

LIQUEFIED WOOD AS A PARTIAL SUBSTITUTE OF MELAMINE-UREA-FORMALDEHYDE AND UREA-FORMALDEHYDE RESINS

Bruno Esteves^{1,2,*}, João Martins³, Jorge Martins^{1,4}, Luísa Cruz-Lopes^{1,2}, José Vicente^{1,2}, Idalina Domingos^{1,2}

ABSTRACT

Maritime pine (*Pinus pinaster*) sawdust was used to produce liquefied wood by the polyhydric method with acid catalysis. The process was optimized to produce the highest amount of liquefied wood. Wood liquefied at 160°C for 90 min was used in the adhesion tests. The bond strength of veneer glued with urea-formaldehyde and melamine-urea-formaldehyde resins and several mixtures of liquefied wood with urea-formaldehyde and melamine-urea-formaldehyde was evaluated by automated bonding evaluation system.

With the increase in liquefied wood content the bond strength decreased. Nevertheless for 20% liquefied wood the reduction of internal bond strength is relatively small and still within the minimum standards required. When 70% of liquefied wood is employed there is a significant decrease in bond strength.

In conclusion it is possible to use a small amount of maritime pine sawdust liquefied wood as a partial substitute of urea-formaldehyde and melamine-urea-formaldehyde resins in the particleboard production, thus decreasing the formaldehyde content.

Keywords: Automated bonding evaluation system, liquefied wood, particleboard, *Pinus pinaster*, resin.

INTRODUCTION

Wood liquefaction is usually done at high pressure and temperature. Recently due to the lack of oil derived products there have been several studies on liquefaction processes using moderate temperatures and a catalyst. The main liquefaction agents are phenol (Zhang *et al.* 2007, Lin *et al.* 2014) with a base or acid catalyst, polyhydric alcohols usually with an acid catalyst (Hrastnik *et al.* 2013) and also cyclic carbonates (Xie and Chen 2005), ionic liquids and dibasic esters. According to the liquefaction process different resins can be produced. When liquefaction is done with phenol, phenolic resins can be produced. Pan *et al.* (2009) used liquefied wood with phenol an acid catalyst to prepare phenolic Novolac type resins while Hassan *et al.* (2009) produced Resol type resins. Alma *et al.* (1998) and Zhang *et al.* (2005) produced the same type of resins but using alkali catalysts. Using polyhydric alcohols as liquefaction agents produces different kinds of resins. Lee and Lin (2008) used liquefied wood to produce a polyurethane adhesive. Also epoxy resins were prepared by Kobaiashi *et al.* (2000) from liquefied wood with polyhydric alcohols. Mansouri *et al.* (2007) studied the possibility of using liquefied wood as lignin-based wood panel adhesives without formaldehyde. The adhesives yielded a bending strength enough to pass relevant international standard specifications for exterior-grade panels and also showed sufficient reactivity to yield panels in press times comparable to those of formaldehyde-based commercial adhesives. The bond performance of specimens of beech wood, bonded with an adhesive mixture made of liquefied wood and phenolic resin, was investigated by Ugovsek *et al.* (2010). The shear strength increased when replacing 25% of the phenol-formaldehyde by liquefied wood, but decreased when immersing or boiling the specimens in water. So for non-structural applications

¹ Polytechnic Institute of Viseu, Viseu, Portugal.

² Centre for the Study of Education, Technologies and Health (CI&DETS). Viseu, Portugal

³ Student in Polytechnic Institute of Viseu, Viseu, Portugal

⁴ Lepae, Laboratory for Process, Environmental and Energy Engineering, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal.

