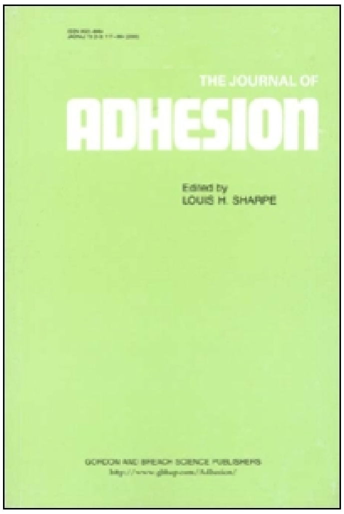

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Improved Water Resistance and Adhesive Performance of a Commercial UF Resin Blended with Glutaraldehyde

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The influence of glutaraldehyde blend on the properties of a commercially available resin in moist conditions was investigated. A UF resin with very low water resistance was blended with glutaraldehyde prior to the thermosetting step and the adhesive performance of the modified adhesive systems was studied. Experiments were performed on birch two-layer co-oriented plywood. It was shown that blending a commercial glue-mix as sold with glutaraldehyde can be an effective way to improve water resistance of the glue without introducing additional –NH_2 moiety. It was also found that glutaraldehyde does not deteriorate properties of the glue in the dry state, while glue susceptibility to boiling water is markedly reduced.

Keywords: Adhesives; Glutaraldehyde; UF

1. INTRODUCTION

Urea-formaldehyde (UF) resin is obtained as a result of condensation of urea with formaldehyde. As Dunky [1] reports, annual production of urea-formaldehyde resin in Europe alone reaches 4.8 million metric tons. Around 60% of that is used for particleboard, 30% for medium

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density fiberboard (MDF) and 10% for laminating furniture or interior flush doors and plywood.

Urea-formaldehyde adhesives are examples of thermosetting resins referred as amino resins. Besides the undoubted and evident advantages of urea-formaldehyde resin, such as low cost, easy application, low cure temperatures, water solubility and excellent mechanical properties when cured, there is one major and serious disadvantage– very low water resistance [2,3]. Moist environments, especially when heated, lead to hydrolysis of methylene and methylene-ether bridges according to the mechanism proposed by Fleischer [4] – Scheme 1.

Ease of hydrolysis makes UF resins useful for interior applications only. Therefore, there has been an urgent need to improve their water resistance. Chemists undertook that challenge, so that there have been numerous attempts to overcome that problem reported in the literature and a wide spectrum of compounds used as modifying-agents. To name just a few: Prestifilippo [5] and Cremonini [6] showed that addition of melamine acetate may affect the UF adhesive water resistance. Hydrolysed waste nylon was also used as a hardener for improvement of UF resin water resistance [7]. Ebewele *et al.* [8–10] showed that incorporation of a hydrophobic chain (urea-capped aliphatic amines and/or amine hydrochlorides as curing agents) into the network resulted in lower resin susceptibility to hydrolytic attack.

The modification of UF resins with latexes was investigated by Glazkov and Boldyrev [11]. Particleboards bonded with latex-modified resin exhibited swelling decreased by 48% and water absorptivity decreased by 40%. Another approach to increase resistance of UF resins against hydrolysis was studied by Park who examined performance of UF resin combined with emulsifiable methylene diphenyl diisocyanate (EMDI) [12].

Wang and Pizzi [13] proposed using succinaldehyde as a modifying agent at the condensation step and found that water resistance of the obtained urea-formaldehyde-succinaldehyde resin (UFSA) could be increased and that that approach could be effective.

Glutaraldehyde is widely used, as a convenient cross-linking agent for biodegradable, biocompatible polymeric materials in biomaterial [14,15] and in pharmaceutical science [16], therefore, it seemed interesting to investigate how glutaraldehyde (GA) would work when

$$\text{—(CO)NHCH}_2\text{NH(CO)—} + \text{H}_2\text{O} \rightleftharpoons \text{—(CO)NH}_2 + \text{—(CO)NHCH}_2\text{OH}$$

$$\text{—(CO)NHCH}_2\text{OCH}_2\text{NH(CO)—} + \text{H}_2\text{O} \rightleftharpoons 2\ \text{—(CO)NHCH}_2\text{OH}$$

SCHEME 1 Mechanism of Methylene and Methylene-ether Bridge Hydrolysis.

added to a commercial UF resin without introducing an additional $-NH_2$ moiety in the form of urea.

