

ABSTRACT

In the recent years, increasing demands have arisen to develop new and/or optimize existing materials. The production and usage of the conventional petroleum-based materials are very damaging to the environment. Therefore, the current research is directed to seeking new bio-based polymeric materials. In the present doctoral thesis, the preparation and characterization of novel polymeric materials, based on polybenzoxazines and epoxy resins, were investigated. The main advantage of polybenzoxazine and epoxy materials is their remarkable flexibility in the field of molecular design. Moreover, their preparation is relatively simple and inexpensive. In the first part of the doctoral thesis, the focus was oriented to the preparation of benzoxazine monomers with surfactant properties. The synthesized benzoxazine surfactants were used to stabilize aqueous epoxy emulsions. From these emulsions, polymer coatings were easily prepared by their drying and curing at an elevated temperature. During curing both epoxy resins and benzoxazine surfactants reacted and crosslinked into a copolymer network. Therefore, no structural voids were formed in the final coating formulation and the mechanical and thermal properties of the so-prepared copolymers were consequently improved.

In the second part of the doctoral thesis, new bio-based benzoxazine monomers were synthesized from raw materials, such as phenols, primary amines and formaldehyde. Since the stocks of fossil fuels are limited, there are needs to develop new bio-based materials. Natural phenols, like cardanol (from cashew nut) and guaiacol (derived from lignin), alongside with natural amines, such as furfurylamine (from vanillin) were used to prepare novel bio-based benzoxazines. One of the main disadvantages of polybenzoxazines is their relatively low crosslink density. This was especially evident for the polybenzoxazines, based on bio-based precursors. However, the crosslink density was significantly improved by the modification with other polymeric groups. New benzoxazine monomers with additional reactive groups, such as oxazine, epoxy and furan ring/groups, were prepared and examined. The sample, where benzoxazine monomer was modified with epoxy groups, has achieved by far the highest value of crosslink density. During the curing process of benzoxazine monomers, the oxazine heterocycle was opened and free hydroxyl groups were formed. Epoxy groups reacted with free hydroxyl groups to form additional covalent bonds, which consequently increased the crosslink density of the resulting copolymer. Both mechanical and thermal properties were considerably enhanced as well.

Another disadvantage of polybenzoxazines is their high temperature of curing. The addition of various accelerators decreased their curing temperatures. Phenolic and amine compounds have proven to be the best accelerators. It was observed that used accelerators were actively involved in the curing process of benzoxazine monomers, and thereby became a part of (co)polymer structure. The addition of toluene sulfonate, as an accelerator for the curing of benzoxazine monomers, reduced the curing temperatures even more significantly, compared to neat benzoxazine monomers. However, the curing mechanism has changed, and the final polymers have become considerably more brittle. Since the excellent mechanical properties of the final polybenzoxazine material are crucial for its usage, the accelerators based on phenolic and amine compounds were used exclusively in the following stages.

In the third and final part of the doctoral thesis, the composite materials, based on polybenzoxazines and/or epoxy resins, were reinforced with the addition of cellulose fibers. The mechanical and thermal properties of resulting composites were enhanced.

Keywords: benzoxazine, epoxy resin, curing, crosslink density, bio-based polymer