*Corresponding author: bruno@demad.estv.ipv.pt

Received: 24.01.2014 Accepted: 30.06.2014

in dry conditions, up to 25% of the synthetic phenol-formaldehyde resins could be replaced by liquefied wood with a satisfactory bond. Kunaver *et al.* (2010) studied the possibility to partially replace resins UF, MF and MUF for liquefied wood for the production of panels and concluded that it would be possible to replace up to 50% of the minimum characteristics required maintaining resins for this type of panels. The main goal of this research was to use liquefied pine sawdust prepared by the polyhydric alcohol process as a partial substitute of UF and MUF resins in particleboard production. The optimization of temperature, time and amount of polyhydric alcohol to obtain the higher liquefaction percentage was presented before by the authors in (Martins *et al.* 2013). The results show that the higher the temperature, the greater the percentage of liquefaction. At the same temperature the percentage increases with the liquefaction treatment time according to a logarithmic curve approximately until it reaches a maximum and then decreases, possibly due to condensation reactions of liquefaction products. The maximum liquefaction was obtained after 30 min at 180° C (about 80%) and 60 min at 160°C (about 70%). It was found that the ratio of wood/ethylene glycol influenced the percentage of liquefaction that ranged between 62% and 88% and the ratio which showed best results was 1: 6.

EXPERIMENTAL

Wood Liquefaction reaction

Maritime pine (*Pinus PinasterAit*) sawdust generated in the circular saw from a local carpentry was used in the tests. The sample was sieved and the 40-60 Mesh fraction was selected for the tests. Ethylene glycol (EG) was used as solvent and Sulfuric Acid (SA) as catalyst. Four parts of EG were used for each part of *Pinus pinaster* dust in dry state adding 3% SA (based on the EG mass). The ratio between EG and wood was optimized before to achieve the highest liquefaction possible (Martins *et al.* 2013). The mixture was placed in a Parr glass 600ml LKT PED reactor (Figure 1) with double jacket with automatic stirrer at ± 70 rpm.

The liquefaction reaction was done at 160°C (temperature of the oil in the jacket) for 90 min. The liquefaction time was optimized to obtain the highest liquefaction (Martins *et al.* 2013). The EG+SA+Wood were inserted inside the reactor when the oil achieved the desired temperature.

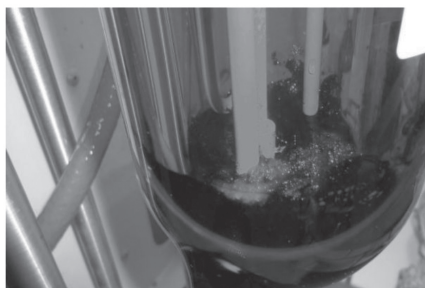


Figure 1. Liquefaction reactor.

After the reaction a mixture of dioxane and water at 4:1 ratio was used to solubilize the liquefied wood. A pump and a Buckner Funnel with a paper filter were used to separate the solid residues that resulted from the liquefaction. This allowed us to determine the liquefaction percentage that was calculated using the following formula:

$$\text{Liquefaction percentage (\%)} = \left(1 - \frac{\text{Mass of residue (g)}}{\text{Mass of dry wood (g)}} \right) \times 100$$

The water and dioxane were evaporated using a Rotary evaporator by using reduced pressure, 700mmHg provided by a vacuum pump.

Determination of Gel time

For determination of the adhesive Gel time, different ratios between the liquefied wood and adhesive were tested, 9:1, 8:2, 7:3, 6:4, 5:5, for a total mass of 10 g. The mixture was stirred with a glass rod until the Gel becomes apparent.

Determination of bond strength by ABES

Wood liquefied at 160°C for 90 min was used in the tests. The bond strength of veneer glued with urea-formaldehyde resin (UF), melamine-urea-formaldehyde resin (MUF) and several mixtures of Liquefied wood (LW) with UF and MUF were evaluated using ABES (Automated Bonding Evaluation System) equipment. Two beech veneer strips with 0,5mm thick, 20 mm wide and 117 mm in length were used. The resins were prepared adding to the MUF resin, LW and ammonium sulphate (as catalyst). For each test 6,7 mg of the mixture were used to glue an overlapping area of 100 mm². ABES gives the force, in N, necessary to break the glue line. The bonding strength (BS) was determined by the following formula.

$$\text{Bonding strength (N / mm}^2\text{) or MPa} = \left(\frac{\text{Force (N)}}{\text{Overlapping area (mm}^2\text{)}} \right)$$

Tests were made for 20, 30, 50, 100, 150, 200, 350 and 600 seconds to allow the analysis of the different phases of deformation curve. Different blends of UF/LW and MUF/LW were tested.

