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ATR-FTIR spectral analysis of modified UF adhesive

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Abstract: This report deals with stability and toxicity of urea-formaldehyde (UF) adhesives for woodworking industry. ATR FTIR method was used to research UF adhesive modified by glutaraldehyde (GA). The glutaraldehyde was added to UF resin to increase structural stability of the adhesive. FTIR spectra of UF adhesives, UF and GA blends hardened at temperature 100 °C are presented in the paper. Formaldehyde released from the adhesive is harmful. Collagen solution was chosen as reaction agent to decrease UF adhesive toxicity. Measured FTIR spectra of UF adhesive modified with collagen hydrolysate approved the creation of bonds between formaldehyde and collagen.

Keywords: UF resin, adhesive, collagen, glutaraldehyde, FTIR

INTRODUCTION

As the aminoplastic adhesives are widely used in woodworking industry, problems of chemical stability of the adhesives, resistance against hydrolysis, and formaldehyde emissions are the main themes of modern research on urea-formaldehyde (UF) adhesives. To influence the quality of curing and the structure of cured resin various substances are added into adhesives. A way of modification of the adhesives is adding such substances, which bond free formaldehyde and so prevent releasing formaldehyde from glued materials (SEDLIAČIK 2005).

At hardening of UF adhesives, acid hardeners influence transformation of dimethylene-ether links (less stable bonds) to the methylene links (more stable bonds). Lowering the number of dimethylene-ether links in cured adhesive film of aminoplastic, it is possible to lower the formaldehyde emission. One of examined chemical substances used for modifying aminoplastic adhesives is glutaraldehyde (GA). There is assumed that GA can be inbuilt into the structure of hardened adhesive and so replace less stable dimethylene-ether links with its 5-carbon chain (MAMINSKI et al. 2006).

In recent years, research on modification of adhesives has been also aimed at utilization of products that are easy to get, and using them the costs in adhesive production can be reduced. Chrome tanned leather waste contains collagen hydrolysate. Collagen (protein) bears a number of amino-groups that are known for their reactivity with formaldehyde.

In our experiments we researched chosen additives and their influence on curing of UF adhesive. We measured and compared FTIR spectra of additives, standard UF adhesive and the adhesive modified with glutaraldehyde and collagen.

MATERIAL AND METHODS

In experimental work we researched UF adhesive KRONORES CB and hardener R-60. Natural polymers (skin collagen hydrolysate HK79) were added into the adhesive in amount of 5 %. The hydrolysate was a liquid containing collagen (26 %). Solid content of the hydrolysate was 43 %, pH = 5.2. Hardener was modified by addition of activator based on glutaraldehyde (GA) (VIPO a.s.) in amount of 3 %.

FTIR spectra were measured with FTIR spectrometer NICOLET iS10 (Thermo Scientific). Collagen hydroysate was researched in liquid form. Formaldehyde (0.2 g 37 % water solution) was added into 10 grams of HK. The mixture was conditioned at temperature of 20 °C for 16 hours. Parallel sample was boiled for 5 minutes (to approximate conditions at

plywood pressing). Spectra of liquid samples were measured immediately after reaction time. Spectra of hardened adhesive samples were measured on tablets.

RESULTS AND DISCUSSION

FTIR spectrum of collagen hydrolysate (HK) is shown in figures 1. In spectral interval 1650–1400 cm^{-1}, the spectrum was characterized by two strong absorption bands (1626 and 1458 cm^{-1}) and in spectral interval 1350–1000 cm^{-1} by four mediate bands (1337, 1246, 1157 and 1083 cm^{-1}).

In interval 3800–2500 cm^{-1} there is a wide absorption band that according MILATA et al. (2007) indicate the existence of peptide bonds (–CO–NH–) in solution (3400 – 3480 cm^{-1}) and hydrogen bonds (inter and intra–molecular bonds NH, OH).

The measured infrared spectrum of collagen hydrolysate used for modification of UF adhesive correlated very well with the spectra measured by BELBACHIR et al. (2009). They compared spectra measured for various collagen types in four spectral intervals: υ(C=O) (1700–1600 cm^{-1}), δ(CH_2) and δ(CH_3) (1480–1350 cm^{-1}), υ(C–N) and δ(N–H) (1300–1180 cm^{-1}), υ(C–O) and υ(C–O–C) (1100–1005 cm^{-1}). Comparing the spectra of collagen and the mixture of collagen and formaldehyde (fig. 1), we investigated interaction of formaldehyde with collagen hydrolysate.

