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Synthesis of Polyurethanes based on 17-Hydroxy-Oleic Acid obtained from Sophorolipids

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Abstract

Due to the worldwide shortage of petrochemical based resources, the usage of renewable bio-based raw materials for established and novel products becomes increasingly important.[1] Such bio-based resources are already used for the fabrication of a variety of products, e. g. paper, lubricants, detergents or cosmetics. In the future they are expected to emerge in many more applications in industry and household.[1]

A very promising approach relies on the use of glycolipids as a source of hydroxy-oleic acid.[2] Microbial glycolipids are produced for instance via fermentation from natural resources such as plant oils and sugar.[3] After fermentation complex product mixtures are obtained with the composition depending on the microorganism, substrate and fermentation time.[3] The successful use of microbial glycolipids and hydroxy-oleic acid (HOA) derived therefrom as bio-based intermediates requires reliable analytical methods as well as robust manufacturing processes for the synthesis and cleavage of bio-based molecules. In order to obtain hydroxy-oleic acids as bio-based intermediates, the acidic cleavage of microbial derived sophorolipid was investigated. In addition the implementation of HOA in polyurethane (PU) systems was explored.

1 Introduction

Bio-based raw materials for polyurethane and polymer synthesis are of great interest. Conventional raw materials are based on petrochemical intermediates.[4] The carbon chains of the polyols used are produced from mineral oil by cracking. Due to their poor biodegradability and their tendency to damage the environment, they have many disadvantages and the interest in sustainable alternatives for polymer synthesis is growing.[5] Bio-based raw materials have various advantages. They are virtually unlimited, inexpensive and environmentally friendly. Their physical properties are very similar to those of petrochemical-based polymers.[4],[6] The three most important plant-based raw materials are proteins, oils and carbohydrates.[7] The polymers most commonly found in nature are polysaccharides like starch and cellulose. However, low-molecular components can also be obtained by fermentation and converted into polymers by chemical

polymerization.[5],[8] For example, polylactic acid, polycaprolactone and other partially sustainable bio-based polyesters such as polybutylene succinates can be synthesized by chemical polymerization[9],[10] Vegetable oils, sugar or algae can be used as raw materials. Some bio-based polymers can already compete with petrochemical-based polymers in terms of price and properties.[6] However, most bio-based polymers are not yet competitive due to the high costs involved in the production of the raw materials and the process technology.

Sophorolipids are promising bio-based starting materials whose production has already been well researched[11],[12] They are microbially produced from bio-based raw materials such as sugar and vegetable oils. Sophorolipids are one of the most promising types of glycolipid biosurfactants, as the production organisms are not pathogenic and characterized by high productivity and substrate conversion.[11] The components of sophorolipids are sophorose, a diglucose and hydroxy-oleic acid. They are linked by a glycosidic bond. The sophorose unit may contain acetyl groups at 6' and/or 6'' positions. Lactonic sophorolipids (L-SL) can be formed by binding the carboxyl group of the hydroxy-oleic acid and the 4'' hydroxyl group of the sophorose moiety.[13]–[16] Derivatives of sophorolipids are promising candidates for novel bio-based polymers such as polyesters or polyurethanes.[17] Through chemical cleavage, such as saponification, sophorolipids can provide further basic building blocks for polymerization (Fig. 1).[2],[18]

