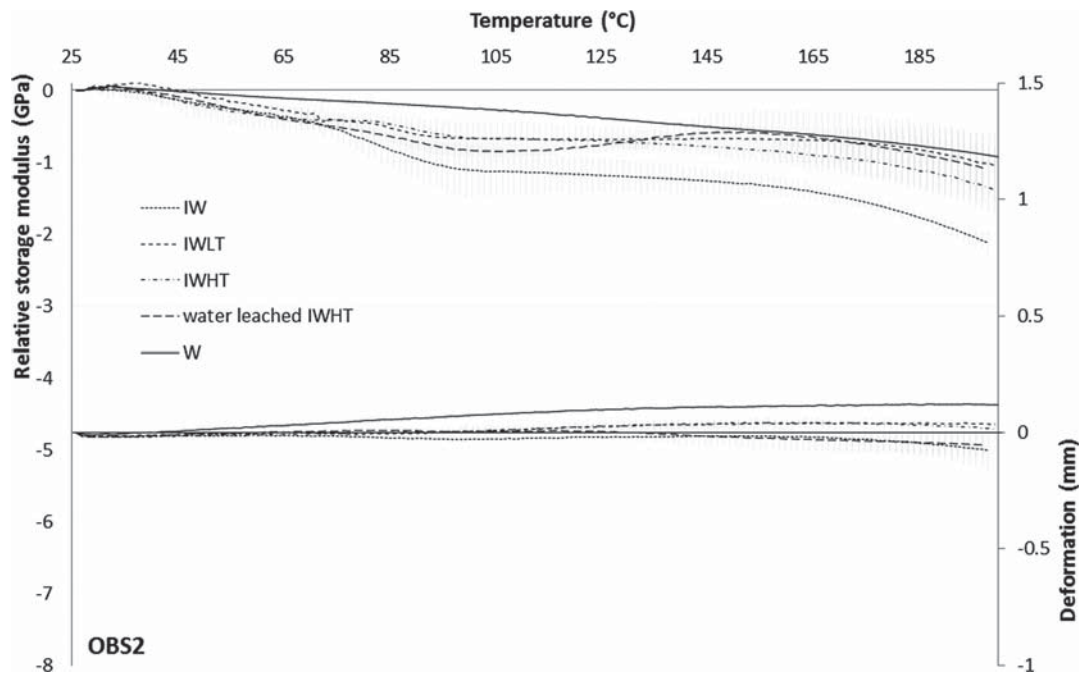


Figure 3c Relative storage modulus E' and deformation along temperature ramp of wood (Radiata pine) impregnated with OBS2 (IW), impregnated and heated (IWLT, IWHT) and impregnated, heated and water leached (water leached IWHT), in comparison to untreated wood (W).

