Formaldehyde-free and bio-based adhesives for the production of wood-based materials

Bunzel, Frauke[1)]; Schirp, Claudia[1)]; Heinrich, Lydia[1)]; Eschig, Steven[1)]

1) Fraunhofer Institute for Wood Research, Wilhelm-Klauditz-Institut WKI, Braunschweig, Germany

Abstract

In view of the fact that formaldehyde has been classified by the European Commission as a mutagen and carcinogenic substance, efforts to develop formaldehyde-free adhesives to manufacture wood-based products are of enormous economic relevance and accordingly of high importance. Furthermore, of great interest in the wood-based industry, however, are adhesives based on renewable materials. These two aspects are topics in our department “Surface Technology” at the Fraunhofer Institute for Wood research, WKI and the presentation will give an overview of bio-based and formaldehyde-free adhesives for the wood-based products industry developed in successful projects and an outlook for further promising approaches:
Reduction of formaldehyde content in adhesives for wood-based materials has been the approach for reducing formaldehyde emissions in the past, but from a current perspective this will no longer be sufficient. On the contrary: focus must be placed on the development of formaldehyde-free resins. There are several requirements, which possible formaldehyde-free adhesives for wood-based materials have to fulfil: Sufficient availability, harmlessness for the environment and health as well as technical and commercial competitiveness. Such a sufficient, economically and technically acceptable formaldehyde-free alternative to the applied formaldehyde-containing amino resins is currently not available.The idea was therefore to develop a formaldehyde-free amino resin by exchange of formaldehyde by alternative aldehydes such as glyoxylic acid and glyoxal. Glyoxal finds application in cosmetics and personal care products, but also in textile, paper and leather finishing. Glyoxylic acid is used for the synthesis of allantoin, antibiotics, complexing agents, pesticides, vanillin, ethyl vanillin and other chemical products. Hence, both are sufficient available, but the price is unfortunately higher than formaldehyde. A formaldehyde-free urea resin is being developed, whereby an attempt is initially being made to replace the proportion of melamine with urea due to the low prize of urea to develop a sufficient, economically and technically acceptable formaldehyde-free adhesive alternative to the applied formaldehyde-containing adhesives. The production and processing of the adhesives correspond to that of formaldehyde-containing amino resins, but under more moderate conditions by a simple three step procedure (max. 60°C). Particleboards were produced using a resin with a ratio of melamine to urea of 70:30, which achieved the requirements of DIN EN 312, type 2. The internal bond strength, bending strength and the water absorption are comparable to a particleboard manufactured with an industrially produced low-formaldehyde UF resin. These initial investigations show promising results in the development of formaldehyde-free urea resins for the production of particleboards with a very low formaldehyde emission.

The goal of another project was the development of an innovative low-formaldehyde and moreover bio-based dispersion adhesive based on polyvinyl acetate (PVAc) for the production of wood-based products. PVAc dispersions are commonly known as white glue and particularly used for surface bonding. PVAc is a less expensive adhesive and therefore selected as starting material. However, their thermoplastic character limits the application of PVAc as adhesive for the production of wood-based materials. Therefore, the starting point is to raise the glass transition temperature through copolymerization of vinyl acetate with a radical polymerizable sugar derivative in order to adjust the thermoplastic properties to a duromer. Within this project, the synthesis of an innovative adhesive based on a copolymer of vinyl acetate and a sugar derivative was successfully performed. Moreover, the scale-up has succeeded so that 60 kg of the adhesive have already been produced. Emission measurements revealed that the finally developed adhesive does not emit any formaldehyde. The developed adhesives were compared to commercial PVAc-adhesives and a conventional formaldehyde containing condensation resin for the application in wood-based products. It has been shown that particleboards produced with a PVAc-sugar-adhesive had approximately the same properties as produced with a conventional formaldehyde-containing condensation resin. However, despite of the addition of wax as hydrophobing agent the swelling behaviour is still a deficit. The advantages of the PVAc-sugar-adhesives are that glued wood particles, -fibers and veneers are storage-stable for further processing. Furthermore, beside wood-based panels dimensionally stable molded medium density fibreboards and molded plywood of beech veneer have been produced and so a formaldehyde-free PVAc for dimensionally stable molded wood-based materials is available.

A very promising raw material to develop bio-based adhesives is lignin, which is recovered in large quantities as a by-product of the pulp and paper industry. Due to its densely cross-linked structure and numerous functional groups including hydroxyl and carboxylic acid groups, it has the potential to develop strong adhesive and cohesive forces. In order to use it in adhesives, a number of challenges such as its low solubility in common solvents and compatibility with other formulation ingredients have to be overcome. In a further project, chemical modifications of lignin with different renewable and non-renewable building blocks, such as succinic acid, 1,2-propanediol, fatty acids and polyethylene glycol were used to yield polymeric materials suitable for different non-condensation adhesive applications. Lignin polymers with melting points up to 99 °C were obtained, while viscosities could be varied between 8 mPas (at 100 s-1, 25 °C) and 18 000 mPas (at 100 s-1, 100 °C). The lignin derivatives were integrated in different types of adhesive formulations, including emulsion polymerisation isocyanates (EPI), 2-component polyurethanes (2K-PU) and polyurethane dispersions. Both the dry and the wet shear strength of the thus obtained adhesives for wood bonding were tested and the results show a good water stability and high shear strength. Hence, the adhesives achieved D3 according to DIN EN 204. By testing these adhesives, a positive effect of higher lignin contents on the adhesive force could be determined. The evaluation showed that lignin derivatives have great potential to replace and complement petroleum-based binders in adhesive portfolios.

There are many other ideas and activities to develop bio-based formaldehyde-free resins by substitution of formaldehyde by other aldehydes. Sugar for example is a basic material for hydroxymethylfurfural (HMF), furfural (FF) and diformylfuran (DFF). Both FF and HMF can be produced from lignocellulose by dehydration using various catalytic processes. Meanwhile, the

estimated annual furfural production is > 400,000 t/a. The price is in the range between 1000-2000 €/t. The commissioning of an industrial plant in Switzerland (AVA Biochem) with a capacity of 100000 t/a is planned by 2023. These aldehydes are promising alternatives for formaldehyde and initial investigation to develop bio-based formaldehyde-free amino resins with these aldehydes have been carried out.