

Evaluation of Properties of New Composite Material Obtained from Wood and Lactic Acid

Marion Noël¹, Emmanuel Fredon¹, Eric Masson², Eric Mougel¹,
Daniel Masson¹, Philippe Gerardin¹

¹ LERMaB, Université Henri Poincaré Nancy 1 - Ecole Nationale Supérieure des Technologies et Industries du Bois, 27 rue du Merle Blanc, BP 1041, 88051 Epinal, France
[email:emmanuel.fredon@enstib.uhp-nancy.fr]

²CRITT Bois, BP 1041, 88051 Epinal, France [eric.masson@cribois.com]

Keywords: Antiswelling efficiency, composites, impregnation, polylactic acid, wood

ABSTRACT

This work deals with the synthesis of new composites made of wood and polylactic acid (PLA). Vacuum pressure impregnation of PLA oligomers, obtained by controlled polymerization of lactic acid, followed by in situ polymerization allowed to improve wood dimensional stability. The polymerization of PLA oligomers was carried out under different conditions with or without a catalyst. The formation of polymer inside the wood structure was confirmed by FTIR experiments. The final properties of PLA wood composites were strongly influenced by the curing conditions. During the first part of the curing process, heating led to a softening of wood, while longer heating periods led to a rigid material. A strong darkening appeared simultaneously during heating, indicating degradation of some wood components. Anti swelling efficiency and mechanical properties were evaluated for the hardened materials. The results showed an improvement of ASE, while enhancement of mechanical properties depended on the catalyst used.

INTRODUCTION

Wood is well known for its good environmental properties. But the most limiting characteristics of wood are its sensitivity to moisture undergoing biological attacks and dimensional instability. That's why stabilization treatments or surface coatings are necessary. More recent treatments consist of resin impregnation into lumens and/or cellular walls. Wood impregnation by isocyanates, polyethylene glycol, formaldehyde resins, styrene or methyl methacrylate can significantly improve the anti-swelling efficiency (Ibach *et al.* 2001, Magalhães *et al.* 2004, Persenaire *et al.* 2004, Roussel *et al.* 2001, Zhang *et al.* 2006). But these additives proved themselves to be harmful towards the environment, in use or at the end of the product life cycle. The environmental concern has also led to the development of new polymers, derived from renewable resources. One of the most produced and processed is polylactic acid or PLA. Concerning polymer composites field, PLA has already been used, associated with flax or hemp fibres, to produce extruded or compressed composite materials with good environmental characteristics. Moreover, the affinity of hydrophilic natural fibres with PLA, is much better than with conventional hydrophobic polymers as polyethylene, polypropylene or polyvinylchloride, avoiding the use of compatibilizing agents. This innovative work deals with the obtention of a biocomposite wood/PLA obtained by an impregnation process: the treatments consist in polymerizing lactic acid oligomers into

wood, so as to densify and increase wood dimensional stability. After describing the process, chemical and physical properties are given and discussed in this paper.

EXPERIMENTAL PART

Sampling

Wood samples ($5 \times 15 \times 50 \text{ mm}^3$) were cut into pine (*Pinus sylvestris* L.) sapwood (520 kg m^{-3}) and beech (*Fagus sylvatica* L.) heartwood (740 kg m^{-3}) timbers. They were preliminary dried in a ventilated oven at $103 \text{ }^\circ\text{C}$ until constant weight. L-(+)-lactic acid 90% aqueous solutions were delivered by PURAC.

Treatment

Lactic acid oligomer and impregnation solution preparation

Lactic acid aqueous solutions (90%) were first dehydrated under vacuum in a $120 \text{ }^\circ\text{C}$ heated bath, and maintained into it for one hour once boiling was over. After cooling, catalysts (0.6 %_w sulphuric acid or 5 %_w Tin (II) 2-ethylhexanoate) was added and the solutions thus obtained were used for impregnation. According to the catalyst added, PLA prepolymer mixtures are named as shown in figure 1: PP if no catalyst added, PPSA for sulphuric acid and PPTO for tin octanoate.