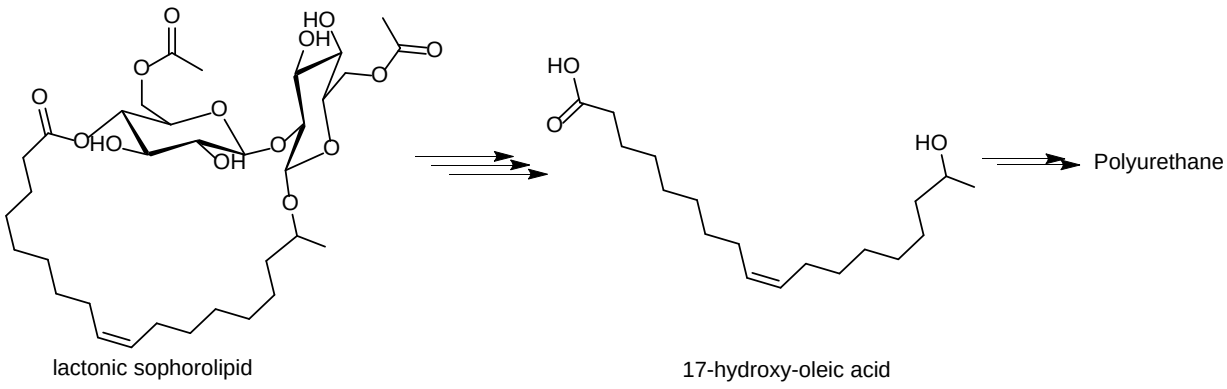

Fig. 1. Schematic illustration of the cleavage of lactonic sophorolipid to obtain 17-hydroxy-oleic acid.

The development of a synthesis route for hydroxy-oleic acids makes these available for further use in polymer synthesis. The special features of hydroxy-oleic acids accessible in this way are that they have terminal carbonyl function and hydroxyl functionality at (ω-1)-position (17-hydroxy-oleic acid). The use of ricinoleic acid, an isomer of the hydroxy-fatty acids (HFAs) synthesized here, is already known in literature.[17],[19]–[21] Ricinoleic acid carries the hydroxyl functionality at the twelfth carbon atom of the chain. This position of the OH group results in polymer chains with six carbon atoms in the side chains, which influence the properties of the polymer in such a way that they act as "plasticizers" by lowering the glass transition temperature. This prevents crystallization, even at very low temperatures[22] It is expected that the absence of side chains in linear HFA polyesters will

provide properties such as higher strength and higher T_G than poly(ricinoleic acid) esters[23] This opens up the possibility of producing polyesters with long hydrophobic carbon chains which can then be incorporated into polyurethane systems.

2 Materials and Methods

2.1 Chemicals

The lactonic sophorolipids used in this work were prepared as described in [24]. The lactonic sophorolipid and the deacetylated acidic sophorolipid were obtained with a purity of 97 %.

Tetrahydrofuran (THF, HPLC grade) and chloroform ($CHCl_3$, purity > 99 %) were obtained from Fisher Chemicals. Acetone (> 99%), acetonitrile (HPLC grade), hydrochloric acid (1M, HCl, grade: for analysis), dibutyltin dilaurate (DBTDL, > 95%), dibutylamine (> 98%), 1,6-hexanediole (1,6-HDO, synthesis grade) and hexamethylene diisocyanate (HDI, purity > 98 %) were purchased from VWR and Sodium hydroxide (purest) was obtained from Bernd Kraft. 4-tert-butylcatechol (99 % purity) was purchased from Acros Organics. Distilled water was taken from the in-house pipeline network.

2.2 Synthesis of 17-Hydroxy-oleic Acid (HOA)

For the synthesis of (ω-1)HFA, lactonic sophorolipid (L-SL) was used as starting material, which was produced *via* fermentation by the yeast strain *Starmerella bombicola*. L-SL with a purity of approx. 97 % dissolved in a 5 molar sodium hydroxide solution at 80 °C. 5 M NaOH was added until a constant pH value was achieved. The pH value was adjusted to 3.5 using HCl. Crystallization of the product was performed at 7 °C. The product was separated and dried by lyophilization. A white powdery product (deacetylated acidic sophorolipid, A-SL) was obtained. Identification was performed by HPLC MS, IR and GPC measurements. 8 mmol of the resulting A-SL were weighed in a 100 mL round bottom flask and dissolved in 50 mL 1 M HCl. The reaction was carried out at 80 °C. The reaction progress was monitored by HPLC measurements. The pH value was then adjusted to 3.5 using NaOH and a liquid liquid extraction (dist. $H_2O/CHCl_3$) was performed. The excess solvent was removed under reduced pressure. The product obtained is yellowish oily (yield: 83.5 %). For the subsequent ester cleavage, a 5 M NaOH solution was used at 80 °C and stirred for approx. 16 hours. This was followed by another liquid-liquid extraction (dist. $H_2O/CHCl_3$). The excess solvent was removed under reduced pressure. A brownish oily liquid was obtained.

