Maastricht University

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

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SUMMARY

Carbohydrates are a widespread class of compounds, which are recognized for their nutritious values and, more recently, as an alternative source of chemicals. In the time when the world struggles with different environmental challenges, exploration of biomass becomes of increasing socio-economical value for the world population.

Polymers (Greek: *poly*-many, *mer* – parts) are macromolecules, which are composed of many repeating units and therefore possess unique properties. Polymers "shape" the world as we know it today. Plastic bags, food packaging, plastic in medicine, in cars, at homes – society consumes vast amounts of plastic items and simultaneously generates piles of plastic waste, which is – in most cases - still non bio-based and/or non-biodegradable.[1] From the early XX century, when first synthetic polymers were intentionally produced, this class of materials developed an extraordinary career. Polyamides, wider known as nylons, share a big part of this popularity. Those synthetic polymers contain peptide bond linkages between the repeating units.

The presented study combines the abovementioned points, focusing on the synthesis of polyamides from carbohydrate-derived building blocks. Specifically, cyclic derivatives of galactaric acid (GalX) are used to prepare bio-based polyamides. The starting molecules are obtained by the extraction and chemical modification of sugar beet pulp, which is, in fact, a waste product generated along the sugar production. The production of galactaric acid does not compete with the production of food and sugar beet can be locally sourced to support local economies.

The polymerization of GalX results in amorphous or semicrystalline polymers with elevated glass transition temperatures in comparison to aliphatic, linear analogues. The crystallinity of polymers can be highly suppressed with increased amount of incorporated GalX. The homopolymers composed of equimolar ratio of diamine and GalX are amorphous. Depending on the rigidity of the diamine, the glass transition temperature (T_g) of such polymers can be tuned from 50 to 220ºC. The reactivity of the different biacetalized monomers towards the diamines greatly depends on the chemical variation of the α carbon substituent. Compared to non-substituted linear monomer, increased reactivity was observed for different biacetal derivatives of galactaric acid. The polymers derived from the modified galactaric acid monomers vary in terms of glass transition temperature, thermal stability, hydrophilicity and

functionality. The utilization of carbohydrate-based monomers for the synthesis of polyamides at high temperature can be challenging due to potentially limited stability of the monomers. Investigation of the chemical structures and the analysis of the side reactions helps to reduce effectively the undesired degradation-related phenomena. When the diacid derivative of GalX is polymerized the internally catalyzed deprotection of acetal leads to cross-linked and/or degraded product. The utilization of diethyl esters of GalX usually eliminates the hydrolysis, but leads to the alkylation of amines, which, in consequence, lowers the molecular weight of polymers therefrom.

The properties of polyamides greatly depend on an interaction between amide protons and the oxygen present in the acyl group. In the acetals of galactaric acid other moieties are present which also possess oxygen. The interactions between amide protons, usually occurring in polyamides, are interfered and the polymers have different properties. Furthermore, cyclic moieties are considerably bulky. Consequently, the incorporation of GalX into aliphatic polyamides decreases the density of hydrogen bonding and suppresses crystallinity.

Once synthesized, GalX polyamides are stable under processing conditions and can withstand exposure to high temperatures. The GalX-based polyamides can be blended with other polyamides to form two-phase systems with increased modulus and lowered elongation at break. The miscibility differs depending on the used polyamides. With aliphatic and aromatic-aliphatic GalX polyamides a two phase blend was obtained, however, blending GalX polyamides containing fully aromatic 1,4-phenylenediamine resulted in a one phase system. The occurrence of transamidation between blend components leads to reactive compatibilization.

REFERENCES

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