

Bio-based alkyds by direct enzymatic bulk polymerization - DTU Orbit (09/11/2017)

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Alkyd coating systems have been largely used to preserve exterior wood applications as well as to provide them with a decorative appearance. In the current stage of sustainability concerns, there has been a stronger focus on development and production of bio-based coating components, heading toward a totally bio-based formulation. In this context, the biggest challenge is development of bio-based analogues to classical alkyd resins (or alkyd), which is up to 50% fossil based. In addition, all the remaining components of an alkyd coating formulation are also needed to be prepared from renewable raw materials before a 100% bio-based alkyd paint can be realized.

In this project an enzyme catalyzed bulk polymerization method for direct production of alkyds has been developed. The objective has been to make it possible to produce binders at much lower temperatures as well as to achieve a higher degree of control over the polymerization reaction. The process was used to prepare new and 100% bio-based resins. The developed enzymatic method is simple to perform, robust and allows the preparation of alkyds with much higher control over the chemical structure compared with the corresponding traditional method. Bio-based alkyds prepared from a combination of glycerol, and tall oil fatty acids, and azelaic acid by enzymatic polymerization show improved hydrophobicity and lower glass transition temperatures compared to an alkyd prepared from the same raw materials by a classical boiling method. The enzymatic method results in a higher degree of control over the polymerization process, making it possible to optimize the binder structure to a specific degree of branching. Alkyd photostability of glycerol-based alkyds can be improved by increasing the alkyd's branching level, and subsequent development resulted in optimized structures. It was aimed for further improvement of alkyd photostability through the development of new pentaerythritol-incorporated alkyds with high degree of branching. In order to make it possible to incorporate pentaerythritol into alkyd structures in enzymatic polymerization, a new type of pentaerythritol derivatized with azelaic acid (or penta-aze) was examined and tested for the production of more branched alkyd systems. A photostability test validated the concept, and the method also resulted in alkyds with improved hydrophobicity and lower glass transition temperatures compared to a corresponding classical reference. In a further development of the system, it has been found possible to use the esters of pentaerythritol and stearic acid in combination with the penta-aze derivative for the preparation of pseudo alkyds containing only pentaerythritol as polyol with high degree of branching. Moreover, the studies on more sensitive monomers such as itaconic acid in enzymatic polymerization has showed that the method is useful in the production of alkyds from such building blocks, which could not be prepared by the corresponding classical boiling method at high temperature. Such systems are considered as a good option for binders with improved curing properties.

In the project various aspects of preparing a bio-based alkyd formulation have also been investigated. In particular, a reaction setup for production of larger amounts of traditional alkyds was designed to allow the production of up to 500 grams of alkyds under inert atmosphere. This system has been used for preparation of a number of bio-based alkyds by classical cooking and provided a selection of physical properties as a function of diacid chain length. The synthesis set up was developed further to enhance reproducibility and emulsification of binders, which ultimately resulted in production of 300 g of a fully biobased alkyd. This binder was efficiently emulsified with a bio-based emulsifier, formulated and subsequently sent to an outdoor exposure, where it will be evaluated over the coming years.

Finally, the project has also been working on the coupling between reinforcement agents and the binder in alkyd coatings. For this purpose, two different types of silica particles were modified with rape seed oil fatty acids or tall oil fatty acids (TOFA-silica), respectively. Tests of TOFA-silica particles have demonstrated that their functionalized surface markedly altered their solubility, but provided only moderate improvement in the mechanical properties of the alkyd.

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