Impregnation and curing

Wood samples were then immersed into lactic acid oligomer mixture. The system was then put in a container and exposed to two successive 2 h periods of vacuum followed by atmospheric pressure. Impregnated wood samples were then taken off and stripped off before curing at $120 \text{ }^\circ\text{C}$ in a ventilated oven. $120 \text{ }^\circ\text{C}$ was chosen as the best compromise to induce PLA polymerization without inducing important degradation of wood cell wall components (Morales 2004). A distinction is done between samples removed after 60 minutes short heating (SH) and those removed after extended heating (EH) until constant mass. Composite preparation and different curing conditions are presented in figure 1.

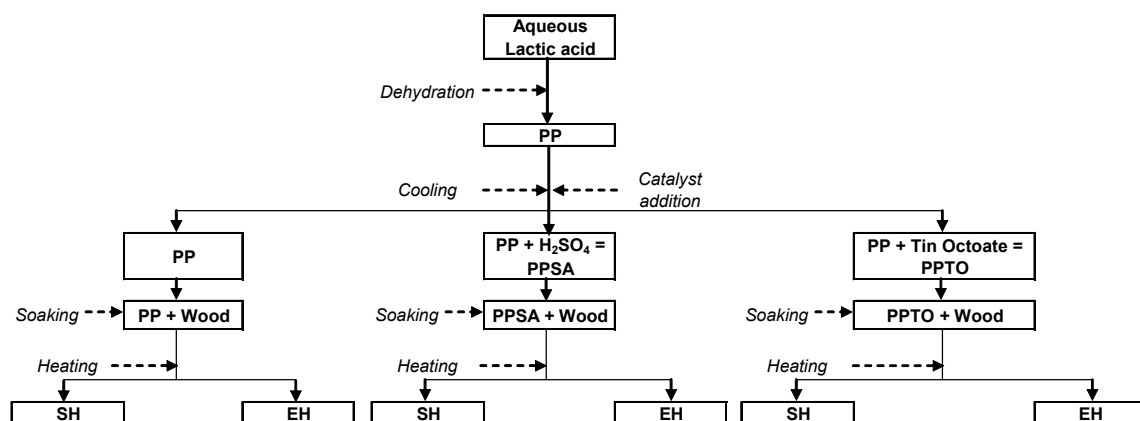


Figure 1 : experimental conditions to make wood-PLA composites

Mass yields and volumetric swellings

Impregnation yield were measured by weighing dry samples before and after impregnation. Block swelling due to impregnation before and after heating are respectively defined as equations 1 and 2 :

$$S_i (\%) = \frac{V_i - V_0}{V_0} \times 100 \quad (1)$$

$$S (\%) = \frac{V_h - V_0}{V_0} \times 100 \quad (2)$$

where V_0 stands for oven dried wood sample volume before impregnation, V_i for wood sample volume after impregnation before heating stage and V_h for heated impregnated samples volume.

Structural analyses of the modificationGel Permeation Chromatography (GPC)

The weight molar mass distribution of the polymers extracted by chloroform was analyzed. It was determined with respect to poly(ethylene glycol) standards by gel permeation chromatography (GPC) equipped with one linear Waters Styragel HR1 column. All samples were analysed at 40°C. N,N-dimethylformamide, solvent and eluent, was delivered at a flow rate of 1.0 mL min⁻¹. Samples were dissolved in DMF at a concentration of 2.0 %_w. The injection volume was 20 µL.

Fourier Transform InfraRed analysis (FT-IR)

FTIR spectra were recorded as KBr disks on a Shimadzu FTIR 8400 spectrometer. Finely divided sawdust (2% in weight) was dispersed in a spectral grade KBr matrix and pressed to form 200 mg pellets.

Scanning electron microscopy (SEM)

Scanning electron microscopy was performed on a MEB Hitachi S-520 apparatus. PPSA SH sample surface has been coated by a gold/palladium blend in a Fisons Instruments Polaron SC7610 sputter coater.