RESULTS AND DISCUSSION

Gel time

Gel time for the mixtures of UF resins and wood liquefied at 160° C and 180° C was similar (Figure 2) for both temperatures. The Gel time decreased initially, from 600s to 100s with increased liquefied wood ratio until it reaches the 5:5 ratio. Then remained constant until 8:2 ratio is achieved and then increase again. The Geltime of Urea-formaldehyde resins (UF) occurs at 50-150s at 100° C in the presence of a catalyst such as ammonium sulphate, but it is also possible using an acid catalyst such as sulfuric acid. Since liquefied wood has about 3% sulfuric acid, the initial decrease of Gel time is justified by the fact that the increase of acid has a higher effect than the increase in liquefied wood content. With a ratio higher than 8:2, the content of liquefied wood no longer allowed a correct gelification of the resin. A similar increase was obtained by Kunaver *et al.* (2010).

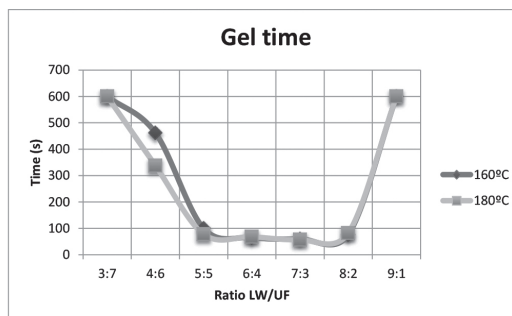


Figure 2. Gel time of mixtures of UF resin with liquefied wood at 160° C and 180° C.

Neutralization

Liquefied wood is highly acidic due, not only, to the sulphuric acid used as a catalyst but also to the acidic nature of most of the wood components. Since the acids acts as catalyst on the UF resins cure, tests were made to estimate the impact of neutralizing liquefied wood before mixing it with the resin. In figure 3 we can see the determination of bond strength by ABES for a resin resulting by mixing UF-LW (50:50), neutralized and non-neutralized and cured at 115°C.

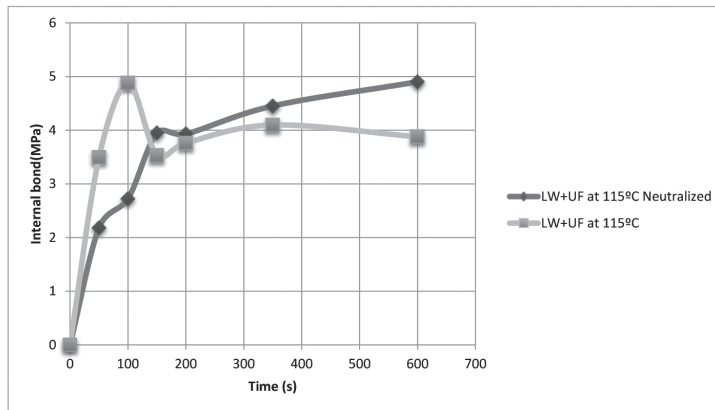


Figure 3. Bond strength of mixtures of liquefied wood not neutralized (LW) and neutralized (LWN) with a urea-formaldehyde resin (UF).

The bond strength of LW-UF resin at 600s was about 4 MPa. However the maximum (5 MPa) was obtained at about 100s which is next to the 80s (100°C) used by the industry. Using the neutralized resin the slope of the linear zone was smaller and the maximum bond strength was also slightly lower although at 600s has been higher (4,5MPa), which means it took longer to activate but the final results were similar.