2.3 Oligomerization of HOA

The synthesis of OH-terminated hydroxy-oleic acid polyester was carried out on the basis of Nefzger et. al.[25] 0.03 mol 17-hydroxy-oleic acid and 0.006 mol 1,6 hexanediol were placed in a 100 mL multi-necked flask, equipped with a Vigreux column, thermometer and distillation bridge as well as a collecting flask. In addition, 0.042 mmol 4-tert-butylcatechol was added as radical scavenger. A heating-agitating unit with a temperature sensor was used for heating. The reaction mixture was heated to 200 °C over a period of approx. 60 min and

the resulting water was distilled off. After 8 h reaction time tin chloride dihydrate was added. After a reaction time of 24 h, the reaction was stopped.

2.4 Synthesis of HOA-PES polyurethane

For the synthesis of HOA-PES polyurethane, 3.5 g of the product prepared according to section 2.3 was dissolved in 25 mL tetrahydrofuran and heated to 60 °C. 0.58 g HDI and 500 ppm DBTDL were added. After 16 h, the NCO content was titrimetrically and the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The product obtained was a dark brown rubber-like lump. Excess HDI was reacted with an excess of a 0.1 M dibutylamine in acetone solution.

2.5 Analytical methods

HPLC (High Performance Liquid Chromatography) measurements were performed with a Shimadzu Nexera XR equipped with a BM-20 A communications bus module, 2 x LC-20 AD XR, a SIL D0ACXR auto sampler, a column oven and a VWR-ELSD 80 light scattering detector (N_2, 3.5 bar, 40 °C). A C18 RP La Chrom II (Hitachi Ltd., Japan), 4.6 x 250 mm, 5 µm column was used. The measurements were performed at 30 °C with an acetonitrile-water gradient with a flow rate of 1.0 mL min^{-1}, starting with 25 min. 50 % acetonitrile, followed by 60 min. with a linear gradient to 99 % acetonitrile. Samples contain approximately 2.5 mg mL^{-1} substance in tetrahydrofuran. The samples are measured without further preparation.

The NCO-content was determined titrimetrically according to DIN EN ISO-11909-2007.[26] A sample of the reaction mixture was mixed with 10 mL of a 0.2 M dibutylamine solution in acetone. The mixture was diluted with 40 mL acetone and titrated against 0.1 M hydrochloric acid. The automatic titration was performed on a TitroLine 7000 titration unit from SI Analytics. The result is given in weight percent of the NCO groups in relation to the sample weight. The NCO value is calculated according to the following formula.

$$\%NCO = \frac{(V_{Blank} - V_{EP}) \cdot f \cdot c(HCl) \cdot M_A}{10 \cdot m_s} \qquad (6\text{-}1)$$

with:

	V_{Blank}	Blank in mL
	V_{EP}	Consumption Titrant at equivalence point in mL
	$c(HCl)$	Concentration Titrant in mol L^{-1}
	f	Titer
	M_A	Molecular weight NCO; 42.02 g·mol^{-1}
	m_s	Sample mass in g

3 Results and Discussion

3.1 Synthesis of 17-Hydroxy-oleic Acid

The comparatively high purity of L-SL (approx. 97 %) provides an excellent starting point for optimizing the synthesis route for the production of 17-hydroxy-oleic acid. The synthesis sequence is based on the opening of the lactone ring[2],[18] and successive separation of the hydroxy-oleic acid fragment from the sugar units by acidic hydrolysis (Fig. 2).

