Biomass as source of furan-based plasticizers: an alternative to phthalates

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1. Introduction

Modern society relies heavily on polymeric materials, of which polyvinyl chloride (PVC) is the third most globally produced synthetic polymer.[1] Its exceptional characteristics (high hardness, good mechanical and insulating properties) make it a highly versatile material. In most cases, the incorporation of additives is required to enhance the polymer performance. In particular, plasticizers are widely used in PVC to improve its flexibility by lowering the glass transition temperature (T_g). The manufacture of soft PVC consumes about 85% of the global plasticizers market, where in 2016 Asia Pacific was the leading consumer followed by North America and Europe.[2] During the last decade, the worldwide annual production of plasticizers was around 5 million tons,[3] and the global market is forecasted to reach US$ 26.3 billion by 2025.[2] The largest class of plasticizers of the 21st century consists of phthalates that are petroleum-based compounds among which di-2-ethylhexyl phthalate (DEHP) and diisononyl phthalate (DINP) are the most used. Nowadays, rising environmental concerns, the increasing awareness of their toxicological effects and the depletion of petrochemical resources are driving the great interest in replacing these traditional plasticizers.[3] Consequently, the scientific community is continuously searching for alternative renewable sources for the production of plasticizers.[4] Driven by the decreasing of oil reserves and its competitive price during the last century, biomass is considered the most promising replacement feedstock for petroleum.[5,6] Lignocellulosic biomass is the most abundant resource on earth with tons of waste being generated annually by forestry, agricultural and agro-industrial activities. Moreover, lignocellulose avoids any conflict with food supplies, therefore its valorization has crucial sustainability advantages that offer access to green chemicals production.[7] Due to their potential as feedstocks for chemicals and fuels, furanic monomers such as 5-hydromethylfurfural (5-HMF) plays an essential role as bio-based key intermediate among the various biomass derivatives.[10] Its production is based on an acid-catalyzed hydrolysis of cellulose to glucose, followed by isomerization to fructose and dehydration under acidic conditions to finally yields 5-HMF. The preparation of 2,5-furandicarboxylic acid (FDCA) *via* oxidation of 5-HMF has received a considerable interest, due to its great potential as platform chemical.[8,9] The use of these bio-based intermediates is a decisive step towards "greener" and non-toxic plasticizers to replace the hazardous and oil based phthalates.

1. Natural plasticizers based on 5-HMF and FDCA

Novel routes as well as scale-up of processes for 5-HMF production are actively being researched. AVA Biochem BSL AG started the first industrial 5-HMF production facility in 2013.[6] The catalytic oxidation of 5-HMF leads to FDCA, reaction which can be carried out chemocatalytically on several supported-metal catalysts.[7,11] FDCA has a high application potential as bio-based intermediate for monomers production,[12] polyesters, polyamides and plasticizers.[8,13,14] The joint venture Synvina,, recently founded by Avantium and BASF, is developing the production technology and marketing of FDCA and polyethylene furanoate (PEF).[15]

The synthesis of esters of FDCA and their use as plasticizers was first described in 1994.[16] Moreover, different esters of 2,5-bis(hydroxymethyl)furan (BHMF) have recently been proposed as potential replacement for phthalates, showing full compatibility with PVC, low migration and plasticizing effect comparable to that of common phthalates.[17] However, furan-based plasticizers are not commercialized yet and the knowledge related to their synthesis and applications still needs to be deepened. A collaborative research project between ITMC (RWTH University of Aachen), DWI and FILK focuses on the development and characterization of a wide library of furan-based plasticizers starting from 5-HMF and FDCA (**Figure 1**).