Solvent extractions

Solvent wood composites extractions were carried out in a Soxhlet apparatus. Composites were divided into thin chips and extracted with chloroform for 80 h, at the rate of 4 to 5 cycles h⁻¹.

Dimensional stability

The anti-swelling efficiency (ASE) was determined in order to evaluate dimensional stability of treated wood specimens. Treated wood blocks (20×20×20 mm³) were stored at a temperature of 20°C and relative humidity of 100% until the samples reached the equilibrium moisture content (EMC). EMC was considered to be reached when the mass variation of the samples within 24h was less than 0.5%. Water volumetric swelling coefficients were calculated according to equation 3, where V_2 is the volume of the water saturated blocks and V_1 the volume of oven-dried blocks :

$$S (\%) = \frac{V_2 - V_1}{V_1} \times 100 \quad (3)$$

The ASE percentage was calculated from the wet and oven-dried volumes of treated and untreated wood specimens according to equation 4, where S_U is the volumetric swelling coefficient of untreated blocks and S_T is the volumetric swelling coefficient of treated blocks.

$$ASE(\%) = \frac{S_U - S_T}{S_U} \times 100 \quad (4)$$

Water leaching

Water leaching was performed according to a method adapted from NF X 41-575 French standard. Ten treated or untreated wood specimens ($5 \times 15 \times 50 \text{ mm}^3$) were placed in a flask filled with 450 mL agitated 20°C distilled water. Water was changed after 1h, 2h, 4h, 8h, 16h, 24h and 48h soaking periods. ASE determination was then determined on leached wood blocks.

Mechanical tests

Axial compression test

Modulus of rupture (MOR) compression test was performed according to NF B 51-007 French standard method, by using a 100 kN capacity universal test machine, and applying a $3 \text{ mm} \cdot \text{min}^{-1}$ constant deflection rate. Ten tests were carried out for each sample type.

Shearing test

Shearing strength parallel to the grain was calculated following a method adapted from NF EN 314-1 European standard concerning the bonding performance of plywood by shearing of a surface prepared by cutting. In this study, the shearing of a radial \times longitudinal oriented surface has been evaluated in treated pine sapwood and control pine samples by using a 30 kN capacity universal test machine, and applying a $3 \text{ mm} \cdot \text{min}^{-1}$ constant deflection rate. Ten tests were carried out for each group.

Hardness tests

Monnin hardness characterizes the wood global hardness, whereas Brinell hardness gives results about the stamping on wood surface, principally used for flooring uses. Brinell hardness was calculated by the following method, adapted from EN 1534 European standard. A 10 mm diameter steel ball was pressed into tangential section of solid wood treated and control specimens ($50 \times 50 \times 5 \text{ mm}^3 \text{ T} \times \text{L} \times \text{R}$). Monnin hardness was calculated by the following method, adapted from NF B 51-013 French standard. A 15 mm diameter steel cylinder was pressed into radial sections of treated wood and control specimens ($20 \times 20 \times 20 \text{ mm}^3 \text{ T} \times \text{L} \times \text{R}$).

RESULTS AND DISCUSSION

Validation of in-situ polymerization

The polymerization of the lactic acid oligomers into wood has been first analyzed by a global FTIR analysis of samples at the different stages (SH and EH), before and after a chloroform extraction. Figure 3a shows control pine sample and PPSA treated pine sample spectra (PP, and PPTO treated wood spectra are quite similar). The two peaks at about 875 cm^{-1} and 765 cm^{-1} (Younes *et al.* 1988), ascribable respectively to PLA

amorphous and crystalline phases, confirms the polymerization of poly lactic acid into wood structure. Band shift from 1746 cm^{-1} (C=O stretching ester groups in wood) to 1764 cm^{-1} and the relative increase of the intensity of this ester band compared to hydroxyl groups absorption band at 3500 cm^{-1} , corroborate the polymerization hypothesis (Younes *et al.* 1988, Kister *et al.* 1998). After chloroform leaching, the PLA polymers issued from a short heating are not durably linked to wood: no polymer characteristic peaks appear in figure 3B(b) : carbonyl band appears at 1741 cm^{-1} , which can be attributed to non extracted lactic acid monomers. Moreover, weight losses after chloroform extractions reach 90 to 100% in the case of SH samples. On the contrary, for PPSA EH extracted sample in figure 3B(c) the high intensity of the 1762 cm^{-1} peak spectrum shows a strong presence of ester groups and the two peaks at 875 and 760 cm^{-1} remain. Weight losses have been measured at about 50%. Indeed, half part of polymers chains is trapped into wood structure.