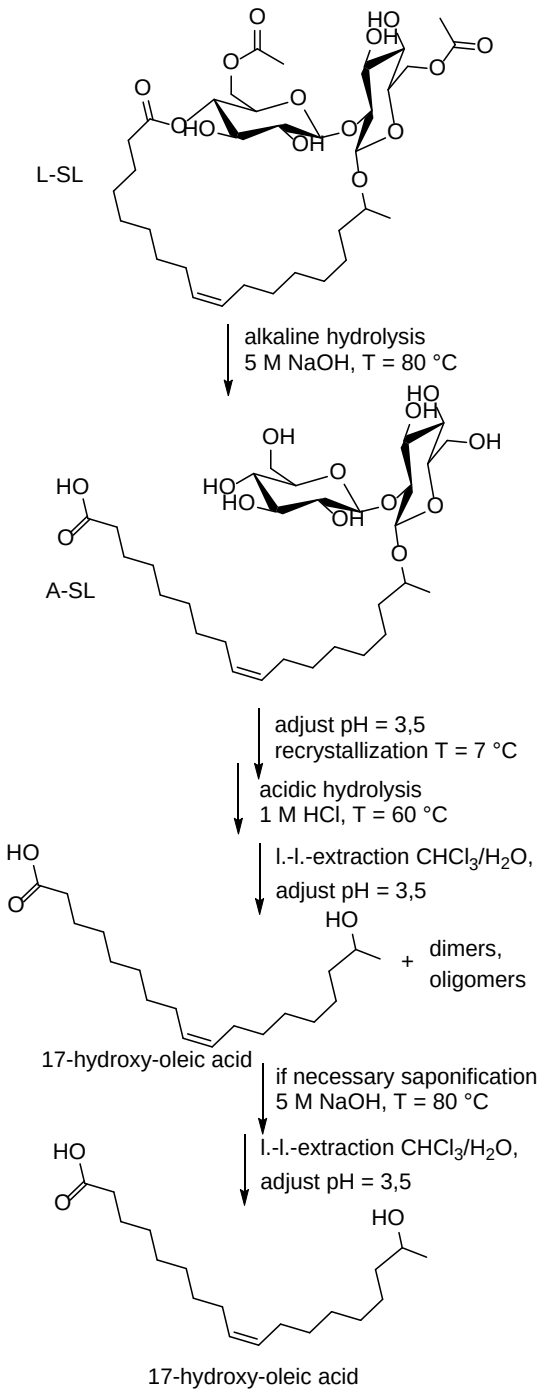

Fig. 2. Synthesis route developed for the production of 17-hydroxy-oleic acid from L-SL.

During the alkaline ring opening, the acetate groups were also removed and free primary hydroxyl groups were formed.[27] The reaction progress was monitored by HPLC-ELSD measurements (Fig. 3). The peaks were identified and assigned by HPLC-MS measurements (Table 1).

S. bombicola not only produced 17-hydroxy-oleic acid but also a small proportion of 18-hydroxy-oleic acid chains, which could be identified by HPLC-MS. Due to their slightly higher hydrophobicity, they are eluted somewhat later. Unidentified peaks are most likely reaction products of 17-hydroxy-oleic acid with monofunctional fatty acids from the initial starting

material mixture. Since this measurement was a reaction tracking measurement and the peaks no longer appeared in the end product after purification, further identification is not necessary.

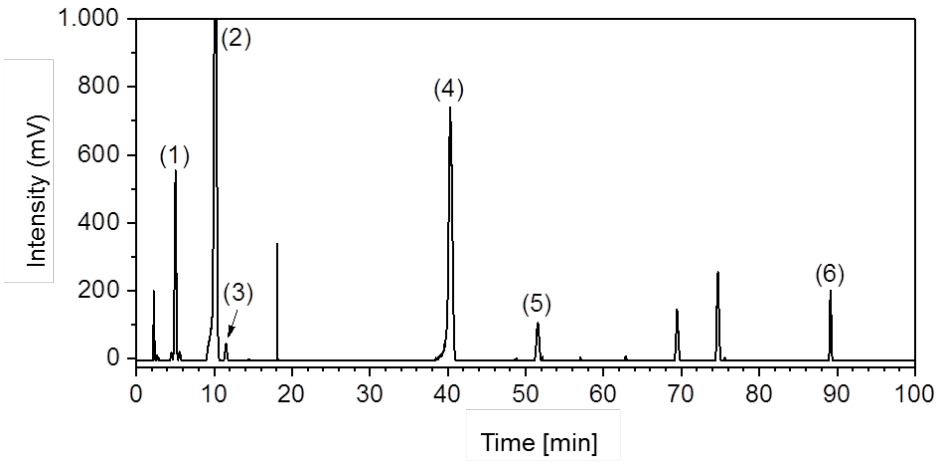

Fig. 3. HPLC-ELSD Chromatogram of the acidic A-SL cleavage with identified peaks after 4 h of reaction time.

Table 1. Assignment of HPLC signals (Fig. 3) to identified substances.