Pressing temperature

In figure 4 we can see the ABES curve for a MUF resin pressed at 105°C and 115°C. In accordance to Heineman (2004) and Ferra *et al.* (2011) the curve has three different stages, an initial delay attributed to the loss of energy due to water evaporation, a second nearly linear stage due to the polymerization reaction by chain-extension and cross-linking processes of the adhesive systems and a last stage is where the curves stabilize reaching maximum values. The initial stage is not shown in these figures because the first point was taken only at 50 s and by that time the initial delay had already occurred. The second, almost linear stage can be seen until around 100-150s for MUF-LW resin at both temperatures. The main difference observed is that at a higher temperature the curves have a higher slope in the linear stage. With longer pressing times the bond strength is similar for both temperatures.

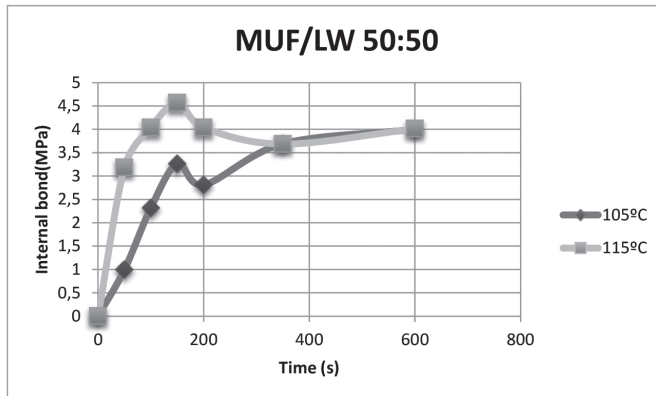


Figure 4. Bond strength determined by ABES for MUF-LW 50:50 at 105°C and 115°C.

Amount of liquefied wood

Figure 5 shows the bond strength of MUF and MUF-LW resins determined by ABES. MUF resin presented the best results reaching a bond strength of about 6 MPa at 105°C and a little lower 5 MPa at 115°C. The maximum was obtained at about 100s which is near the 80s (at 100°C) used by the particleboard industry. With the increase in liquefied wood content bond strength decreased as expected. Nevertheless for 115°C and 100s the bond strength reached around 4 MPa for MUF-LW with 20% of liquefied wood. Comparing to MUF resin MUF-LW (20%) had about 30% of bond strength decrease. At higher temperature (115°C) the bond strength decreased less for 100-150s reaching a maximum of around 4,5MPa. The mixture MUF-LW with 50% liquefied wood presented lower bond strength for 105°C pressing temperature. The maximum bond strength 3,2 MPa was almost half of the bond strength of the pure resin (6 MPa). For 115°C however the decrease was lower. When 70% of liquefied wood is employed there is a significant decrease in bond strength for both temperatures with a maximum of about 2 MPa at 115°C and a little lower for 105°C.