It was hypothesized that addition of glutaraldehyde would result in: (1) formation of 5-carbon bridges, (2) reduced hydrophilic character of the resin, (3) increased water resistance and (4) increased reactivity towards wood constituents.

2. EXPERIMENTAL

2.1. Materials

Commercially available urea-formaldehyde resin Silekol, the U/F molar ratio of which is proprietary information, was obtained from Zaklady Azotowe "Kedzierzyn" SA (Kedzierzyn-Kozle, Poland). Content of solids 65% mass, viscosity at 20°C 250 mPas.

Glutaraldehyde as a 50% aqueous solution (GA) was purchased from Aldrich (Milwaukee, WI, USA). Ammonium chloride was purchased from Polskie Odczynniki Chemiczne SA (Gliwice, Poland). H-40 hardener was obtained from Zaklady Azotowe "Kedzierzyn" SA (Kedzierzyn-Kozle, Poland). Ammonium chloride solution was prepared in distilled water. Ready-to-use glue formulations were prepared in tap water. Birch wood with 7% moisture content was used as substrate. Fourier transform infrared (FTIR) spectra were recorded in KBr on a Bio-Rad FTS165 instrument (Bio-Rad, Hercules, CA, USA). Viscosity was measured on METTLER RM180 Rheomat at 20°C (Mettler-Toledo, Columbus, OH, USA). Failure location was determined by light microscopy. The statistical difference between results obtained a in shear strength test were evaluated by p-values calculated in the Student t-test with 95% confidence interval.

2.2. Blend Preparations

Silekol resin/GA blends were prepared according to Table 1 as aqueous solutions. To a weighed portion of Silekol, hardener (10% NH_4Cl aqueous solution or H-40) and a calculated amount of water were added. The formulation was mixed 1 min at ambient temperature with a mixer speed 60 rpm and then a calculated amount of a 50% aqueous solution of GA was added. The formulation was mixed for 4 min.

2.3. Sample Preparations

Test specimens for shear strength were prepared from a birch wood log that was cut into pieces (100 × 20 × 8 mm). Then, in order to determine

TABLE 1 Studied Blend Formulations – % of Total Composition Weight

	Silekol, % mass	GA 50% sol, % mass	NH_4Cl, % mass	Water, % mass
Series 1				
SGA00	80.6	–	3.0	16.4
SGA31	80.6	3.1	3.0	13.3
SGA57	80.6	5.7	3.0	10.7
SGA82	80.6	8.2	3.0	8.8
SGA162	80.6	16.2	3.0	0.2
Series 2			H-40, % mass	
SGA00	80.6	–	1.8	17.6
SGA38	80.6	3.8	1.8	13.8
SGA60	80.6	6.0	1.8	11.6
SGA91	80.6	9.1	1.8	8.5
SGA150	80.6	15.0	1.8	2.6

the bonding strength of the blended adhesive system, ready-to-use glue (formulations according to Table 1) was applied by spreading onto the samples. The spread rate was 100 g/m^2. Two glue-coated pieces of birch wood were put together to form a two-ply assembly (sample) and hot-pressed. The area of bonded overlap was 2 cm^2.

2.4. Pressing Conditions

Bonding was performed on AB AK Eriksson (Mariannelund, Sweden) press. Hot-pressing parameters were set as: temperature 180°C, pressure 3.2 kgf/cm^2, time 300 s. 60 samples for each formulation were bonded.

2.5. Sample Treatment

After bonding, all the samples were conditioned in a climate room (20°C, 65% humidity) for 24 hours. Then 20 conditioned and dry samples were subjected to shear strength tests, 20 samples were immersed in water (20°C) for the next 24 hrs, and the last 20 samples were kept for 15 min in boiling water. Samples after 24 hour soaking or after 15 min boiling were tested wet.

