In-depth study of polyamides containing galactaric acid-derived building blocks

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Chapter 8 VALORIZATION

Inspired by the possibility to transform waste generated along the food production into useful materials, the author led a reader of this thesis through the straightforward synthesis of homo- and copolyamides from natural resources. During this research, attention was given to the properties of polymers as well as to the in-depth analysis of undesired phenomena occurring during the synthesis. Through different parts of this research dissertation, the potential problems regarding the synthesis and subsequent processing of carbohydrate-derived polyamides were discussed and solutions for those problems were proposed. The presented family of compounds, being built from not-yet commercialized building blocks, logically complements the existing set of materials with new combinations of functionalities. In case of building blocks used in this study, belonging to the “GalX” family, these functionalities predominantly encompass high rigidity and good thermal resistance. The incorporation of GalX building blocks generally elevates the glass transition region of copolyamides, while lowering their melting point. Lower melting point facilitates processing which is of considerable significance in the plastics industry. A higher built-in content of cyclic and irregular moieties results in amorphous and transparent polyamides, which adds the esthetic value as it can be used in decorative elements or in manufacturing of materials, for which transparency is a requirement i.e. lamp shades.

The utilization of the renewable sources for the purpose of polymer production has a significant socio-economical aspect. The vast majority of world-wide plastic production is based on the non-renewable fossil industry.\(^1\) In order to provide sustainable growth of society the long-term availability of resources must constitute the inherent part of the development strategy including alternatives to non-sustainable sources.\(^2\)\(^-\)\(^3\) One efficient strategy is based on the utilization of the biomass to mine chemical compounds, however, not all forms of this approach are entirely justified e.g. plantations require large areas to sustain, which might interfere with agricultural area for food production. Similarly to other fields, the technology to develop this branch of industry started from a not very sustainable but highly efficient route based on the utilization of the world food plantations like the production of bioethanol from sugar-cane.\(^4\) Naturally, shortly after those plans were executed the monitoring agencies started to send alarming messages regarding the foreseen repercussions of the competition between food resources and the industry. This 1\(^{\text{st}}\) generation biomass is currently slowly
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replaced by 2\textsuperscript{nd} generation biomass, e.g. sugar beet pulp which is a waste product from sugar production. The notable aspect of this transition includes the elimination of the competition between the world food supply and industry, and a clever waste management.

Overcoming humanitarian challenges certainly constitute one of the most important aspects of this research and is part of the long-term crisis prevention. In order to develope usable technology the possible materials from biomass have to be critically evaluated and the optimization of the bio-based materials in such a way that allows achieving the ultimate performance must be performed. Hereby, technology assessment is performed for each section of this research dissertation.

The synthesis of polymers from carbohydrates is often problematic due to the “caramelization” of monomers at higher temperatures. Furthermore, the acetals are compounds, which are generally susceptible to degradation in acidic conditions, thus the adjustment of the synthetic methods is necessary. In Chapter 2 and in Chapter 4 it is presented in detail which obstacles can be encountered during the preparation of polyamides and alternatives to more troublesome procedures. The presented alternative procedures are industrially relevant and, as a consequence, are foreseen to be predictively transferred to upscaling procedures.

A vast amount of bio-based polyamides contain characteristic amber-like appearance, which by itself is not a major issue except that understanding the origin of the underlying phenomena is of fundamental value. Having better insight into the nature of side reactions further improves the control level over the polymerization and this was analyzed in Chapter 5.

The bio-based polyamides containing a high content of cyclic moieties can be considerably rigid, which could cause the loss of mechanical performance. The produced polymer must be thermally stable not only during the synthesis, but during the processing as well, in order to obtain ready-to-use specimens. The improvement of mechanical properties of materials and their thermal processing is described in Chapter 7 and delivers important information about how to handle bio-based polyamides.
Figure 8-1 The graphical representation of the valorization of the developed technology. GalX polyamides prepared in this project were valorized as lamp shades (left and right bottom pictures).

Lastly, this work can drastically expand the scope of applications of carbohydrate-based materials. Based on the inherent acetal chemistry of GalX building blocks, it might become possible to control which and how many functional groups can be incorporated into a singular monomer structure to be polymerized. This allows for further functionalization of polymers therefrom as well as modification of important parameters i.e. glass transition region or hydrophilicity of polymers. Additionally, the introduction of those moieties into polyamides is changing the balance in different interactions between molecules and chains in the polymeric macro-material. This balance finally helps to determine the general properties of the material. The fundamental understanding of the influence of the protection group onto the reactivity of the flanking carboxyl groups, besides the influence of the cyclic moiety on interactions between polymeric chains, is the topic of Chapter 3 and Chapter 6.

With this valorization addendum this thesis comes to an end. After 4 years of experiments, a simple sugar beet was transformed into a material. Regardless of some left-over flaws, which still need to be solved and a couple of questions, which still need to be answered, the project eventually resulted in the development of technology that is useful and even necessary to
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manufacture an expanded set of bio-based polyamide articles, ultimately sourced from local sugar beet resources.
REFERENCES