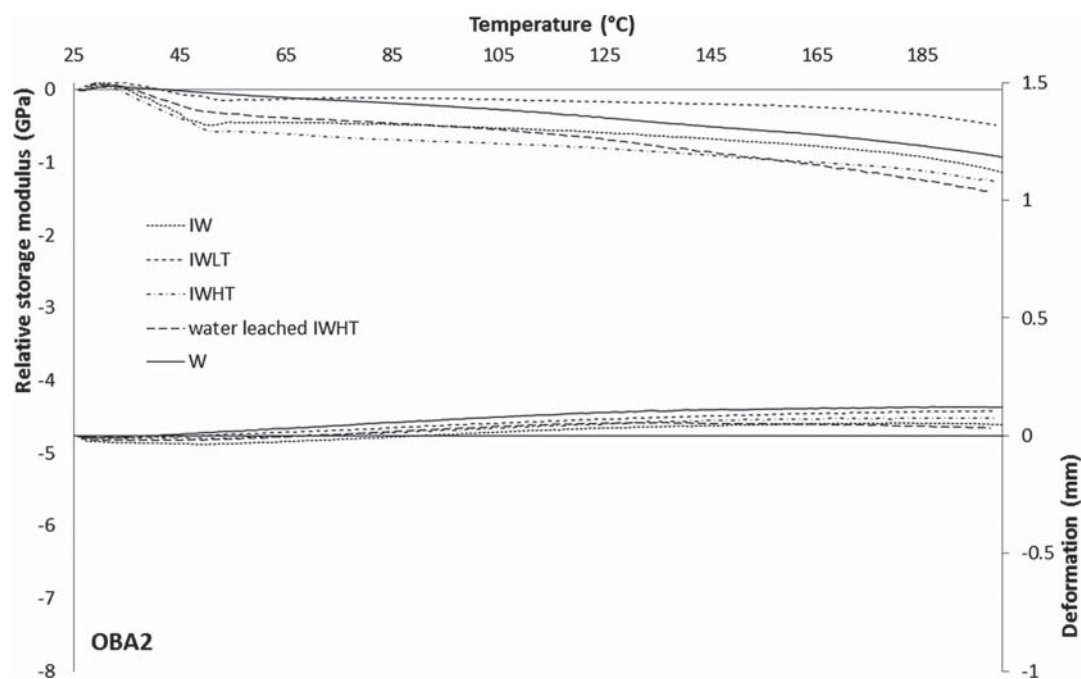


Figure 3d Relative storage modulus E' and deformation along temperature ramp of wood (Radiata pine) impregnated with OBA2 (IW), impregnated and heated (IWL, IWHT) and impregnated, heated and water leached (water leached IWHT), in comparison to untreated wood (W).

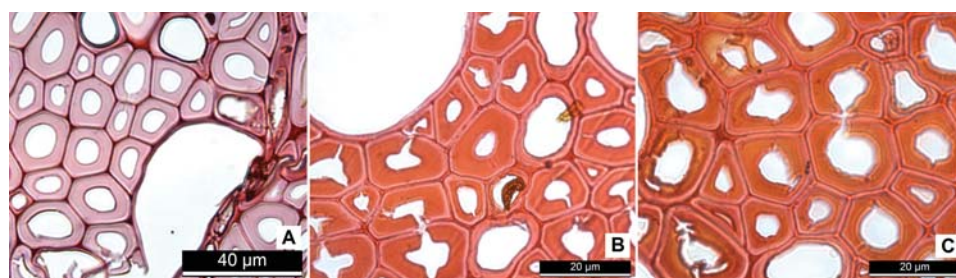


Figure 4 Micro-slices of untreated wood (Beech) (A), wood treated with OBA2 (IWHT) (B) and wood treated with OLA1 (IWHT) (C).

variation in dye intensities for this sample may be due to the presence of oligomers in the cell wall or lumens, with the extent of cell wall degradation explained by *in situ* polymerization. However, across these samples, no cell delamination was observed, indicating that the middle lamella remained intact after treatments.

3.4 Modification of Wood Properties on Water Soaking

Given that some *in situ* polymerized material can be extracted from the treated wood [12,13], the 120°C treated samples were extracted by water leaching

(water leached IWHT). Water leaching removed up to 30% of the oligomer uptake (Table 1), typically removing residual monomeric and short-chain oligomers, but this leaching can also hydrolyze and remove higher M_w polymeric fractions [13] (Figure C and Figure D, Supplementary Materials). Analysis by DMTA (Figure 3a) suggests that the extracted OLA1 IWHT sample has relatively similar properties to the original treated sample despite water leaching and removal of polymeric components. Potentially, the remaining *in situ* polymerized material could be hydrolyzed by water and could also act as a plasticizer, but to a lower extent than observed by oligomers in OLA1

Table 2 storage modulus at 25°C of DMTA samples (E') and Young modulus of macro-samples tested in 4-point bending (MOE).

Ref.		E' (GPa)	MOE (GPa)
W		5.89 ± 0.16	22.96 ± 1.05
OLA1	IW	5.50 ± 0.41	16.41 ± 0.84
	IWLT	4.09 ± 0.55	
	IWHT	3.80 ± 0.36	
	Water leached IWHT	4.54 ± 0.46	
OGA1	IW	3.85 ± 1.26	4.28 ± 1.33
	IWLT	3.79 ± 0.17	
	IWHT	3.27 ± 0.11	
	Water leached IWHT	4.63 ± 1.32	
OBS2	IW	5.46 ± 0.17	22.52 ± 1.29
	IWLT	6.37 ± 0.44	
	IWHT	5.30 ± 0.39	
	Water leached IWHT	4.49 ± 0.95	
OBA2	IW	4.59 ± 0.35	25.40 ± 3.01
	IWLT	5.39 ± 0.10	
	IWHT	5.26 ± 0.91	
	Water leached IWHT	4.91 ± 0.05	

IW. Furthermore, the removal of leached OLA1 components gave a greater ambient storage modulus at 25°C (4.5 GPa) compared to treated samples (3.8 GPa; Table 2). As already reported [13], with such treatments oligomers and polymers are most likely entangled around cellulosic fibers and fibrils within the wood structure. This interlocking of OLA1 polymers within the lignocellulosic matrix likely increases the free volume contributing to wood reinforcement.