2.6. Gel Time and Pot-Life Measurements

Gel times were measured according to Polish Standard BN-80/6321-05. A glass test tube with 10 g of the glue was immersed in boiling water. The glue was being mixed with a glass rod until gelation occured. Measurement was made in triplicate. Pot-lives were determined on a viscosity basis. The critical value was 300 mPas.

2.7. Glutaraldehyde-Wood Interaction

A mixture of powdered birch wood with 50% aqueous glutaraldehyde solution (1:2, wt/wt, pH 3.0 adjusted with 1 M HCl) was sealed in a glass tube and stored at 55°C for 72 hours. Then wood powder was dried in vacuo and the FTIR spectrum was measured.

3. RESULTS AND DISCUSSION

Ten formulations of the commercial UF resin hardened with the two different hardeners were blended with various glutaraldehyde content (Table 1) and the properties of these adhesive systems were investigated.

3.1. Gel Time

Gel time is defined as the time it takes for the system to cease exhibiting any liquid-like characteristics. An influence of GA addition on gel

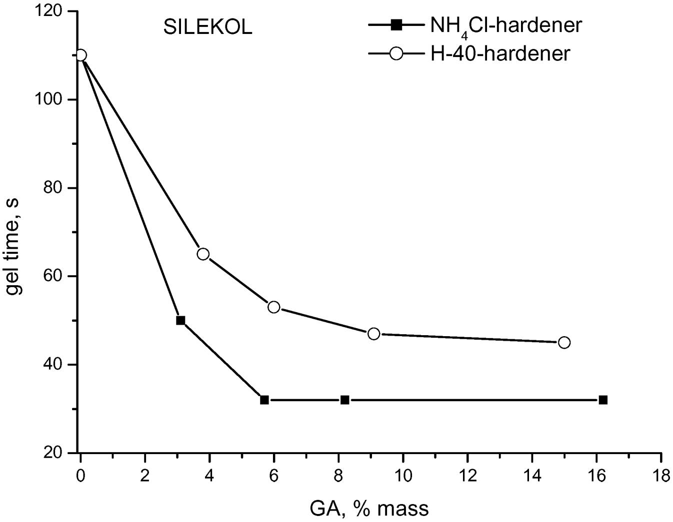

FIGURE 1 Effect of GA addition on gel time of Silekol-GA blend hardened with ammonium chloride or H-40.

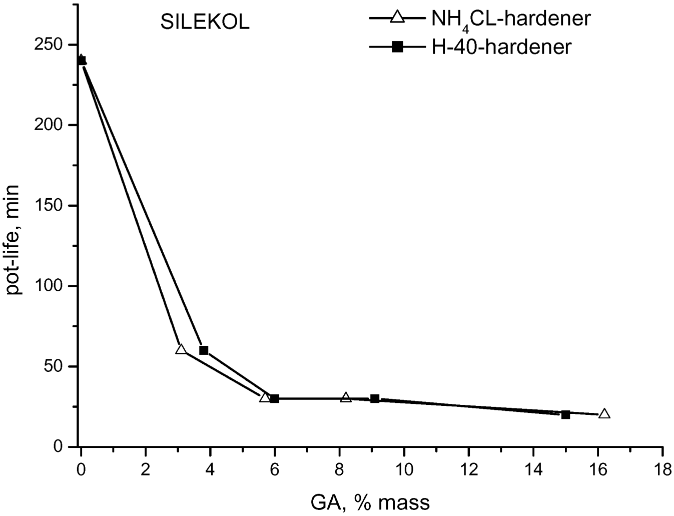

FIGURE 2 Effect of GA content on pot-life of Silekol-GA blend hardened with ammonium chloride or H-40 at 20°C.

time of the adhesive systems was observed. Figure 1 illustrates how glutaraldehyde addition decreases gel time at 100°C.

Since GA is a tetra-functional reagent the effect seen in Figure 1 could be ascribed to a high rate of cross-linking reaction. The ability of the modified resin to cross-link quickly even at ambient temperature becomes a serious disadvantage – blended resins exhibited a pot-life <1 hr (critical viscosity 300 mPas was achieved) while the pH was 6.2–6.4, but it must be stressed that no gelation occurred when no hardener was added.