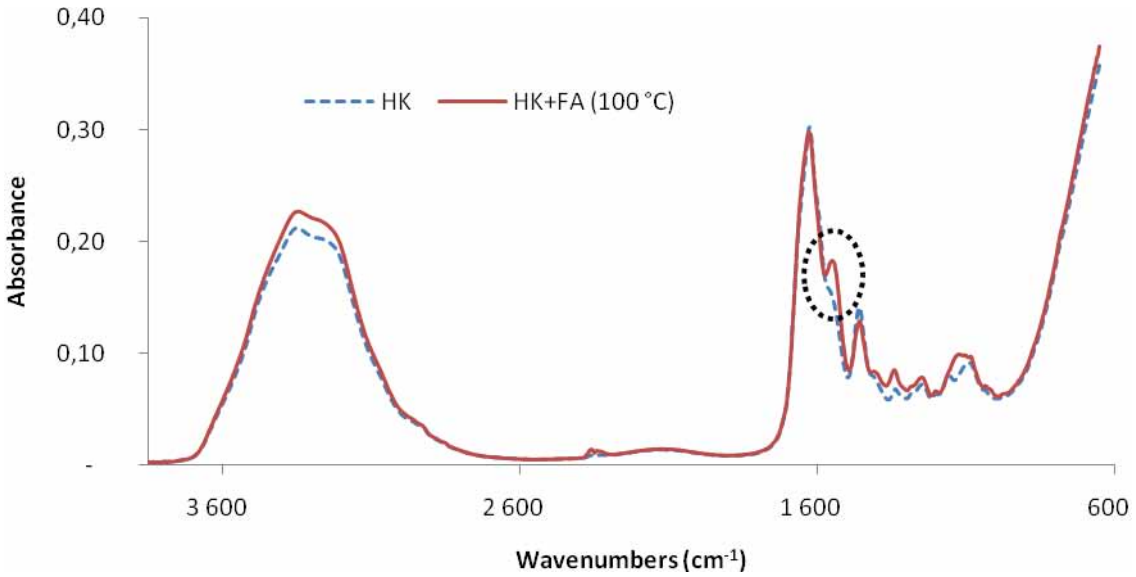

Fig. 1 FTIR spectrum of collagen hydrolysate after reaction with formaldehyde.

The change in spectral curve is evident in interval 1550 cm^{-1}, and a new band and increased absorption is evident in interval 1160–1080 cm^{-1}. Intensity of band in HK spectrum at 1626 cm^{-1}, characteristic for amines, lowered after reaction with formaldehyde and at the same time intensity of bands at 3346 cm^{-1} increased (–OH groups; intra and inter–molecules hydrogen bonds). It can be considered the result of possible chemical interaction between researched substances and a product containing higher number of –OH groups. Samples conditioned at temperature 100 °C showed more intensive bands at 1550 cm^{-1}; we can assume that the reaction rate at higher temperature is higher.

Comparing the spectra of standard UF adhesive with UF modified with HK, high similarity is noticeable (fig. 2).

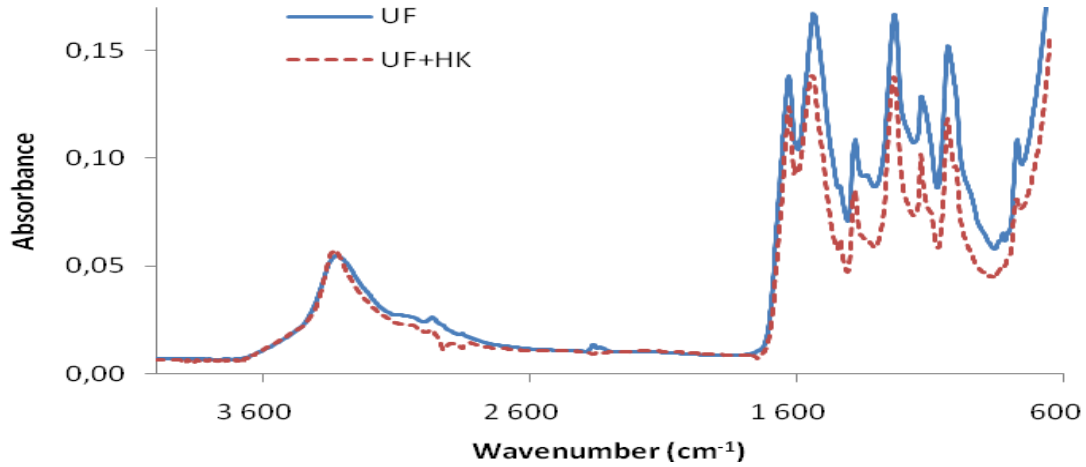

Fig. 2 FTIR spectrum of UF adhesive and UF adhesive with collagen hydrolysate.