In the case of OGA1 oligomers, this treatment had a greater impact on wood properties (Figure 3b; Table 2). Oligomers penetrate the cell wall, inducing a lower stiffness of the treated wood at ambient temperature (ca. 35/45% E' decrease compared to untreated samples), as well as contributing to sample failure > 150°C. A weaker wood structure was also manifested in macroscopic samples after HT treatment with an approximate 80% decrease in MOE (Table 2). The very high weight uptakes and the higher residual acidity of the OGA1 treatment may explain this observation. However, as with the OLA1 treated samples, water leaching led to a recovery of ambient E' and MOE values, with the latter

being higher than for untreated samples. In contrast, wood samples impregnated or heat-treated with OBS2 or OBA2 do not have any significant water leaching, nor do they undergo any resulting change in MOE (Figure 3c; Figure 3d; Table 1; Table 2).

The glass transition temperature of wood components lies in wide intervals due to degree of crystallinity or extraction procedure of components [19]. The T_g was reported to lie between 200°C and 250°C for cellulose, between 150°C and 220°C for hemicelluloses, and between 140°C and 210°C for lignin [19]. A thermal transition seen between 80°C and 150°C in Figures 5a-d for untreated wood could be assigned to T_g values for hemicelluloses or lignin. This thermal transition appeared to be reduced upon the impregnation of oligomers and was significantly decreased by OLA1/OGA1 treatments (−15/5°C, 0/30°C for OLA1, OGA1 respectively). Both water leaching and solvent extraction led to intermediate T_g values for these wood components (30/70°C). OBS2/OBA2 treatments did not significantly affect the thermal transitions of wood properties, as observed with DSC thermograms of solvent extracted samples (Figures 5a-d).

4 SUMMARY

The oligomer treatments used to treat wood were prepared as liquid impregnation materials and were able to further polymerize, as either pure polymers or *in situ* within wood. Treatment and *in situ* polymerization contributed different properties to the treated wood. DMTA revealed that impregnation with cell wall bulking OLA1/OGA1 treatments led to sample softening and plasticization, most likely facilitated by weakened cohesive forces and mobility of lignocellulosic matrix constituents [9]. Heating and *in situ* polymerization of the OLA1/OGA1 treatments gave increased E' values. In contrast to OLA1/OGA1 treatments, impregnation with OBS2/OBA2 gave a lumen filling treatment. DMTA indicated that this treatment gave only a small decrease in sample stiffness, which was attributed to the onset of the polymer melt. No treatment contributed to any significant wood reinforcement at ambient temperature, but the OLA1/OGA1 treatments do confer greater softening upon heating, as demonstrated by DMTA. However, water leaching of lower M_w OLA/OGA components can reduce this softening effect in treated samples. These treatments also impacted wood softening with a significant decrease in T_g values observed for wood components.