As can be seen in Figure 2, the type of hardener had little effect on pot-life of glutaraldehyde-blended UF resin.

3.2. Shear Strength

Shear strength measurements were performed on a Hackert FP 10 (VEB Thüringer Industriewerk, Chemnitz Germany) instrument with 120 mm/min shear rate. The results for the relevant adhesive are shown in Figures 3 and 4.

As it can be seen in Figures 3 and 4, average shear strength values for the Series 1 and 2 differ significantly. Although the increase in average shear strength of wet samples increases with GA content for both series, shear strength values remain unsatisfying. Such behavior of the adhesives may be explained by two opposite effects – on the one

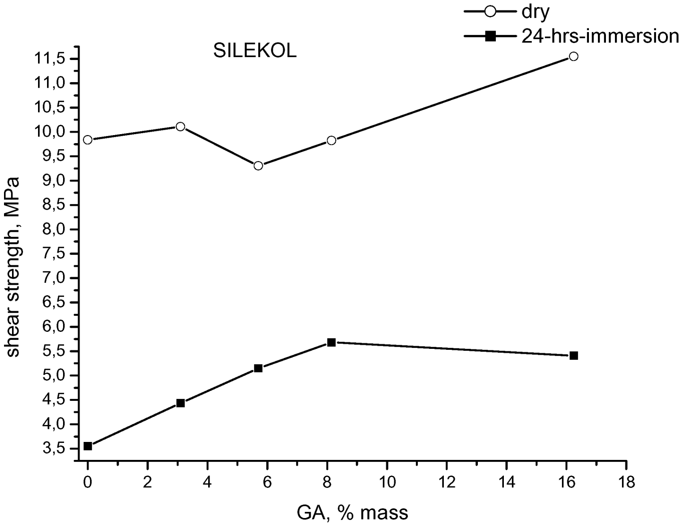

FIGURE 3 Shear strength of NH_4Cl-hardened blend *vs*. GA content.

hand, there is still too high hydrolysis susceptibility which suggests that glutaraldehyde incorporation into the resin structure resulted in easy-to-hydrolize structures. On the other hand, GA contribution

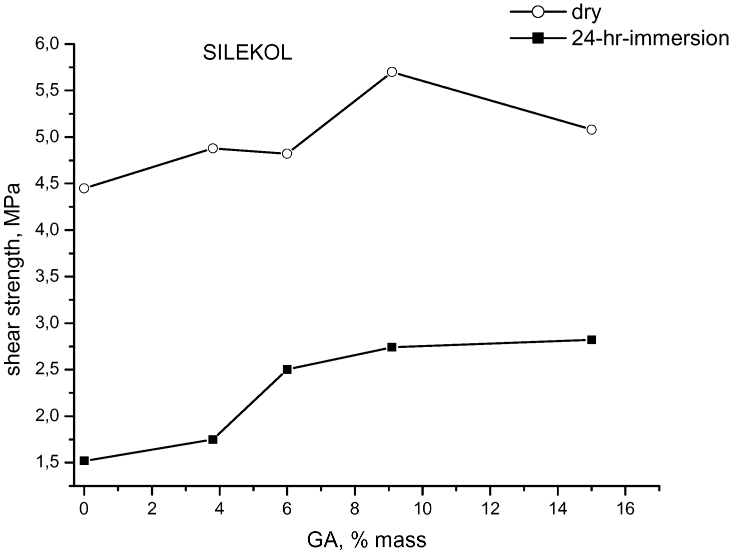

FIGURE 4 Shear strength of H-40-hardened blend *vs*. GA content.

to overall hydrophobicity of the adhesive is observed. These effects counterbalance each other, so that effective water resistance is improved, but remains at a low level.

For Series 1, improved water resistance in cold water is clearly observed (Figure 3) – all changes in adhesive strength are significant - p-values are smaller than 0.05 (Table 2). On the other hand, performance of the adhesive in the dry state was not changed significantly except for SGA162-bonded samples (16.2% mass GA content).

