been planned by participating parties, including first patent applications, which have been prepared with regard to material and processing, as part of an envisaged of a patent forest. This is an attempt to keep market competition in check until appropriate production quantities are achieved. Additionally, the general opinion is the following: active political support and committed business action will accelerate the cascading use and reintegration of materials towards a circular economy and thus lead eventually to economic success on the long term.

The market for products based on biochar, proteins from animal wastes or PLA is very large in theory. Nevertheless, Styrofoam in applications such as greenhouses, reforestation, packaging cannot be replaced by the considered value chain. However, it is already possible to penetrate niches in the areas mentioned and secure market shares there. It is therefore agreed that a USP defensively exists, which has already been protected as intellectual property.

The respective biolink would take over parts of the existing production, thus hardly any new jobs are created in industrial applications. In the procurement of materials for the carbonation process and in the production of biochar, however, a large number of new jobs can be created, especially in the agricultural and forestry sectors, which give both unqualified employees and technically and economically qualified specialists the opportunity to find employment. With regard to government financing and subsidies or grants to support the biolink depend on size, turnover, number of employees and are therefore very heterogeneous in the Europe-wide context. For the specific participating companies, research is underway on The Central Innovation Programme for small and medium-sized enterprises (ZIM), Horizon 2021 and fiscal research allowance.

CASE STUDY 4



https://www.youtube.com/watch?v=WJfocB6 7Lg

Replacement of Castor Oil in Polyurethanes

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Involved Project Partners

LP - Plastics Innovation Competence Center



Involved Actors

Conica Centravo

Note

We use generic company names throughout this case study. A list with complete company names can be found at the end of the case study.



Background

Polyurethanes (PU or PUR) are extremely versatile polymers which are formed by the reaction of two components: Di- or polyisocyanates and di- or polyalcohols react in a poly-addition reaction to form the characteristic urethane group as shown in figure 4 below. The choice of the two components, i.e. the use of more rigid or flexible chemical base structures for isocyanates and alcohols, results in an

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[13] AlpLinkBioEco Lead Partner, Plastics Innovation Competence Center, University of Applied Sciences and Arts Western Switzerland - School of Engineering and Architecture of Fribourg (HES-SO//FR HEIA-FR) extremely wide range of possible combinations. In addition, the functionality of the two components can be two or more, so that linear, slightly branched or three-dimensionally cross-linked polyurethanes can be produced. As a result, meltable and thermoset

polyurethanes which can be soft and rubber-like or hard and brittle can be produced (Beck et al., 1993; Adam et al., 2005; R. Leppkes, 2005; J. Cowie., 1991; L. Shen., 2009;).

Chances		
Regional source	(CO ₂)	Low transportation cost, lower CO2 footprint from transportation, short delivery times lead to low inventory and ease order to needs
	ΦΦΦ //11/\\	Reduction of land consumption for plantations in the tropics
		Reduced dependency on variations in harvest and seasonality in case animal based replacement can be found
		Increased security of supply and predictability of cost
Challenges		
Specifications		Physical properties need to be close; especially the viscosity needs to be between 100 – 400 mPa*s
		Chemical properties need to be close; especially the number of functional groups per molecule needs to be above 2 and below 4
	%	Specifications must be reproducible and below 5% variation
Reformulation	(A)	The mix of components within the formulation needs to be adjusted, leading to reformulation costs; the closer the replacement to castor oil, the lower the cost and the shorter the testing time
Cost		Needs to be in the range of castor oil or slightly higher
Supply		Security of supply needs to be given all year round
		Quantities of several 100 tons/year for every mid-sized player are needed. Big players will need several thousand tons/year

Table 2.1. Chances and challenges replacing polyalcohols (castor oil) in a polyurethane formulation

Table 2.1 shows, chances and challenges to be considered when components are to be changed in this value chain. Thus, the idea came up, to replace mostly imported bio-based castor oil with a (residual) animal-based fat or oil. It is crucial that the substitute features similar physical properties as the initial component castor oil, to replace it like a dropin chemical. Some of these properties are listed below and needed to be examined and discussed in detail within the piloting session:

- Viscosity
- Water content
- · Clear liquid
- Low acid content
- UV-stability
- OH-group-content
- Functionality
- Flammability
- Availability
- · Reproduce-able specifications

The more the properties are comparable, the easier it is to reformulate and to mix the two components needed to produce polyurethanes. The considered animal fat / oil -source is a side stream of slaughterhouses, which is collected and processed. Consequently, it can be stated that in this envisaged value chain, a bio-based, mainly imported raw material is replaced by a regionally available animal oil or fat. Thus, any additional higher value application then e.g. bio-diesel out of this side stream of slaughterhouses, is beneficial for the society. Figure 2.4 shows the two mentioned

molecular components, as a basis for the forming of the polyurethane polymer, e.g. a foam (Figure 2.5).