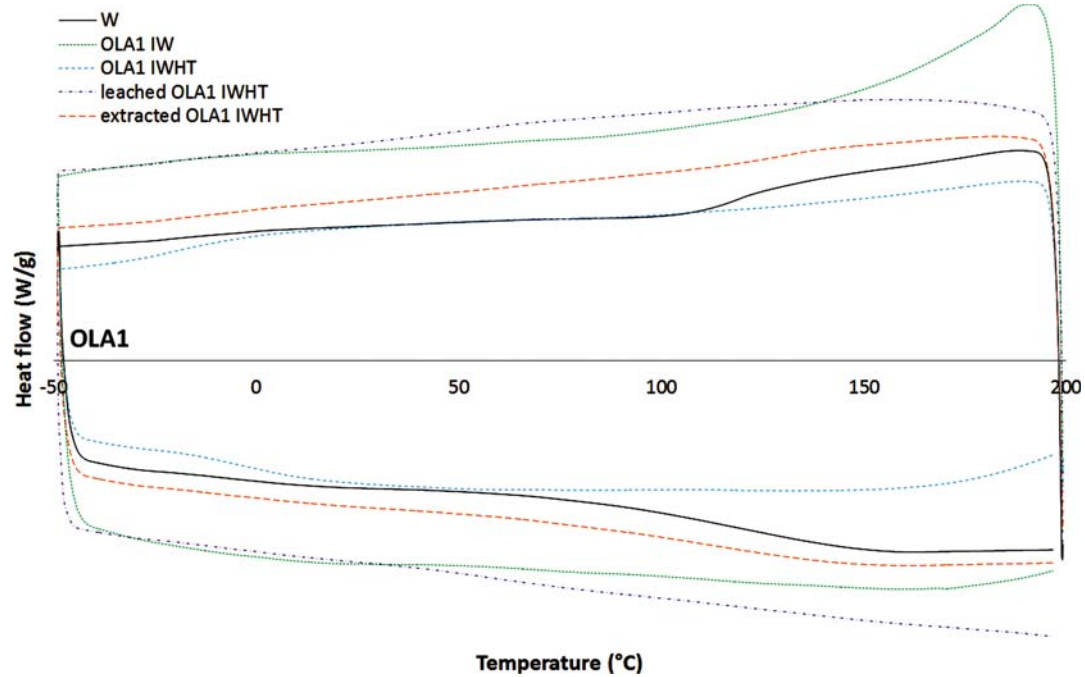


Figure 5a DSC thermograms of untreated wood (Beech), wood impregnated with OLA1 (IW), treated (IWHT), treated and water leached (leached IWHT) and treated and solvent extracted (extracted IWHT).

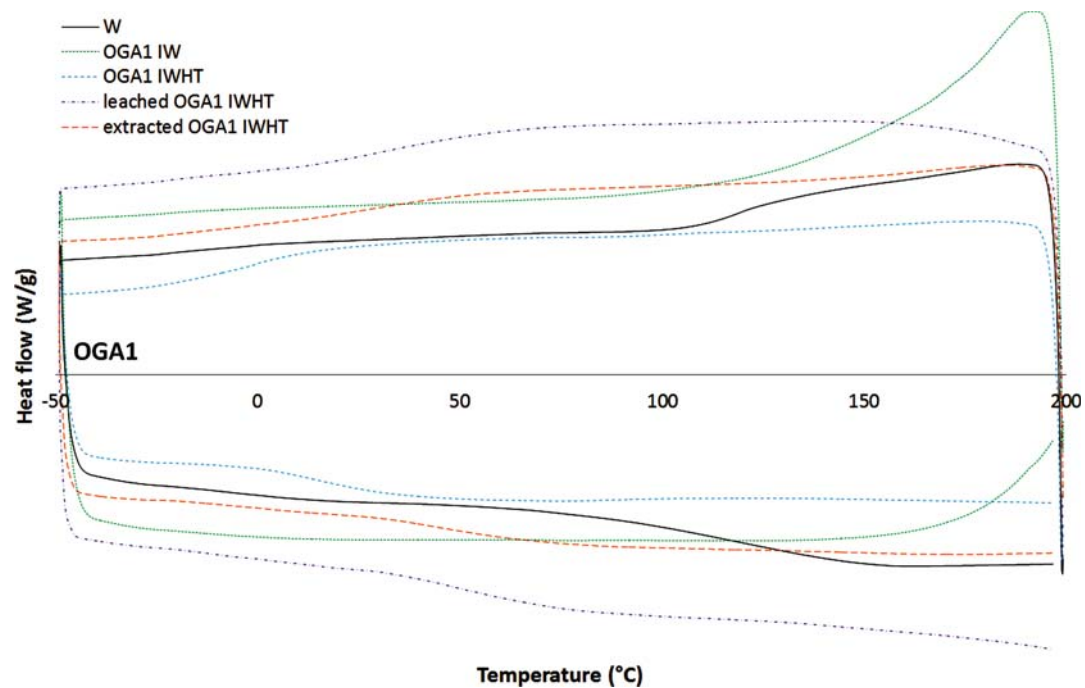


Figure 5b DSC thermograms of untreated wood (Beech), wood impregnated with OGA1 (IW), treated (IWHT), treated and water leached (leached IWHT) and treated and solvent extracted (extracted IWHT).