For Series 2 (H-40-hardened Silekol), statistical analysis of shear strength values also showed that glutaraldehyde did not affect performance of the glue in the dry state, while water resistance of the glueline after 24-hr-immersion in cold water is increased significantly (Table 3).

Improved water resistance can be explained by incorporation of GA into the resin structure (spectral data verifying that hypothesis is presented in 3.3) and formation of 5-carbon bridges during the curing step, so that water repellency of the resin is increased. In addition, 5-carbon chains induce lower crosslink density as well as higher flexibility of the network which may affect mechanical properties of the cured resin.

The ammonium chloride hardened series show 2-fold higher shear strength than their respective H-40 hardened series when gel times at 100°C differ about 35%. Moreover, the ammonium chloride hardened Series 1 treatment with boiling water resulted in 100% of the samples cleaving spontaneously, thus, these data were not presented on the chart. H-40-hardened Series 2 exhibited increasing percentage of the uncleaved samples on boiling depending on GA content in the formulation (Figure 5).

TABLE 2 p-Values Calculated for NH_4Cl-Hardened Silekol-GA Blends (Series 1)

	p-value
Dry state	
SGA00 vs. SGA31	0.6399
SGA00 vs. SGA57	0.3147
SGA00 vs. SGA82	0.9800
SGA00 vs. SGA162	0.0033
24 hrs immersion	
SGA00 vs. SGA31	0.0194
SGA00 vs. SGA57	8.74E-05
SGA00 vs. SGA82	4.04E-08
SGA00 vs. SGA162	1.71E-07

TABLE 3 p-Values Calculated for H-40-Hardened Silekol-GA Blends (Series 2)

	p-value
Dry state	
SGA00 vs. SGA38	0.2140
SGA00 vs. SGA60	0.3152
SGA00 vs. SGA91	0.0015
SGA00 vs. SGA150	0.0698
24 hrs immersion	
SGA00 vs. SGA38	0.1452
SGA00 vs. SGA60	7.40e-07
SGA00 vs. SGA91	2.60e-09
SGA00 vs. SGA150	7.41e-09

That phenomenon can be reasoned by the different mode of action of the hardeners. One of the H-40 components is free urea which allows formation of a urea-glutaraldehyde resin network, more hydrophobic than a urea-formaldehyde network, thus water penetration into the bondline is weaker. However, in order to completely explain the role of GA in the resin network some additional spectroscopic measurements for structural characterization and a detailed study of mechanical and physiochemical properties are necessary.

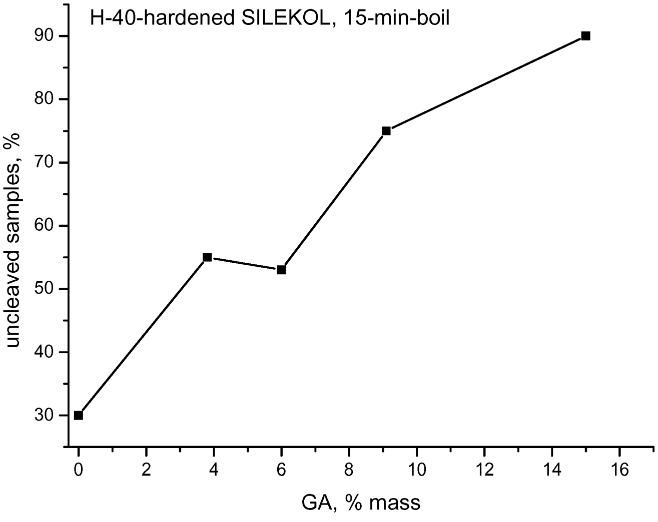

FIGURE 5 Effect of GA content in blend on percentage of spontaneously cleaved samples during 15-min boiling.

