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Biobased, thermoreversibly crosslinked polyesters

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Summary

Thermoset materials are widely employed due to their superior chemical resistance and mechanical properties. The reason these materials perform so well is due to the fact that they consist of a three-dimensionally crosslinked network. One example of such a thermoset are unsaturated polyester resins which are able to form this network via the *in situ* polymerization of styrene. Unfortunately there are two main drawbacks tied to the use of these resins: styrene is a hazardous chemical which requires special precautions to work with. Furthermore the crosslinked network which gives the material its superior properties also ensures it is not recyclable in any way. Fortunately due to uncertainty in oil prices and availability and an increasing understanding of the effects of carbon emissions there is a global increase in awareness regarding the use of materials obtained from sustainable resources. In the polymer industry in particular large strides are being made to implement green alternatives for currently employed materials. While this might yield a less toxic alternative to styrene, this approach does nothing to address the problems that arise at product end of life, namely the waste generated upon disposal. The first chapter of this thesis gives an overview of some of the processes that have been successful in going green as well as various strategies to address the waste generated by enabling the recycling of the final material.

While the added functionality which is common in most biobased compounds often presents difficulties both in obtaining a pure compound as well as controlling any side reactions, they can sometimes present opportunities that were otherwise unavailable. An example of this is diphenolic acid, a diol obtained from the platform chemical levulinic acid which is a structural analogue to bisphenol A apart from an additional pendant acidic functionality. Realizing the potential of diphenolic acid, chapter 2 describes its modification along with the subsequent incorporation into a polyester. The modification consisted of the addition of a furan group, utilizing the acidic functionality present. Polymerization was performed with terephthaloyl chloride which gave an alternating polyester in good yields. As every other monomer in this polymer contained a pendant furane functionality the material could be easily crosslinked by the addition of

bismaleimide. The bismaleimide was able to react via the Diels-Alder reaction in order to create a three-dimensionally crosslinked material and due to the reversible nature of the Diels-alder reaction the material obtained could be decrosslinked by elevating the temperature. Unfortunately the temperature needed was too close to the degradation temperature resulting in loss of material properties.

The degradation of the polymer upon decrosslinking is tackled in chapter 3, which describes the optimization of reaction conditions during polymerization. As expected, the addition of phenol, which can act as a chain stopper during the polymerization reaction, results in short-chain polyesters. The reduction in chain length leads to a reduction in glass transition temperature of the uncrosslinked polymer, which in turn lowers the temperature of the decrosslinking reaction. As the processing and degradation temperature now lie further apart, the polymer no longer undergoes any degradation during processing. This is shown by successfully reworking spent polymer by grinding and remolding, resulting in samples with identical material properties as the original material.

Despite the excellent reworkability, the crosslinked polymer is very brittle, limiting its potential applications. Chapter 4 describes the efforts made to improve this by modifying the impact properties of the crosslinked polymer. In this chapter the preparation of various blends of the polyester with furan functionalized EPDM rubber is described. The furan functionality on both polymers enables covalent interactions via the Diels Alder reaction between both components in the polymer blend, reducing phase separation. A blank experiment with a non-functionalized EPDM rubber was performed which showed no improvement on mechanical properties, whereas a correlation between rubber content and impact strength could clearly be seen for the furan functionalized EPDM. This is a strong indication for successful covalent interaction of the two components.

In order to further control the mechanical properties of the crosslinked polymer, compositions containing various bismaleimide crosslinkers in various amounts were prepared. The results of which are described in chapter 5. Upon analysis of the different compounds it became apparent that crosslinking was possible with a wide range of bismaleimide molecules. However for all formulations it was obvious that not each maleimide group participates in Diels-Alder coupling with a

furan in the final product. Even when half of the stoichiometric amount of bismaleimide relative to the furan groups present was added there was no visible effect on material properties.

Finally, chapter six briefly addresses the largest steps that need to be taken on the road to a truly sustainable product, namely the synthesis of the main precursor: diphenolic acid, as well as the implementation of the final polymer in fiber containing formulations. The synthesis of diphenolic acid could be greatly improved by the implementation of heterogeneous catalysts. Some preliminary experiments have shown that the use of immobilized heteropolyacids in combination with diethylaminothiol could be a good candidate for this reaction. Furthermore the compatibility of sustainable fiber materials (flax and jute) with the polymer matrix was tested. As the base polymer proved too brittle to be properly tested on a tensile machine only qualitative conclusions could be drawn from these compounds: the use of flax and jute improves the toughness of the resulting compound, also the use of jute mats yielded a compound which was able to withstand 5 kN of tensile force, a significant improvement.

Overall, the work in this thesis covers nearly the complete chain from platform chemical levulinic acid up until real life application in fiber reinforced materials. The successful recyclability and reworkability indicate that this polyester might be a sustainable alternative to the currently employed polyester resins.

