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Simple urea-glutaraldehyde mix used as a formaldehyde-free adhesive: effect of blending with nano-Al₂O₃

M. Ł. Mamiński*, M. E. Król, M. Grabowska, P. Głuszyński

*Warsaw University of Life Sciences – SGGW, Faculty of Wood Technology,
159 Nowoursynowska St., 02-776 Warsaw, Poland*

**corresponding author: mariusz_maminski@sggw.pl*

Abstract. A formaldehyde-free adhesive based on urea (U) and glutaraldehyde (GA) was developed. High reactivity of the urea-glutaraldehyde mix at ambient temperature allows for its cold setting. The glues of GA/U molar ratio between 0.8 and 1.2 were examined. It was found that for the satisfactory performance of the system, blending with nano-Al₂O₃ was necessary.

Introduction

Since formaldehyde has been classified as carcinogenic to human (IARC 2004), the requirements urea-formaldehyde resins must meet have become stricter and an urgent need for a reduction of its content and emission from wood based materials and adhesives occurred. E0 (known as F***) class means formaldehyde emission below 3 mg/100 g while that for Super E0 (also known as F****) is below 2 mg/100 g (JIS A 5905, JIS A 5908:2003). There are several approaches allowing to overcome that problem: (1) development of adhesives based on renewable resources – e.g. soy proteins (Kumar et al. 2002), tannins (Ballerini et al. 2005) or chitosane (Umemura et al. 2003); (2) replacement of formaldehyde-emitting adhesives – namely urea-formaldehyde – with other types of adhesives (e.g. polyurethanes); (3) addition of formaldehyde scavengers to the glue formulation (e.g. liquefied wood (Medved et al. 2009), acetoacetyl moieties (Dziurka and Łęcka 2004) or urea

which is used in industry up to date); (4) adhesive reformulating and/or partial substitution of formaldehyde with other aldehydes. In literature, there are some reports on the application of succinaldehyde or propionic aldehyde in adhesives (Manosuri and Pizzi 2006; Wang and Pizzi 1997).

In the proposed solution, formaldehyde was replaced by glutaraldehyde – an industrial aldehyde used as a disinfecting agent or proteins-crosslinking agent (Kupeć et al. 2003) – so that urea-glutaraldehyde (UGA) adhesive was obtained. However, it must be stressed that glutaraldehyde is less toxic than formaldehyde. Glutaraldehyde LD₅₀ value (oral, rat) is 1470 mg/kg (Sigma-Aldrich 2008), while that for formaldehyde is 100 mg/kg (NTIS 2005).

Also, since it is known that nanoparticles may greatly improve adhesive interactions with a substrate (Zhai et al. 2007) the prepared urea-glutaraldehyde mix was blended with Al₂O₃ nanopowder. The approach allowed for the development of a cold setting formaldehyde-free urea-based adhesive for wood bonding.

Materials and methods

The raw UGA mix was prepared by simply dissolving a calculated amount of urea in a respective amount of 50% aqueous glutaraldehyde solution (Aldrich) to finally achieve the required molar ratio of the reagents (e.g. 30 g of urea in 100 g of 50% GA solution for 1.0 GA/U molar ratio). Mixing (100 revolutions per minute) was kept at room temperature until complete dissolving of urea, so that the procedure required no typical and laborious resin synthesis.

Formulations with GA/U molar ratio of 0.8, 1.0 and 1.2 were prepared. 1%wt or 3%wt of nano-Al₂O₃ (Aldrich) dispersions – based on solids – were obtained by addition of nanomaterial to the urea / glutaraldehyde solution followed by 30-min-ultrasonication. 1% aqueous oxalic acid (10 g of solution in 100 g of glue composition) used as hardener was

added to the UGA mixture prior to bonding. Final solids contents were as follows: 58%, 56% and 60%, respectively, for 0.8, 1.0 and 1.2 GA/U molar ratio. After the time necessary for the system to achieve application viscosity of 1000 cP (Table 1), the glue was applied onto the specimens. Glue load was 160 g/m². Solid beech specimens (density 620 kg/m³, 5.6% moisture content) cut according to EN 205 were bonded at ambient temperature (30 min, 1.5 N/mm²). The manufactured samples – after 7 days in controlled climate (20°C, humidity 65%) – were subjected to dry shear strength tests (no. of samples was 20).

Results and discussion

From the data shown in Table 1 it is clear that reactivity of the adhesive is high – even at ambient temperature gelation occurs in 70 - 100 min without any hardener. However, it can be easily shortened to minutes with small addition of an acid. The gelation experiments and physical analysis of the adhesive after curing showed that GA/U = 1.0 molar ratio was most suitable. The 0.8 and 1.2 options provided poor mechanical performance and brittleness of the cured polymer. Thus, wood bonding and blending with nano-Al₂O₃ was performed for GA/U = 1.0 only. The strengths of the gluelines are shown in Table 2. The presented values obtained for the acid-cured series with Al₂O₃ exceeded shear strength of the substrate and 100% wood failure was observed, while the controls exhibited adhesive failure and strengths lower by 52 and 34%. By comparing strengths of non-Al₂O₃ blended series with and without hardener, it can be noticed that values of the hardened series are much higher, which suggests that acid hardener is necessary for the system. On the other hand, low strength values of the Al₂O₃ blended series without hardener suggest that sole presence of nanoparticles did not provide significant changes in shear strengths.

Table 1

Table 2

Conclusion

Thus, the observations allow for withdrawing the conclusions that by simple dissolving of urea in glutaraldehyde solution a formaldehyde-free cold-setting adhesive system can be made. Its acid-curing significantly improves the adhesive performance, however, a synergetic effect of small addition of Al_2O_3 nanoparticles and acid curing is necessary for satisfactory shear strengths exceeding that of the substrate.

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Table 1. Gelling times and application viscosity development of the studied UGA glues at 20°C

Tabelle 1 Gelierzeiten und Dauer bis zum Erreichen der geordneten Viskosität der untersuchten UGA-Klebstoffe bei 20°C

GA/U molar ratio	Gelling time		1000 cP achieved after [min]
	1% oxalic acid [min]	no hardener [min]	
0.8	7.5	70	5
1.0	10	70	8
1.2	16	100	13

Table 2. Shear strengths of GA/U = 1.0 glue blended with Al₂O₃
Tabelle 2 Scherfestigkeiten von GA/U = 1,0 Klebstoff gemischt mit Al₂O₃

Al ₂ O ₃ [wt%]	Shear strength [N/mm ²]	
	1% oxalic acid	no hardener
0.0	2.83 ±0.83	1.40 ±0.51
1.0	5.91 ±0.78	0.90 ±0.22
3.0	4.85 ±0.90	0.85 ±0.25