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Non-toxic, zero emission tannin-glyoxal adhesives for wood panels

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Abstract In this study different tannin-glyoxal glue mixes for particleboard were studied.

Gel times at 100 °C of 45% water solutions of commercial pine tannin extract (Pinus radiata ex Diteco Ltda, Chile) with respectively 8% paraformaldehyde and 9% glyoxal were done at different pHs. Duplicate one layer laboratory particleboards were prepared by adding 12% total resin solids of adhesives composed of commercial pine tannin extract (Pinus radiata ex Diteco Ltda, Chile) with paraformaldehyde, or glyoxal or polymeric 4,4' diphenylmethanne diisocianate (pMDI), respectively.

It was found that tannin-glyoxal panels which do not contain formaldehyde and with an emission equal to that of unbounded wood can be obtained by the use of glyoxal as hardener.

1 Introduction

Tannin adhesives have been used extensively in several countries in the Southern Hemisphere and are starting now to be used industrially in Japan and there is also interest for their use in Europe. The quest to decrease or completely eliminate formaldehyde emission from wood panels bonded with adhesives, although not really necessary in polyflavonoid tannin adhesives due to their already low emission (as for most phenolic resins), has nonetheless promoted some research to further improve their formaldehyde emission. As part of the quest for zero formaldehyde emission adhesives, tannin adhesives based on tannin autocondensation (Pizzi et al. 1995), on hexamine as hardener (Pizzi et al. 1994, Pizzi et al. 1995, Pizzi et al. 1996, Pizzi et al. 1998, Pichelin et al. 1999) and on nitroparaffins as hardeners (Trosa and Pizzi 2001) have already been proposed and some of these technologies are now already in commercial use. Glyoxal is a non-volatile, reactive aldehyde which is qualified as non-toxic with a $LD_{50} > 7000$ mg/kg body weight and is as such a prime candidate for use as a hardener for exterior grade tannin adhesives. In this study different tannin-glyoxal adhesives were studied.

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2 Materials and Methods

Gel times at 100 °C of 45% water solutions of commercial pine tannin extract (*Pinus radiata* ex Diteco Ltda, Chile) with 8% paraformaldehyde and 9% glyoxal respectively were done at the different pHs shown in Fig. 1. Duplicate one layer laboratory particleboard of 350 × 350 × 14 mm dimensions were prepared by adding 12% total resin solids of adhesives composed of commercial pine tannin extract (*Pinus radiata* ex Diteco Ltda, Chile) with paraformaldehyde, or glyoxal or polymeric 4,4' diphenylmethane diisocianate (pMDI) respectively according to the relative percentages by weight shown in Table 1. The percentage moisture content of the resinated particles was of 20%–22%. Total pressing time was 7.5 minutes and the press cycle was 2 minutes from panel contact to maximum pressure of 3.5 MPa and holding, followed by a descending pressing cycle of 2.5 minutes at 1.6 MPa and 3 minutes at 0.8 MPa, at 190 °C–195 °C press

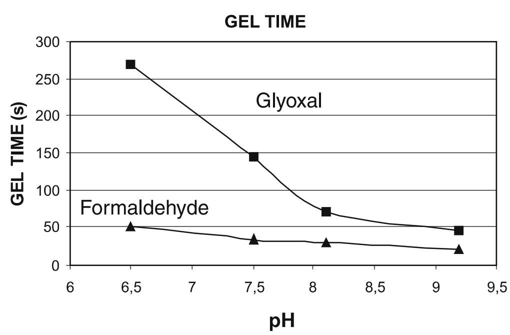

Fig. 1 Comparison of gel times as a function of pH of pine tannin + 8% paraformaldehyde and of pine tannin + 9% glyoxal
Abb. 1 Vergleich der Gelierzeiten in Abhängigkeit vom pH für Kieferntannin mit 8% Paraformaldehyd sowie für Kieferntannin mit 9% Glyoxal.

Table 1 One-layer laboratory particleboard results of panels bonded with different tannin-glyoxal gluemixes. Total resin load = 12% on dry wood

Tabelle 1 Ergebnisse einschichtiger Laborspanplatten gebunden mit verschiedenen Tannin-Glyoxal-Leimzusammensetzungen. Harzanteil = 12% auf atro Holz

	Density (kg/m^3)	Dry IB strength (MPa) ± Standard Deviation	Formaldehyde emission (mg/100 g)
95%Tannin + 5%paraformaldehyde	728	0.65 ± 0.10	4.7
88%Tannin + 12%glyoxal	721	0.44 ± 0.02	0.6
85%Tannin + 12%glyoxal + 3%triacetin	714	0.44 ± 0.05	0.6
70%Tannin + 21%PMDI + 9%glyoxal	730	0.60 ± 0.04	0.6

temperature. After light surface sanding the panels were tested for dry internal bond (IB) strength, and for formaldehyde emission according to the perforator method. The results obtained are shown in Table 1.

3 Results and Discussion

The quest to decrease or completely eliminate formaldehyde emission from wood panels bonded with adhesives, although not really necessary in polyflavonoid tannin adhesives due to their already low emission (as for most phenolic resins), has nonetheless promoted some research to further improve their formaldehyde emission. Among the aldehydes used for resins of some type there is one, glyoxal (OHC−CHO), other than formaldehyde which is used consistently today for application with a number of polycondensation resins other than for wood use. Glyoxal presents several major advantages over formaldehyde. The toxicity of glyoxal is so low that it is classified as non-toxic by all the major health agencies. Thus, while the LD_{50} of formaldehyde is around 70–140 mg/kg body weight, the oral LD_{50} of glyoxal value ranges from 3000 to 9000 mg/kg body weight (World Health Organisation 2004). This is the reason why glyoxal is classified as non-toxic. It is readily biodegraded and quickly transformed enzymatically by bacteria and fungi. Furthermore glyoxal is not volatile, contrary to formaldehyde, eliminating in this manner the possibility of noxious gas emission either during board manufacture or by the board in service. It is produced in great amounts and it is consequently as inexpensive as formaldehyde. Its main disadvantage is its reactivity towards phenols, urea and melamine which is lower than that of formaldehyde.

However, the results in Fig. 1, comparing the gel times of a pine tannin solution as a function of pH when curing with either formaldehyde or glyoxal, indicate that in the pH range 8–9.5 the tannin-glyoxal adhesive system presents the same gel time, hence the same rate of curing of the tannin-formaldehyde system in the pH range 6–7. This means that in principle in the 8–9.5 pH range the tannin-glyoxal adhesive can deliver results similar to pine tannin-formaldehyde adhesives. The results in Table 1 for one layer laboratory particleboards appear to confirm this. In Table 1, the Internal Bond (IB) strength of panels prepared using pine tannin and glyoxal are lower than those obtained using pine tannin and paraformaldehyde, except in the case where a low percentage of polymeric isocyanate (pMDI) is used to increase IB strength. The formaldehyde emission results are, however, considerably lower than those observed for the tannin-formaldehyde system. Emission values of 0.6 mg formaldehyde on 100 g panels in Table 1 are only due to the formaldehyde generated just by the heating of wood, and are not due to the resin, as can be seen by the constant value regardless of changes in the proportion glyoxal.

In conclusion tannin-glyoxal panels that do not contain formaldehyde and with an emission equal to that of unbounded wood can be obtained by the use of glyoxal as hardener.

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