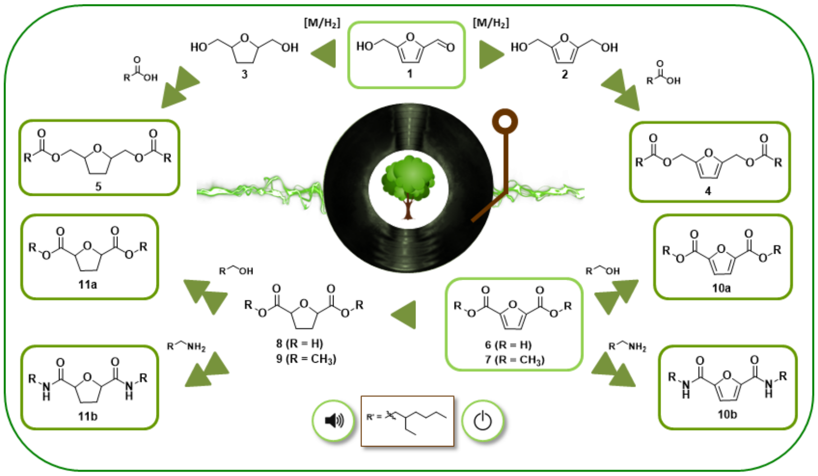

Figure 1. The library of furan-based plasticizers

5-HMF (**1**) yields BHMF (**2**) and ultimately to BHMTHF (**3**) *via* metal-catalyzed hydrogenation.[6,18] Moreover, their respective esters **4** and **5** are accessible *via* acid-catalyzed esterification (e.g. with 2-ethylhexanoic acid). Similarly, FDCA (**6**) and its diester FDCA-Me_2 (**7**) can be hydrogenated to THFDCA (**8**) [19] and THFDCA-Me_2 (**9**), respectively. Subsequently, the diesters **10a** and **11a** are accessible *via* acid-catalyzed esterification or transesterification from FDCA and THFDCA or FDCA-Me_2 and THFDCA-Me_2 respectively in the presence of a certain alcohol (e.g. 2-ethylhexanol). In the same way, the diamides **10b** and **11b** can be obtained reacting the respective furanic intermediates with an amine, for example 2-ethylhexylamine. Moreover, this class of plasticizers can be broaden reacting each bio-based intermediate with alcohols and amines presenting different linear or branched carbon chains. The development of "greener" and harmless plasticizers *via* atom efficient synthetic routes based on 5-HMF and FDCA was successfully achieved. Furthermore, performance and application potential of furan-based plasticizers for coated textiles and plastic webs were evaluated.

2. Properties of furan-based plasticizers

In addition to the sustainable production based on biomass derivatives, furan-based plasticizers have a chemical structure that is similar to phthalate and cyclohexane plasticizers. Therefore, it is expected that furan-based plasticizers have similar application properties. For furan-based amides a high permanence due to a stronger adhesion in the PVC-plasticizer blend could be demonstrated.[14] Preliminary tests reveal that the compounds prepared in the project are able to lower the Tg of PVC in a better or similar way to the phthalate plasticizer DINP. Their thermal stability is comparable to several phthalates used as reference while the cold fracture resistance is moderate. The furanic diesters tested showed a much higher gelling capacity than phthalates, of which tetrahydrofuranoates tend to gel faster. The same behavior has been confirmed for plastisol and dryblend of PVC in the plasticizers and in particular compound **9a** has properties very similar to the phthalate DINP. In addition, these additives formally fulfil the requirements for synthetic coating application and show a very good foaming behavior with the possibility to produce imitation leather with foam layer. Furanic diamides **9b** and **10b** are suitable as potential co-plasticizers able to facilitate the dissolution of PVC in a plasticizers mixture due to a synergistic effect. In general, the specific properties of furan-based compounds make them suitable for a wide range of applications.

3. Conclusion

The future of the polymer industry is threatened by concerns regarding sustainability, environmental effects and human health combined with the depletion of oil resources. In this scenario, where the global request of plasticizers is increasing over the years, furan-based compounds are a promising alternative to the toxic and petroleum-based phthalates plasticizers. This collaborative project used 5-HMF and FDCA as biomass-based intermediates to develop a wide library of furan-based plasticizers obtained in high yields through easily scalable and reproducible synthetic routes. This class of compounds are suitable to be used as plasticizers for PVC since they have the ability to lower the Tg of the polymer and show thermal stability comparable to phthalates. In particular, furanic diesters present valuable properties such as high gelling capacity, good foaming behavior, moderate cold fraction resistance. They can be used for synthetic coating and imitation leather production. In conclusion, aiming to the replacement of phthalates, this research is considered a first step towards a green and sustainable alternative to broaden the range of commercially long-term plasticizer and increase the market share of bio-based compounds.

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