Nr.	molecular weight [g·mol^{-1}]	substance
1	622	A-SL
2	460	Glucose-(ω-1)HFA
3	460	Glucose-ωHFA
4	298	17-hydroxy-oleic acid
5	300	18-hydroxy-oleic acid
6	578	17-hydroxy-oleic acid-dimer

The total reaction time of the acid hydrolysis was between 24 and 72 hours. Since the sophorolipids obtained from fermentation are always product mixtures and the purity of the lactonic sophorolipid was approx. 97 %, substances may be present that inhibit or interfere with acid hydrolysis.[2],[11],[13],[16],[18]

Sugar residues and other impurities were removed from the final product mixture by a liquid-liquid extraction with water/chloroform. Monomers (50.7 % according to HPLC) and dimers (17-hydroxy-oleic acid (49.3 % according to HPLC)) were isolated from the chloroform phase and identified by HPLC. To obtain 17-hydroxy-oleic acid monomers, ester cleavage was performed with 5 M NaOH. The pH value was then adjusted to 3.5 and another liquid-liquid extraction with water/chloroform was carried out. No more dimers were detected in the final product. A small proportion (approx. 4 % according to HPLC) of HFAs bound to glucose residues could not be removed from the end product. By acid hydrolysis of A-SL,

good yields (81.2 - 89.4 %) of 17-hydroxy-oleic acid and 17-hydroxy-oleic acid oligomers mixtures can be obtained. After saponification, the yield was reduced to approx. 54.3 %. The purity obtained was approx. 95 % (according to HPLC).

Due to the poor solubility of 17-hydroxy-oleic acid in NaOH solution, agglomerates formed in the reaction mixture which could not be removed from the reaction vessel. For this reason, ester cleavage results in high yield losses. It should be noted that high purities of the starting materials are necessary for chemical polymerization reactions. The L-SL used was produced by microorganisms and, depending on the batch, may contain different impurities which can influence and interfere with the subsequent reactions.

The purity of the substance mixture is also an important factor in the extraction of 17-hydroxy-oleic acid from sophorolipids. Repeated execution of the synthesis route developed showed that the composition of the educt must have an influence on the reaction time and its products. Already in the recrystallization of the L-SL it became clear that this process was not always reproducible, as disturbing substances were potentially present in the reaction mixture. Possibly these are also inorganic impurities, which could not be detected in further detail. These substances probably also have an influence on the duration of acid hydrolysis. In addition, it was observed that the cleavage process was incomplete and the reaction time was extended when the preparations were scaled up. This increased the formation of di- and oligomers and made it increasingly difficult to process the products. Solubility in chloroform was reduced and a third phase was formed during liquid-liquid extraction.

Ester dissociation is necessary to obtain hydroxy-oleic acids in highest quality. Since ester cleavage is associated with high yield losses and the quantities of starting material present were very small, ester cleavage was only carried out for the final characterization of the hydroxy-oleic acid. 17-hydroxy-oleic acid mixtures of monomers, di- and oligomers were used for polymerization. The yields of 17-hydroxy-oleic acid without ester cleavage are 81.2 to 89.4 % based on A-SL as educt. After ester cleavage, the yield decreased significantly.

The developed route shown in Fig. 2 is quite complex and needs approximately one week of preparation time considering all purification steps. Nevertheless, the synthesis route results in a bio-based building block whose carbon consists of 100% renewable raw materials and that can be used for the synthesis of novel polymers.

3.2 Oligomerisation of 17-Hydroxy-oleic acid

In order to use 17-hydroxy-oleic acid (HOA) as linear polyester building blocks, it must be converted into hydroxyl-terminated polyesters. Hydroxyl-terminated polyester polyols with functionalities of 2 can be obtained by application of a "one-pot" synthesis published by Nefzger et. al. [25] (Fig. 4). Note that the amounts given in section 2.3 lead to molecular weights of ca. 2250 g mol^{-1} and therefore represent the typical molecular weight range of commercially available polyester polyols.