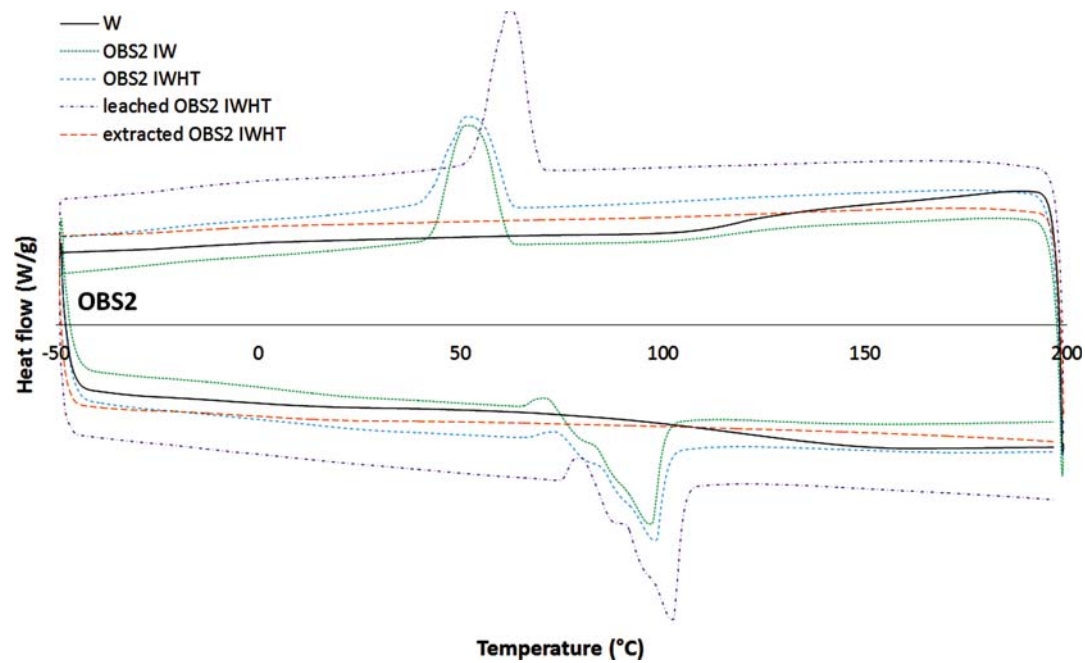


Figure 5c DSC thermograms of untreated wood (Beech), wood impregnated with OBS2 (IW), treated (IWHT), treated and water leached (leached IWHT) and treated and solvent extracted (extracted IWHT).

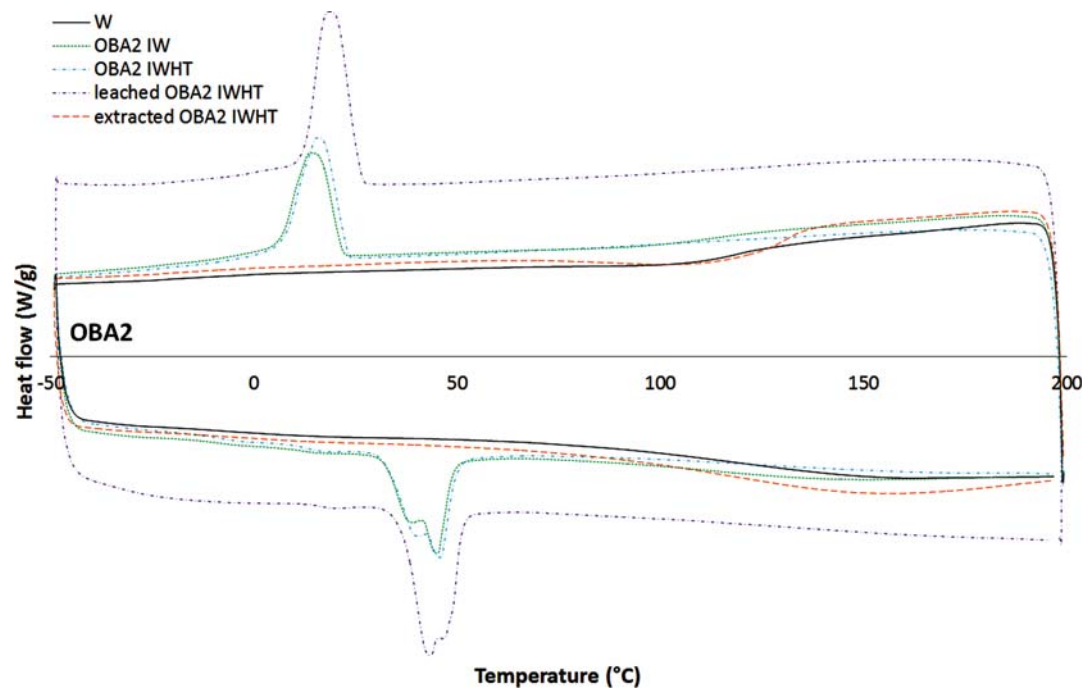


Figure 5d DSC thermograms of untreated wood (Beech), wood impregnated with OBA2 (IW), treated (IWHT), treated and water leached (leached IWHT) and treated and solvent extracted (extracted IWHT).

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