

Поскольку потеря массы при горении образцов отвержденного связующего с добавкой серы уменьшилась, ДСтП, модифицированные добавкой серы, будут иметь пониженную потерю массы при горении.

Водостойкость отвержденного связующего меньше при любой температуре отверждения. Это доказывает, что добавка серы блокирует носители гидрофильных свойств в отвержденном связующем – метилольные группы ($-\text{CH}_2\text{OH}$), таким образом снижая водопоглощение связующего.

Проведенные экспериментальные исследования на малых образцах отвержденного КФС с модифицирующей добавкой серы (и контрольных – без добавки) подтверждают теоретические исследования процесса структурообразования связующего и вывод об углублении поликонденсации КФС при добавке серы.

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INVESTIGATIONS FOR IMPROVING THERMAL STABILITY AND DELAMINATION RESISTANCE FOR ADHESIVES USED FOR GLUE LAMINATED TIMBER

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В работе исследуется возможность улучшения качества склеивания древесных конструкций строительного назначения.

Bonding of wood today is one of the most important joining techniques in timber construction and allows constructions to be built that would otherwise only be feasible with stronger materials such as steel or reinforced concrete. In times of limited natural resources, wood, as a renewable resource, is becoming more and more important for constructors, architects and engineers, due to its material specific advantages, such as its high strength to density ratio along with its positive eco-balance.

Since the evolutional development of wood does not t engineering demands in all cases, solutions must be found to optimize the material for civil engineering. The invention of glulam by Otto Hetzer in 1906 was a milestone for structural wood construction. Due to bonding, it was possible to improve the properties of the material significantly by grading and removing defects to apply the strength properties to full capacity.

Apart from wood, the adhesive is the second integral component. During Hetzer's time, one relied on high class casein adhesives made from acid milk casein, which was added with calcium compounds. This biological adhesive is interesting from an ecological view, however it is not resistant against moisture and therefore not capable of resisting delamination loads. Synthetic resins, such as phenol-resorcinol-formaldehyde (PRF) and melamine-urea-formaldehyde (MUF), which furthermore can be cost-efficiently produced from petrochemical raw materials, quickly replaced biological adhesives and are currently the most used adhesives for the bonding of timber.

In the late 1980's, a new type of reactive adhesives based on polyurethane was developed and introduced on the local market. The polymerization of polyurethanes goes back to developments made by Otto Bayer in 1937. By using polyurethane as an one-component adhesive, isocyanateterminated polyurethane-prepolymers react with water from the substrate or the surrounding air humidity. Thus the system is completely different to water-based polycondensation adhesives

such as urea-, melamine- or phenol-resin in that they include water as a solvent and use an additive hardening component for curing at room temperature.

Even though one-component polyurethane (1C PUR) exhibits favorable characteristics, such as its ductile material behavior or its modifiability in terms of reactivity and viscosity, deficits existed regarding its thermal stability in comparison with PRF or MUF. In the past, the resistance of 1C PUR in a re situation has been doubted. As a result, research facilities, standardization organizations and the industry have strived towards developing new standards and test methods.

The developed tests partly require that the adhesive must perform equally or better than the bonded wood. 1C PUR adhesives, developed in the 1990's, were not able to pass these tests.

Knowledge regarding the thermal resistance of wood bonding with 1C PUR was limited and available publications on the topic were mostly based on commercially available adhesives without knowledge of the chemical composition. Due to this lack of suitable data, a research project by the adhesive producer Purbond in Switzerland and the raw material producer Bayer MaterialScience in Germany together with the Wood Physics Group of the Institute for Building Materials at ETH Zurich, was initiated to increase the state of knowledge of bonding with 1C PUR. Within this dissertation, basic investigations on the structure-property relationships of one-component moisture-curing adhesives under thermal load were initiated to create a basis for new developments by the adhesive producers.

About 10 years ago the majority view regarding the thermal stability of 1C PUR adhesives was as a disqualifying characteristic for its use in structural applications. Publications by different authors presented results of adhesive tests at elevated temperatures, which revealed deficits in the adhesive strength compared to polycondensation resins, such as PRF or MUF for example.

However, investigations within this thesis clearly showed that a one-sided view on this type of adhesive can not sufficiently answer the question if polyurethane adhesives in general are appropriate for use in structural applications at elevated temperatures. The differentiated view on prepolymers, which are the basis for the application oriented adhesives, reveals that as a result of the wide variety of PUR chemistry, a wide variety in the resulting properties is also possible.

By systematic modification of the hard segment content and the cross-linking of the prepolymers, the thermal stability could significantly be increased.

In the further formulation of the adhesives it could be shown that the use of selective types of inorganic and organic filler materials also significantly improved the thermal stability of 1C PUR adhesives. These findings were directly incorporated into the ongoing development of new products of the adhesive producers. The new standard for adhesive testing at elevated temperatures in the USA (ASTM D 7247, 2007), which requires a thermal stability of the adhesive that is higher than that of wood, close to its ignition temperature, was in fact a hurdle on which previous polyurethane systems failed. This thesis contributed to the development of a new generation of 1C PUR adhesives that are able to outperform the thermal stability of wood as measured by the aforementioned standard and pass the test.

From the scientific point of view the thesis provides findings in the special field of 1C PUR adhesives for structural applications of engineered wood products that have not been previously published and therefore extends the knowledge of adhesives directly. Furthermore, results of previous publications have been partly reconfirmed, however, some generalized statements regarding the thermal stability of 1C PUR adhesives have been disproved or revised. The close collaboration between the raw material producer Bayer MaterialScience, the adhesive producer Purbond and the wood physics group at ETH has enabled a scientific process that otherwise would hardly be possible.

From these perspectives, the thesis provided a valuable contribution to the development of 1C PUR adhesive for structural applications on the one hand and to the wider usage of the natural resource of wood on the other.