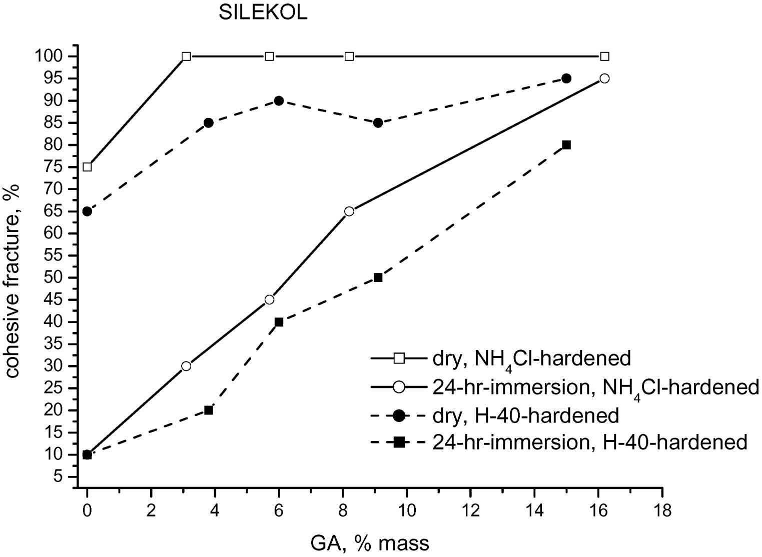

FIGURE 6 Percentage of cohesively fractured samples for Series 1 and 2 *vs*. GA content in blend.

Although increased water resistance was achieved for both Silekol series, another effect was observed – increased percentage of cohesively fractured samples (Figure 6).

GA-modified blends, in comparison with the unmodified ones, exhibit an increased percentage of cohesively fractured samples. That means that the adhesive strength of the glueline is higher than the cohesive strength of the wood substrate. Since unmodified resin exhibits a higher percentage of adhesively fractured samples, it can be reasoned that addition of GA to the commercial glue effects stronger wood-adhesive interactions and reinforcement of wood cell layers near the bondline, so that wood failure occurs. For both investigated series, as small as 3–4% mass addition of glutaraldehyde markedly improves performance of the resin. This supports the essential role of glutaraldehyde in the reinforcement of wood cell layers near the contact zone.

GA reactivity towards functional groups of the substrate (see 3.3) as well as an interpenetrating network can be an explanation of the phenomenon.

3.3. FTIR Spectra

In Figure 7 one can clearly see that there is no C=O group band in the FTIR spectrum of NH_4Cl-hardened Silekol/GA blend, while on a

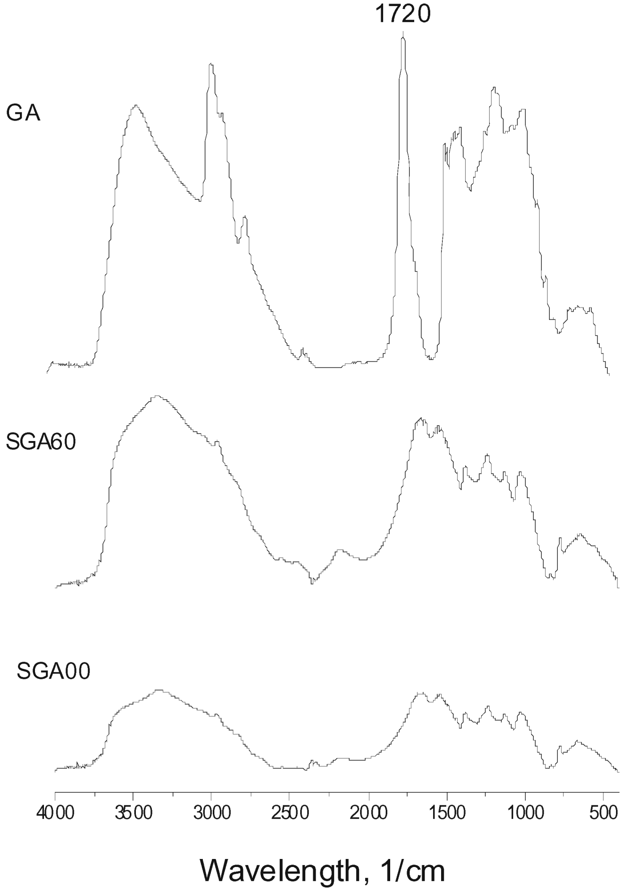

FIGURE 7 FTIR spectra of NH_4Cl hardened resins: SGA60 – Silekol + 6.0% mass GA, SGA00 – Silekol + 0.0% mass GA and GA - pure glutaraldehyde spectrum.