Some differences are evident in bands intensity in interval 2800–2950 cm^{-1}, where two new bands appeared (–CH_2– groups) (MILATA et al. 2007, ESSAWY et al. 2009), changed intensity of spectral band at 1600 cm^{-1} (primary amides) (BELBACHIR et al. 2009), and intensive band at 1438 cm^{-1}. The band in interval 1590–1450 cm^{-1} is resolved into two absorption bands: 1538 cm^{-1} υ(C=O) (carboxyl acids) and 1547 cm^{-1} υ(C=O) (peptide bonds –NH–CO–NH–). The peak 1338 cm^{-1} disappeared. Weak change of the spectra appeared in interval 1000–1150 cm^{-1}; it can point at reduced number of C–O–C bonds in UF adhesive.

Comparing the spectra of standard UF adhesive and UF modified with GA (fig. 3) we can see high similarity in „fingerprints“ interval.

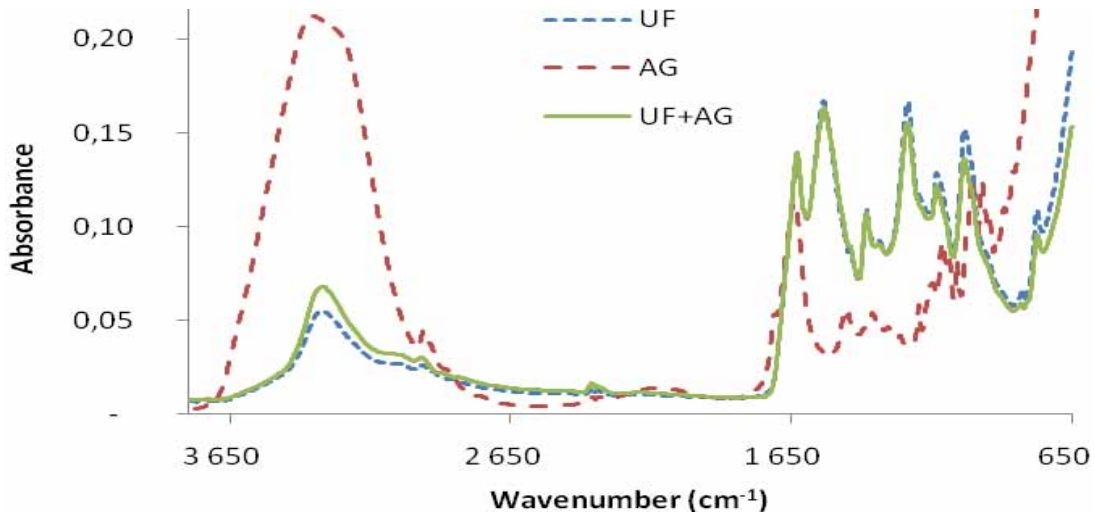

Fig 3 FTIR spectra of UF adhesive and UF adhesive with GA

Some differences are found in interval 2980–2820 cm^{-1}, where two distinguishable bands are shown. According to MILATA et al. (2007) and ESSAWY et al. (2009) strong bands in interval 2950–2850 cm^{-1} belong to alkanes and their –CH_2– groups, and in interval 2900–2700 cm^{-1} to aldehydes (–CHO). We assume that main structure of cured UF adhesive was changed when GA was added. GA is able to react with free aminogroups of the adhesive and incorporate into the structure of cured adhesive; 5-carbon chain contributes to the strength, hydrophobic properties, and stability of adhesive network. The assumption was

confirmed by the fact that the peak at 1720 cm^{-1} from the spectrum of GA (carbonyl group C=O) disappeared from the spectrum of cured adhesive.