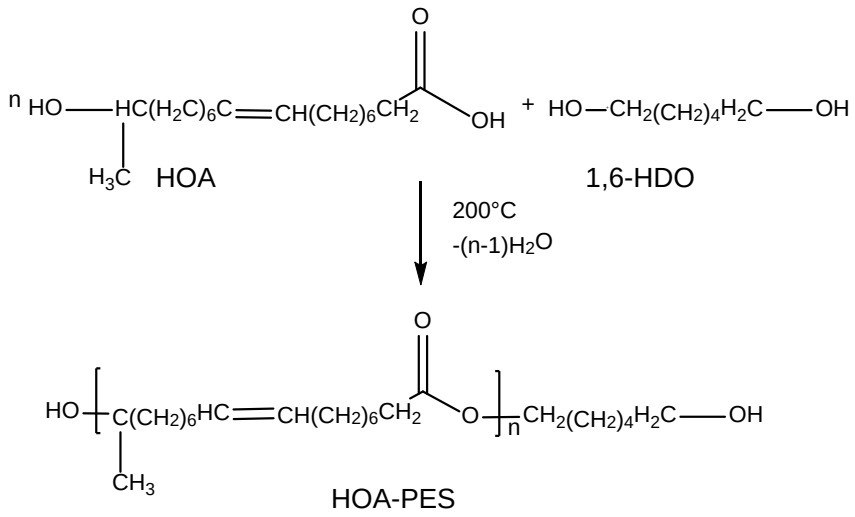

Fig. 2. Schematic reaction equation of the polycondensation of 17-hydroxy-oleic acid and 1,6-hexanediol using the „one-pot“ method.

4-tert-butylcatechol was used as radical scavenger to avoid crosslinking via the double bonds.[28]–[30] Note that the radical scavenger also carries hydroxyl groups and may react with the carboxylic acid functionalities of HOA as well. However, the amount of 4 tert butyl catechol added is insignificant small (1/50 mol%) and can therefore be neglected. The product obtained was of high viscosity and not completely soluble in THF. The soluble part was analyzed by GPC revealing a monomodal distribution for all samples with no 1,6-hexanediol signal observable. Also IR confirmed the formation of the ester groups (results not shown). The acid number was 2.8 mg KOH/g in comparison to ≈ 86 mg KOH/g for the monomeric HOA. All these findings strongly suggest that the majority of the acid groups were esterified and thus the synthesis of the HOA-PES was successful.

3.3 Synthesis of HOA-PES Polyurethanes

For the synthesis of HOA-PES polyurethanes (Fig. 5), the HOA-PES from section 3.2 was used as educt. The molecular weight of the polyester was determined by GPC and used to calculate the required HDI quantity for a NCO/OH ratio of 1.5. After completion of the reaction, the excess isocyanate groups were reacted with a dibutylamine solution. The resulting PU was dark brown and rubbery and no longer entirely soluble in THF. The soluble fraction was further examined by GPC measurement. The GPC chromatograms showed a signal in the molecular range for the product form the conversion of HDI with DBA. The number average molecular weight for the main peak of HOA-PES-PU is 3532 $g \cdot mol^{-1}$. Additionally, molecular weights > 10^6 $g \cdot mol^{-1}$ could also be detected. It seems that during the reaction of HOA-PES with HDI networks were formed leading to a rubber-like product.

The formation of unintended networks may be caused either by crosslinking of the molecules via the double bonds or by increased functionality of the HOA-PES. Latter may be caused by glucose residues.

A comparison of the FT-IR spectra of the polyurethane and monomeric HOA (Fig. 6) show that the signal for the double bond remains visible for HOA-PES-PU. This indicates that no

formation of a network via the double bond had occurred. In addition new bands become visible. The band at about 3330 cm^{-1} is the N-H oscillation of the excess di-butyl amine. The deformation oscillation of the secondary amine at approx. 1621 cm^{-1} can be seen. A band at approx. 1533 cm^{-1} can be assigned to the NH band of the urethane group.

