TAL TECH

Synthesis of thermoplastic cellulose derivatives in environment of ionic liquids

Summary

Sustainable thermoplastic polymers are developed and investigated to partly or fully replace non-renewable-resources-based materials for melt processing technologies. Cellulose appears to be a nearly unlimited renewable resource for polymeric materials. Discovery of dissolution processes of cellulose in ionic liquids opens several new routes for functionalization. Thermoplastic cellulose derivatives can be prepared without use of plasticizers, by attaching long-chain ester branches to the macromolecule of cellulose. The research challenge is to find chemically stabile, efficient and recyclable solvent(co-solvent) systems and functionalization routes, which have also potential for industrial upscaling. Also, the functionalization route should provide control over degree of substitution and mixed branching if necessary.

Research field:	Chemical, materials and energy technology
Supervisors:	Andres Krumme Elvira Tarasova
Availability:	This position is available.
Offered by:	School of Engineering Department of Materials and Environmental Technology
Application deadline:	Applications are accepted between November 16, 2020 00:00 and December 16, 2020 23:59 (Europe/Zurich)

Description

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The most important renewable resource for producing polymeric materials and composites is cellulose. Its annual production in biosphere is estimated 90 gigatons. Still, it has some drawbacks for processing: it is hard to dissolve cellulose and the material is not thermoplastic in its natural state. Melt processing, however, has several advantages over solution processing, such as high productivity, simplicity and flexibility. Melt processing needs cellulose to be made thermoplastic by functionalizing and this needs the material to be dissolved at first.

Novel and developing solvents for dissolving and functionalizing cellulose in homogeneous conditions are Ionic Liquids (ILs). They are considered to be more sustainable compared to well-known Viscose, CarbaCell and LycoCell processes which are still considered as harsh solvent systems. ILs are highly polar and therefore can break the hydrogen bonds between macromolecules of cellulose. Besides, ILs can be easily regenerated by several methods depending on their composition. IL can act both as a solvent and a functionalization medium.

The first generation of ILs for cellulose dissolution was mostly imidazolium based. However, these ILs have be found to be of low stability and destructive for cellulose macromolecule. Nearly missing vapour pressure of these ILs is preferable for simple systems, as they are not volatile and anti-solvent (water or alcohol) can be easily removed by destilation after precipitation of cellulose. Still, this can be also an issue if more complex dissolving systems, as biomass or cellulosic waste, are in use as several organic or inorganic constituents of low or missing volatility tend to stay in the IL-s.

Therefore, a new generation of ILs is developed in recent years for improving stability and recyclability. Distillable acid–base conjugate ILs were developed, which dissociate back to their original components, organic acid and base at higher temperatures. The components have significantly higher vapour pressure than the ionic compound and are therefore distillable. The most common acids are propionic or acetic acid and several bases are described as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,1,3,3-tetramethylguanidine (TMG). These distillable ILs vary regarding dissolving capacity, viscosity, susceptibility to hydrolysis and price but all are relevant candidates for dissolution of cellulose and development continues. Probable one of the most studied distillable IL is [DBNH][OAc] which is the main solvent for IonCell process (ioncell.fi), which should start in industrial scale on year 2025 for producing cellulosic fibres.

Distillable IL is a suitable medium for homogeneous esterification of cellulose. One can use classical routes for esterification with carboxylic acid chlorides or anhydrides. Acid side products can still damage the cellulose polymer by hydrolysis. One can use iso- or vinyl esters instead which lead to ketones or aldehydes as side products. Those are also volatile and can be easily removed by conducting the esterification at low pressures. Moreover, the modern distillable IL based systems allows to overcome several issues related to synthesis of long chain branched cellulose esters. For example DBU/DMSO/CO2 system allows efficient transesterification with fatty vinyl esters, producing long chain branched cellulose esters of high degree of substitution. Most of the above described shorter-chain branched amidinium ILs are considered as nontoxic.

One can conclude that ILs are the future of sustainable processing of cellulose. Still, describing relations between structure and physical properties of the materials produced by several ways listed above, just begins. The above-mentioned materials differ significantly from commercialized products due to different dissolution mechanisms and functionalization patterns and should be therefore carefully studied. The research challenge is to find chemically stabile, efficient and recyclable solvent(co-solvent) systems and functionalization routes, which have also potential for industrial upscaling. Also, the functionalization route should provide control over degree of substitution and mixed branching if necessary.

Responsibilities and tasks
The Ph.D. student has the following tasks as an active member of the thematic research group:

- Composing comprehensive literature survey of the state of the art in the field of functionalization routes of cellulose in environment of ionic liquids.
- Active participation in elaboration of the most feasible solvent systems and functionalization medium, also consulting research collaborates abroad (University of Helsinki, etc.)
- Synthesis and characterization of the derivatives, esters and mixed esters in laboratory scale, chemical characterization of the derivatives, finding relations between functionalization conditions and properties of the novel materials.
- Participation in upscaling of the most relevant functionalization routes for producing the derivatives for technological trials.
- Participation in elaboration of recycling methods of the solvent systems.
- Publishing of the results as journal articles and conference presentations.

Qualifications:
MSc in organic chemistry / biochemistry /polymer chemistry

The applicants should fulfill the following requirements:

- The candidate should be familiar with methods, procedures and safety of laboratory of organic chemistry, which allows to work independently.
- Previous experience in cellulose chemistry would be highly appreciated.
- Previous experience in the most relevant characterization methods (FTIR, NMR, titration, GPC, DSC, rheology) is also expected.

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