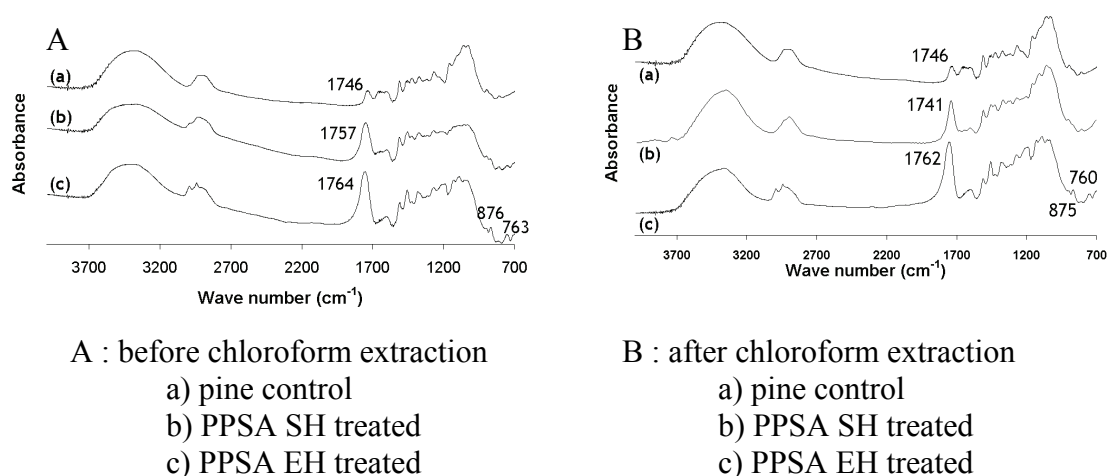


Figure 2 : FTIR spectra of PPSA samples before and after chloroform extraction

GPC analysis of chloroform extracts were carried out in order to control PLA molecular weights distribution. Extracted polymers present molecular weights comprised between 200 g/mol to 5000g/mol. Mass profiles are very broad and all with a maximum intensity under 500g/mol: most products extracted by chloroform were small oligomers that were not trapped into the wood. Surprisingly, all chromatograms reveal the existence of more or less broad signals above 10000 g/mol (exclusion limit of the column). Such signals should be issued from depolymerised lignocellulosic polymer fragments. A rather high intensity of these last signals observed for extracted SH polymers may suggest a degradation probably promoted by acidic conditions (presence of lactic acid and catalysts) when the mixture penetrates the cell walls.

Characterization of composites

Physical analysis

Impregnation yield were measured by weighing dry samples before and after impregnation, giving 120 % and 70 % respectively for pine and beech samples. After extended heating, mass yields reach respectively 50% and 20%, showing a loss of product during heating period. Swelling percentages are gathered in table 1.

Table 1 : Pine and beech impregnated samples swelling

Treatment		PP		PPSA		PPTO	
Swelling [%]		Mean [%]	SD ^d [%]	Mean [%]	SD [%]	Mean [%]	SD [%]
Pine samples	S _i ^a	0.7	0.3	1.6	0.3	1.1	0.4
	S _{SH} ^b	18.5	0.7	24.8	0.7	23.7	2.5
	S _{EH} ^c	18.0	0.8	25.3	0.6	19.9	1.8
Beech samples	S _i	1.0	0.5	2.0	0.5	1.9	1.4
	S _{SH}	28.2	1.2	26.7	1.6	24.4	1.5
	S _{EH}	27.4	1.1	24.1	1.4	15.8	1.7