standard glutaraldehyde spectrum a carbonyl group stretching band is observed at $1720\,cm^{-1}$. Glutaraldehyde-induced cross-linking goes through hemiacetal-acetal intermediates [17], so disappearance of the C=O band could be attributed to formyl group conversion into the ether form. Although disappearance of the $1720\,cm^{-1}$ peak cannot be considered as evidence for complete GA incorporation into the resin network, it must be stressed that neither glutaraldehyde nor a low molecular glutaraldehyde derivative was detected by High Performance Liquid Chromatography (HPLC-MS) technique in extracts obtained after extraction of the cured resin with water in a Soxhlet apparatus.

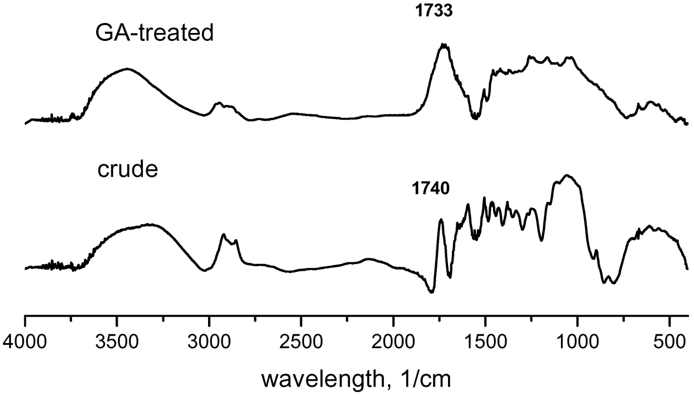

FIGURE 8 FTIR spectra of crude and GA-treated birch wood.

In Figure 8, spectra of powdered crude birch wood and birch wood treated with 50% glutaraldehyde solution are compared. The peak at 1740 cm^{-1}, that is ascribed to C=O stretching of the carboxyl group in crude wood, broadens and moves to 1733 cm^{-1} after GA treatment, which can be attributed to ester formation [18]. Also, crude wood and GA-treated wood spectra differ significantly in 1600–900 region, thus, formation of new ether moieties during wood-glutaraldehyde reaction can be postulated and the observation supports the concept of glutaraldehyde reactivity towards wood constituents.

4. CONCLUSIONS

Water resistance of a commercially available amino resin hardened with two different hardeners was investigated with respect to glutaraldehyde content. For both series improvement of water resistance in cold water was achieved. It must be stressed that GA addition to UF glue did not deteriorate performance of the adhesive in the dry state. Significant change in the performance of the adhesive systems for the samples in boiling water was observed – increasing GA content in the formulation decreases the percentage of spontaneously cleaved samples. Possibly, this is caused by increased hydrophobicity of the adhesive induced by GA 5-carbon chains incorporated into the resin network.

Both for ammonium chloride- and H-40-hardened Silekol, wood layers near the glue-wood contact zone were strengthened; their adhesive strength was higher than that in the bulk adhesive or in the bulk wood substrate. Subsequently, the percentage of cohesively fractured samples was increased when compared with the samples bonded with the unmodified species. The effect was ascribed to glutaraldehyde reactivity towards wood functional groups. The conception was supported by FTIR measurements.

It was shown that a commercial glue-mix can successfully be blended with glutaraldehyde and that addition of an amine-moiety in the form of urea is not necessary for upgrading water resistance of the glue.

By FTIR spectroscopy it was shown that glutaraldehyde was incorporated into the resin structure.

The results presented in this paper were found interesting and promising. It lead us to undertaking more detailed studies with full spectroscopic, rheological and physicochemical characterization of the adhesives. It can also be concluded that further studies on wood-glutaraldehyde interactions, as well as on application of glutaraldehyde in self-prepared resins with precisely controlled F:U:GA molar ratios, are reasonable and are currently under investigation.

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