The sample of cured UF adhesive with GA and HK gave the spectral curve shown in fig. 4. The spectrum showed all of above mentioned differences. The band at 1720 cm^{-1} was not present; we assume that GA was incorporated into the structure of cured UF adhesive.

At 1544 cm^{-1} there is the band, which was not in the spectrum of collagen. The presence of it we can explain by possible formation of structures of C–OH during the reaction of free $–NH_2$ groups with aldehydes. This is confirmed by decreased intensity of band at1630 cm^{-1} when compared with the band at 1544 cm^{-1}; this reflects decreased number of free $–NH_2$ groups.

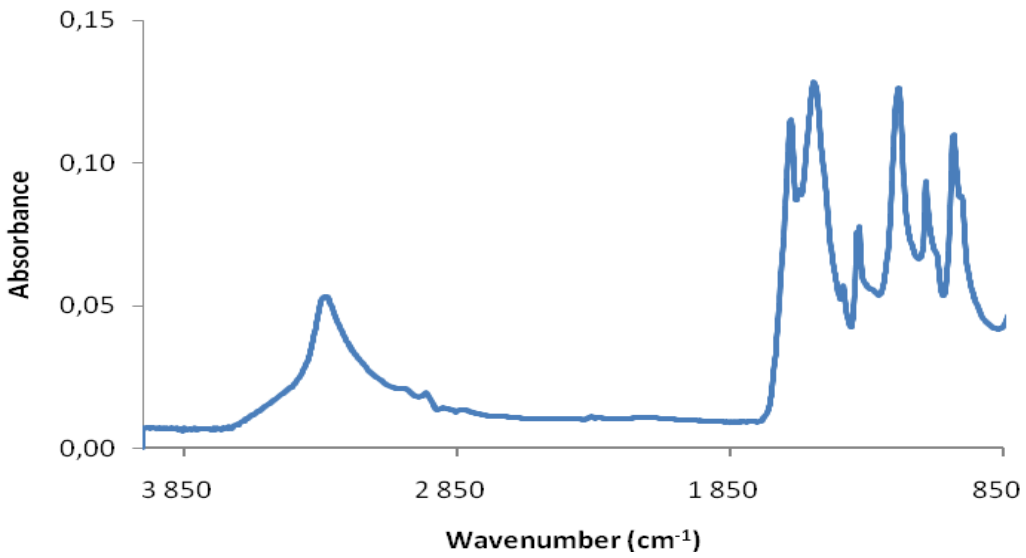

Fig 4 FTIR spectra of UF adhesive and UF adhesive with GA and HK

Based on our experiments, it is very hard to qualify the measure of how the particular components of such a complicated system (macromolecule of cured adhesive, present peptide chains, and presence of standard and modified hardener) are bonded by chemical links. It would also be interesting to know how all the system works on the wood surface.

CONCLUSION

The final adhesive mixture is a mixture of two adhesives – aminoplastic and protein. The curing of UF adhesive is combined with network formation of protein. At the same time, we assume the direct chemical bonding between macromolecules of protein and the resin. The assumption was confirmed with recognizing the structure of cured adhesive mixture by FTIR spectroscopy method. Evaluating the spectra of particular systems present in final adhesive mixture we can confirm that proteins from collagen hydrolysate react with their free $–NH_2$ groups with free formaldehyde and bond it by covalent chemical link. At 1544 cm^{-1} there is a band, which was not visible in the spectrum of collagen. We can consider this fact as a result of formed C–OH structures at reaction of free $–NH_2$ groups with aldehydes. The same is confirmed by reduced absorption at 1630 cm^{-1}, which is the result of decrease of $–NH_2$ groups. Also the ratio of unstable dimethylen-ether links in the structure of cured UF adhesive lowered. Glutaraldehyde present in adhesive mixture was inbuilt into the structure of adhesive, the band at 1720 cm^{-1} indicating (C=O) group of GA disappeared from the spectrum of cured UF adhesive.

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Streszczenie: *Analiza spektralna ATR-FTIR modyfikowanej żywicy mocznikowej*. Praca dotyczy stabilności i toksyczności klejów mocznikowych dla przemysłu drzewnego. Testowano żywicę modyfikowaną aldehydem glutarowym, dodanym w celu zwiększenia stabilności strukturalnej. Używano kolagenu w celu zmniejszenia toksyczności żywicy mocznikowej, potwierdzono powstawanie wiązań pomiędzy kolagenem oraz formaldehydem.

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