^abefore heating, ^bafter short heating, ^cafter extended heating, ^dstandard deviation

Maximum swelling of samples due to impregnation, measured before heating, reaches only 1,6% in the case of pine samples, and 2,0% in the case of beech samples. After heating, swelling can reach 25% for pine samples and 28% for beech samples. The increase of swelling after short heating stage means that lactic acid based products enter wood cells lumens by vacuum impregnation, and can only enter wood cell walls during heating. This might be due to the decrease of the viscosity during heating, and good chemical affinity between wood and lactic acid oligomers. After an extended heating stage, oligomers and polymers are still into the cell walls. In the case of PPTO treatment, the swelling is less effective compared to other impregnation solutions.

Physical changes

As shown in figure 3, after a short heating, all samples were darkened and softened, allowing a high deformation according to radial and tangential directions (sample A). After extended heating, which was attained within about 96 h, the samples were then hardened again (sample B).

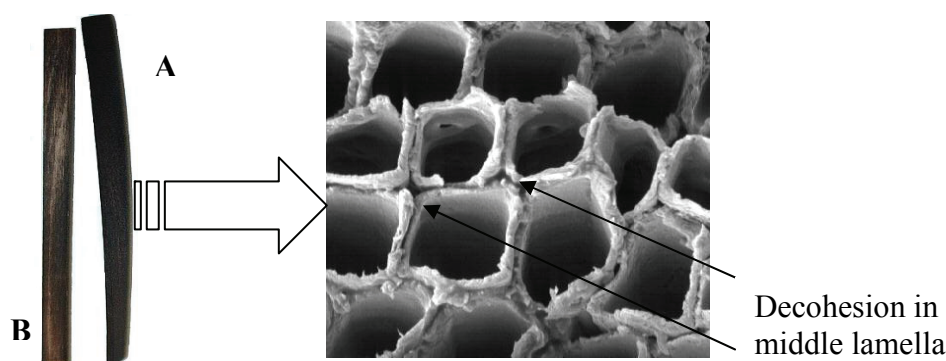


Figure 3 : photographs of PPSA- SH(A) and EH (B) samples and transverse section of SH specimen

SEM observation (figure 3) of softened samples (A) confirms that there is a kind of unsticking in SH specimen middle lamella. From these preliminary experiments, the following hypothesis can be proposed: lactic acid monomers and oligomers easily penetrate the cell walls when short heated, and causes damages to lignocellulosic polymers, involving darkening and softening. Acids are indeed well known lignin depolymerising and darkening agents and lactic acid for instance has been already used for liquefying wood (Heitz, 1994).

PROPERTIES OF HARDENED COMPOSITE

Anti swelling efficiency

Only hardened specimens treated for an extended heating time were tested. The results are presented in Table 2. Averaged ASE value with and without leaching are 72.2 % and 65.8 % respectively. Weight losses after water leaching range from 10 to 25%, respectively. ASE enhancement after leaching can be explained by loss of non polymerized hydrophilic monomers and small oligomers. Classical stabilization treatments performed on wood usually reach similar 60 to 70% ASE values (Ibach 2001, Magalhães 2004, Roussel 2001). Yet, results show stabilized ASE after leaching, which ensures good outside stability. The addition of catalysts does not systematically enhance ASE.

Table 2. Anti-Swelling efficiency of treated and leached specimens

Specimen reference	ASE (%)	ASE _L ^a (%)	Weight loss (%)
Pine samples			
PP EH	67.6	71.3	16,0
PPSA EH	58.4	72.4	24,5
PPTO EH	58.8	61.2	14,4
Beech samples			
PP EH	70.2	58.8	12,7
PPSA EH	67.1	83.5	9,9
PPTO EH	72.9	80.1	19,1

^a ASE measured on 48h water leached samples

Mechanical properties

The results obtained for compression, shearing and hardness tests performed on hardened samples are given in table 3.