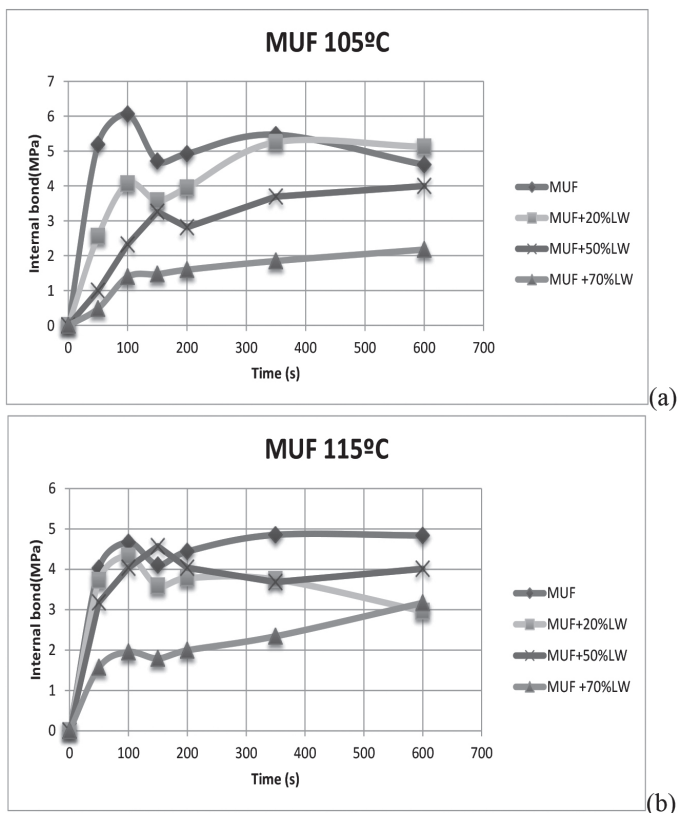


Figure 5. Internal bond strength determined by ABES for MUF and MUF-LW resins at 105°C (a) and 115°C (b).

When UF resins are used rather than MUF resins, the results are similar. Figure 6 shows the bond strength of UF and UF-LW resins determined by ABES. The main different is that MUF resins have somewhat higher bond strength than UF resins which have maximum bond strength around 4,5MPa. This also affects the mixtures of UF resins with liquefied wood which present smaller bond strength than the mixtures with MUF resin. With 20% liquefied wood the bond strength reduced about 33% and 13% for pressing temperatures of 105°C and 115°C. For 70% of liquefied wood the reduction is higher attaining a 66% and 62% for 105°C and 115°C respectively.

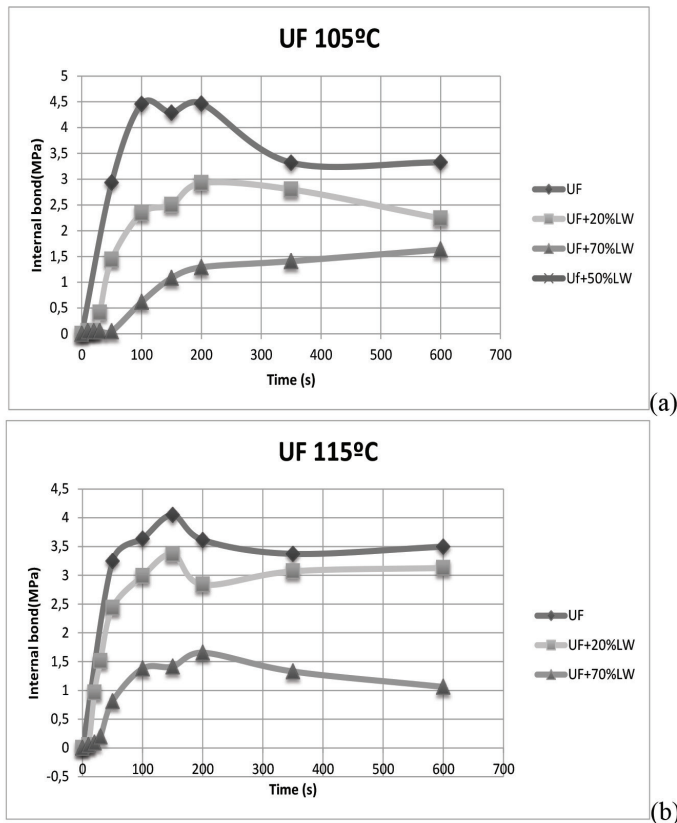


Figure 6. Bond strength determined by ABES for UF and UF-LW resins at 105°C (a) and 115°C (b).