Process

Medium-sized formulators such as Conica (SIKA, Huntsman) of two-component polyurethanes isocyanates from isocyanate suppliers, which are mainly large conglomerates such as BASF and DOW. Consequently, they are either mixed or chemically partly converted into so called prepolymers, depending on the needs and requirements of the process to produce the final polyurethane and the product itself. In either case, component A contains isocyanate (-NCO) groups. Furthermore, they buy polyolyalcohols mostly from the same suppliers or from importers. These represent the second component B. A polyalcohol that is used in many 2-component polyurethane formulations, is castor oil which is imported from the tropics. All different polyolyalcohols from a specific formulation are mixed and sometimes additives, fillers, dyes etc. are added. In any case, component B contains in minimum 2 alcohol groups (-OH) per molecule in average. Components A and B are sold to processors who mix and process the components. After mixing/casting, the chemical reaction between isocyanate and alcohol groups forms the final polyurethane, in most cases a soft or hard rubber-like product.

$$O = C = N$$

$$\downarrow H$$

Figure 2.4:
Production of polyurethanes with the characteristic urethane group from diisocyanates such as diphenylmethane diisocyanate (or polyisocyanates) and dialcohols such as ethanediol (or polyalcohols)



Figure 2.5: Mattress foam with 24% biogenic content from castor oil. Courtesy of BASF Polyurethanes GmbH



Results

The workshop took place in May 2020 between Centravo and Conica. Samples and specifications were exchanged. The specifications of castor oil and the price range of castor oil need to be met by a replacement (close to drop-in), to be technical and economical feasible. The discussion on the technical parameters that are important in order to use the substitute effectively led to the following ranges:

- Viscosity between 100-500 mPa*s
- Functionality between 2,5-4 (average number of OH - groups per molecule)
- Reproduce-able specifications; variation below 5%.
- Availability above 300 tons per year, all-year round
- Cost range 0.5-1 CHF per kg

The fat or oil from slaughterhouse waste is available in quantities above 500 tons per year without

seasonal fluctuations. The quantity reported should be sufficient for a medium-sized player. If the project can be transferred to other actors, quantities must be substantially higher and in the range of several thousand tons per year. Due to the independence of the envisaged substitute from imports, which is not depending on harvest conditions, typical for castor oil, an improved or in minimum more stable profitability should be achieved.

There is no doubt among the parties involved, that in case higher added value chains can be found for animal-based oils / fats there will be conflicts of interest regarding available volumes with impact on pricing, consequently.

Since there are other vegetable oils - apart from the already used castor oil - there would still be bio-based alternatives to the animal based one in consideration, but they would have to be analyzed more closely in order to ensure an optimal drop-in replacement. These were identified in the initial scientific research. The discussion showed that plant oils show lower viscosity in general then animal fats- or oils. Low cost- or high-volume products are rape seed oil or sunflower seed oil, which are

both regionally available. The functionality rsp. the average number of OH groups per molecule or the potential to chemically convert other functional groups into OH groups of both needs to be evaluated though, according to the parameters mentioned above.

It is generally assumed that customers will accept a higher price if security of supply and an improved cost predictability can justify a slightly increased pricing. However, there is an existing market for animal-based fats and oils, in case they work as drop-in chemicals for polyurethanes, which are massively demanded in a wide variety of applications. Formulations for polyurethanes based on animal oils or fats and processing may need to be adapted. This depends on the exact specifications of the substitute and the product. It is therefore imperative that the new formulations are tested. In further consequence, this will lead to expenses that will have to be covered as an additional cost, which have an important impact on the profitability of polyurethane-chemistry. Raw materials cover typically between 15-60% of the costs of the final product turnover. Following features of the biolink are generally considered as Unique Selling Proposition (USP):

- Regional supply
- Ecological responsibility, as there is no need to cultivate reforested areas
- Less transportation (-costs) and thus less greenhouse gas emissions
- Higher added value for the producer of animal-based fats and oils, as side-stream of slaughterhouses

Since it is envisaged that the components used will be directly substituted (drop-in chemicals) and therefore existing production processes would be altered only marginally, it is assumed that no additional jobs can be created from the current perspective. To date, no suitable subsidies have been identified to support the implementation of biolinks. No legal hurdles are expected to impede implementation.

Finally, it turned out that the viscosity of the animal fat was too high to be used in this application for a simple drop in solution. Otherwise, the project could easily have been transferred to other 2-component polyurethane formulators such as SIKA, Huntsman, etc.

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Company List

BASF: BASF SE, Ludwigshafen, Germany Centravo: Centravo Holding AG, Lyss, Switzerland Conica: CONICA AG, Schaffhausen, Switzerland DOW: The Dow Chemical Company, Midland, USA Huntsman: Huntsman Corporation, Salt Lake City, USA SIKA: Sika AG, Baar, Switzerland UetlibergPartners, UetlibergPartners GmbH, Lachen, Switzerland