Table 3 : compression, shearing and hardness tests results

Specimen reference	σ_c (MPa)	f_v (MPa)	HB (MPa)	N
Beech control	72		4.3	11.9
PP B EH	97		5.2	15.3
PPSA B EH	107		4.6	19.4
PPTO B EH	92		1.1	19.3
Pine control	47	2.7	1.6	3.7
PP P EH	66	2.2	1.9	3.3
PPSA P EH	64	1.1	2.3	7.8
PPTO P EH	54	1.2	0.4	5.2

The results show an increase in compression strength (σ_c) of catalysed and uncatalysed specimens. Monnin and Brinell tests were performed on EH treated specimens in order to evaluate their flooring performances. Hardness testing according to Monnin standard characterizes a local compression of fibres whereas hardness testing according to Brinell standard is related to fibres cohesion. PP treatment gives satisfying results for Monnin

hardness (N), while PPSA and PPTO treatments highly increase this property. Thereby, PPTO treated samples show a strong decrease of Brinell hardness (HB) resulting in stronger fibres cohesion degradation. The shearing strength f_v of EH treated pine sapwood specimens shows that treatment weakens the fibres cohesion, particularly PPSA and PPTO treatments. Therefore, it seems that uncatalyzed treatment (PP) leads to a minor degradation.

CONCLUSION

For the first time, a biocomposite material has been synthesised by lactic acid oligomers impregnation into wood followed by thermally induced polymerization. A short heating leads to a softened material, which, once hardened by extended heating, is dimensionally stable. Acid catalysed treatments damage the wood components and lead to a softened material. Its use for flooring applications is conceivable, principally because of high density and good hardness results. Biological resistance tests are currently in progress. Improvement in the process should lead to less leachable material.

REFERENCES

- Heitz, M., Brown, A. and Chornet, E., (1994). Solvent effects on liquefaction : solubilization profiles of a Canadian prototype wood, populus deltoids, in the presence of different solvents, *The Canadian Journal of Chemical Engineering*, **72**, 1021-1027.
- Ibach, R.E. and Rowell, R.M. (2001). Wood preservation based on in-situ polymerization of bioactive monomers. *Holzforschung*, **55**, 365-372.
- Kister, G., Cassanas, G. and Vert, M. (1998). Effects of morphology, conformation and configuration on the IR and Raman spectra of various poly(lactic acid)s. *Polymer*, **39**, 267-273.
- Magalhães, W.L.E. and Da Sylva, R.R. (2004). Treatment of caribbean pine by in-situ polymerization of styrene and furfuryl alcohol. *Journal of Applied Polymer Science*, **91**, 1763-1769.
- Moraes, D., Rogaume, Y. and Triboulot, P. (2004). Influence of temperature on the modulus of elasticity (MOE) of *Pinus sylvestris*. *Holzforschung*, **58**, 143-147.
- NF B 51-007 (1985). Axial compression test. *AFNOR Standard Test Method*.
- NF B 51-013 (1985). Monnin hardness determination. *AFNOR Standard Test Method*.
- NF B 53-646 (2000). Punching resistance determination of wood flooring (Brinell) - test method. *AFNOR Standard Test Method*.
- NF EN 314-1. (2005). Bonding grade of plywood - Part 1: Test method. *AFNOR Standard Test Method*.
- Persenaire, O., Alexandre, M., Degée, P., Pirard, R. and Dubois, P. (2004). End-grained wood-polyurethane composites, I Synthesis, morphology and characterization. *Macromolecular Materials and Engineering*, **289**, 895-902.
- Roussel, C., Marchetti, V., Lemor A., Wozniak, E., Loubinoux, B. and Gerardin, P. (2001). Chemical modification of wood by Polyglycerol/Maleic anhydride treatment. *Holzforschung*, **55**, 57-62.
- Younes, H. and Cohn, D. (1988). Phase separation in poly(ethylene glycol)/poly(lactic acid) blends. *European Polymer Journal*, **24**, 765-773.
- Zhang, Y., Zhang, S.Y., Yang, D.Q. and Wan, H. (2006). Dimensional stability of wood-polymer composites. *Journal of Applied Polymer Science*, **102**, 5085-5094.