CONCLUSIONS

With the increase in the percentage of LW there is a decrease in the Gel time until it reaches the ratio 5:5 and remained until a ratio of 8:2, increasing afterwards. The neutralized resin reacted slower but with similar maximum bond strength. With the increase in LW content bond strength decreased as expected. With 20% LW the reduction of bond strength is relatively small and still within the minimum standards required but when 70% of LW is employed there is a significant decrease in bond strength. In conclusion it is possible to use a small amount of maritime pine sawdust liquefied wood as a partial substitute of UF and MUF resin in the particleboard production, thus decreasing the formaldehyde content.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Portuguese Foundation for Science and Technology (ref. PEst-OE/CED/UI4016/2011) and the Centre for Studies in Education, Technologies and Health.

REFERENCES

- Alma, M.H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. 1998.** Preparation of sulfuric acid-catalyzed phenolated wood resin. *Wood Sci Technol* 32:297–308.
- Ferra, J.M.M.; Ohlmeyer, M.; Mendes, A.M.; Costa, M.; Carvalho, L.; Magalhães, F. 2011.** Evaluation of urea-formaldehyde adhesives performance by recently developed mechanical tests. *International Journal of Adhesion & Adhesives* 31:127–134.
- Hassan, E.B.; Kim, M.; Wa, H. 2009.** Phenol–formaldehyde-type resins made from phenol-liquefied wood for the bonding of particleboard. *J Appl Polym Sci* 112:1436–43.
- Heinemann, C. 2004.** Characterization of the curing process of adhesives in wood-particle matrices by evaluation of mechanical and chemical kinetics. Hamburg: Institute for Wood Technology, University of Hamburg.
- Hrastnik, D.; Budija, F.; Humar, M.; Petrič, M. 2013.** Influence of liquefied and CCB containing liquefied wood on growth of wood decay fungi. *Maderas. Ciencia y tecnología*, 15(1): 105-118.
- Kobayashi, M.; Tukamoto, K.; Tomita, B. 2000.** Application of liquefied wood to a new resin system-synthesis and properties of liquefied wood/epoxy resins. *Holzforschung* 54(1): 93-100.
- Kunaver, M.; Medved, S.; Cuk, N. 2010.** Application of liquefied wood as a new particle board adhesive system. *Bioresource Technology* 101(4): 1361-1368.
- Lee, W.; Lin, M. 2008.** Preparation and application of polyurethane adhesives made from polyhydric alcohol liquefied Taiwan acacia and China fir. *Journal of Applied Polymer science* 109: 161-177.
- Lin, R.; Sun, J.; Yue, C.; Wang, X.; Tu, D.; Gao, Z. 2014.** Study on preparation and properties of phenol-formaldehyde-chinese fir liquefaction copolymer resin. *Maderas. Ciencia y tecnología* 16(2): 159-174.
- Mansouri, N.; Pizzi, A.; Salvado, J. 2007.** Lignin-based wood panel adhesives without formaldehyde. *Holz Roh Werkst* 65: 65-70.
- Martins, J.; Cruz Lopes, L.; Esteves B. 2013.** Otimização da liquefação da madeira de Pinus pinaster com poliálcoolis. (In Portuguese). *Silva Lusitana* 21: 177-185.
- Pan, H.; Shupe, T. F.; Hse, C.Y. 2009.** Characterization of novolac type liquefied. *Eur J Wood Prod* 67: 427–437.
- Ugovsek, A.; Kariz, M.; Sernek, M. 2010.** Bonding of beech wood with an adhesive mixture made of liquefied wood and phenolic resin, *Hardwood Science and Technology. The 4th Conference on Hardwood Research and Utilisation in Europe.*
- Xie, T.; Chen, F. 2005.** Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from liquefied product. *Journal of Applied Polymer Science* 98: 1961-1968.
- Zhang, Q.; Zhao, G.; Jie, S. 2005.** Liquefaction and product identification of main chemical compositions of wood in phenol. *Forestry Studies in China* 7(2): 31-37.
- Zhang, Q.H.; Zhao, G.J.; Yu, L.L.; Jie S.J. 2007.** Preparation of liquefied wood-based resins and their application in molding material. *Forestry Studies in China* 9(1): 51-56.