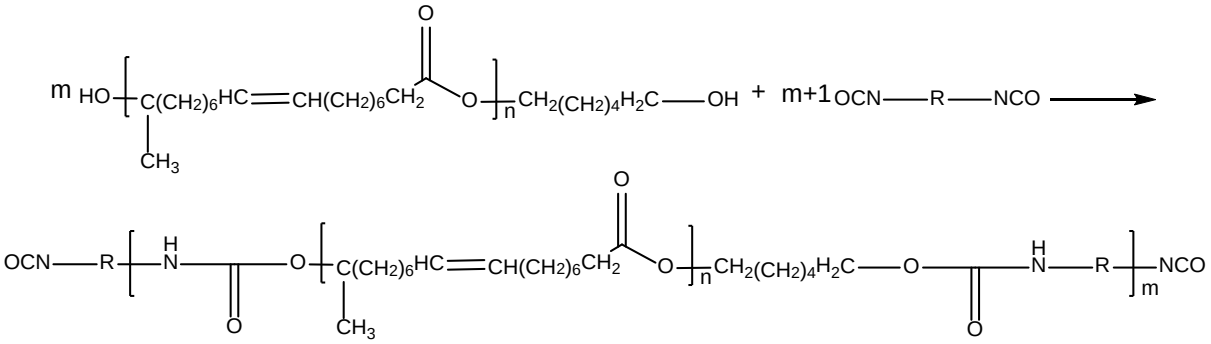

Fig. 3. Equation for the reaction of HOA-PES with HDI to HOA-PES-PU with R = C_6H_{12}.

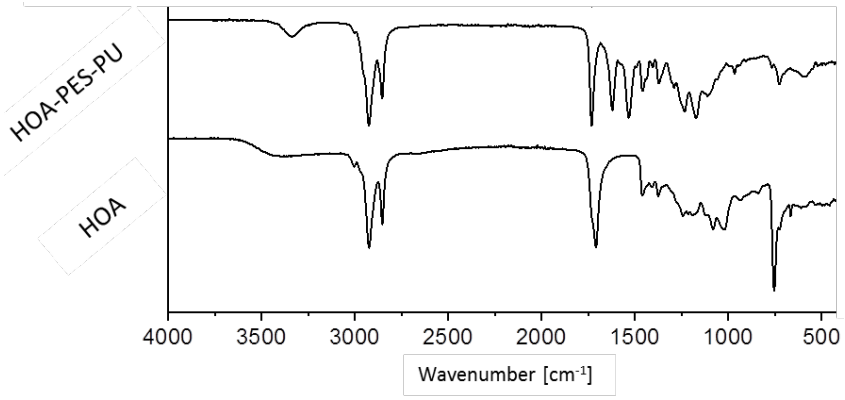

Fig. 4. FT-IR spectra of the HOA-PES polyurethane as well as 17-hydroxy-oleic acid.

DSC measurements showed that HOA-PES-PU has a glass transition temperature (T_G) at -42.85 °C, in contrast to HOA-PES which has no T_G in the temperature range from -60 to 150 °C. The reaction of polyester polyol with HDI and the accompanying formation of hard segments therefore lead to a change (increase) in the glass temperature compared to polyester HOA-PES.

As a conclusion, HOA-PES-PU could successfully be produced. Thus, the synthesis route is generally feasible for the production of polyurethane prepolymers from hydroxy-fatty acids. However, crosslinking occurs to a significant extent most likely due to free glucose impurities in 17-hydroxy-oleic acid raw material. Thus, the quality of 17-hydroxy-oleic acid seems not yet appropriate for the synthesis of polyurethanes and further optimization is required.

Conclusions

Within the scope of this work, a synthesis route for the production of bio-based 17-hydroxy-oleic acids from sophorolipids was successfully developed. The synthesis included an alkaline ring opening of the lactonic sophorolipid to obtain a deacetylated acidic sophorolipid. Subsequent acid hydrolysis cleaved the sophorose unit or the individual glucose units off the molecule and the 17-hydroxy-oleic acid was obtained. In addition to the desired monomers, the product mixture also contained dimers and higher oligomers. In order to obtain pure 17-hydroxy-oleic acid, saponification was necessary; however, the yield was significantly reduced by the ester cleavage step. It was shown that it is possible to obtain 100% bio-based 17-hydroxy-oleic acids from sophorolipids with the developed "one-pot" synthesis based on Nefzger et al.[25] and it was possible to synthesize hydroxyl-terminated polyesters. The resulting bio-based polyester was used to synthesize polyurethanes by conversion with HDI. The products showed a significant crosslinking most likely due to glucose impurities. As a conclusion, polyurethanes containing 17-hydroxy-oleic acids derived from sophorolipids could principally be synthesized. Upon further optimizing the purification strategy these bio-based building blocks could be used in future in high-performance applications, such as low-energy adhesives.

Acknowledgements

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