SUGARS AND FATTY ACIDS FOR PSA APPLICATIONS

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Background

We will describe a fully bio-based soft polymer network synthesized for usage in pressure sensitive adhesives applications. By using different sugars and different fatty acid based monomers we were able to tailor the viscoelastic and adhesive properties of our produced materials.

During the latest few decades, the chemical industries have been facing a redesign of their synthetic routes to minimize the impact on the environment. The increased environmental awareness has attracted the interest of many researches searching and testing alternative chemical pathways for formation of old and new materials. To become sustainable these new greener pathways also need to be designed in a cost-efficient manner. Vegetable oils are considered one of the most attractive and feasible sources of raw materials due to low production costs, and high availability makes them a feasible and attractive source of green raw materials. [1-3] The chemical structure with unsaturated bonds of many natural fatty acids makes them flexible with branching sites for polymerization. Additionally, the structure opens new possibilities for formation of network structures.

The polymer architectures from epoxidized vegetable oils can be fine tuned to form specific materials traditionally made from fossil-based resources, *e.g.* pressure sensitive adhesives[4] (PSA). PSAs are special kinds of adhesives which adhere to a surface under application of small external load and achieve enough joint strength to resist it from detaching, which is done with perfect balance between viscous and elastic properties. PSAs are usually soft polymer networks designed to present T_g much lower than the intended usage temperature[5]. The formation of a covalently crosslinked network provides elasticity to the material which ensures cohesiveness and recovery after stress. At the same time, the incorporation of a soft component is required to ensure mobility to give ability to flow and "wet" the surface. As previously reported in literature, the formation of polymer networks from[6] or in combination with epoxidized vegetable oils[7-8], represent a good strategy to reach PSA properties.

To evaluate the potential use of a combination of sugars and fatty acids for PSA applications, selective synthesis of fully bio-based and biodegradable soft polymer networks is done. First monomers consisting of epoxidized fatty acids and sugars are synthesized through lipase catalysis. We anticipate that the selectivity of the method allows for the formation of ester-based epoxy-functional monomers with varying OH-content. In a second step, a bio-based di-acid is reacted with the epoxy-functional monomers in a step-growth fashion to form polyester networks, leaving the hydroxyls intact. The different rheological properties resulting from variations in the hydroxyl content and the network structure were examined in order to tailor the adhesive properties.

Materials and Methods

Materials

Samples of epoxidized linseed oil and epoxidized soybean oil were kindly supplied by Ackross chemicals. Novozyme 435 (Candida antarctica lipase B immobilized on an acrylic carrier. Activity ≥ 5000 U/g, recombinant, expressed in Aspergillus niger) was purchased from Sigma-Aldrich. Pripol 1009 was kindly supplied by Croda. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich. Deuterated solvents ($CDCl_3$) were provided by CIL (Cambridge Isotope Laboratories, USA).

Synthetic strategies

General procedure for the extraction of methyl esters from natural oils. The extraction of the fatty acid methyl esters was performed following procedures previously reported in literature[9-10].

General procedure for the synthesis of the macromers through lipase catalysis. Selected methyl ester fatty acid, *i.e*. EMLO or EMLEN, and diol, *i.e.* sorbitol, erythritol or 1,4-butandiol, were put in a round bottom flask (2:1 eq; methyl ester:diol) and heated up to: 100 °C for sorbitol, 110 °C for erythritol and 80 °C for 1,4-butandiol under stirring. After that, molecular sieves (25% w/w of the total amount of reactants) and CALB (10% w/w of the total amount of reactants) were added to the melt. The flask was then connected to a vacuum line and left at the mentioned temperature for 48h. The reaction was stopped by dissolving the product in a small amount of $CHCl_3$ and filtering out the enzyme. The solvent was then removed under pressure.

*General procedure for polymer networks formation.*100 mg of monomer were mixed in a vial with the corresponding stoichiometric amount of Pripol (see Table 1) and mixed thoroughly with a spatula at room temperature. When a homogeneous mixture was obtained, the samples were degassed repetitively under vacuum. After the degassing 4 wt% of DBU was added to the mixture, stirred with a spatula and degassed again. Fully cured samples were obtained after heating the mixtures at 130 °C for 30 min.

Table 1. Stoichiometric ratios and reaction conversion.

Product	Initial feed composition diol: fatty acid[a]	Final composition diol: fatty acid[b]
E-4E	1:2	1:2.4
S-4E	1:2	1:1.9
S-6E	1:2	1:1.8
B-4E	1:2	1:2.2

[a] Due to the poor solubility of the unreacted sugars, the initial feed composition is theoretic.

Instrumentation

Nuclear Magnetic Resonance (NMR). ^1H NMR spectra were recorded on a Bruker AM 400 MHz using deuterated chloroform ($CDCl_3$) as solvent. The solvent signal was used as reference.

Real Time-FTIR Analysis (RTIR). The RTIR analysis were made using a Perkin-Elmer Spectrum 2000 FT-IR instrument (Norwalk, CT) equipped with a single reflection (ATR: attenuated total reflection) accessory unit (Golden Gate) from Graseby Specac LTD (Kent, England). RT-FTIR continuously recorded the chemical changes over the range 4000-600 cm^{-1}. Spectroscopic data were collected at an optimized scanning rate of 1 scan per 1.67 seconds with a spectral resolution of 4.0 cm^{-1} using Time Base® software from Perkin-Elmer.

Differential Scanning Calorimetry (DSC). A differential scanning calorimeter (Mettler Toledo DSC 820 module) was used to analyze the thermal properties of the produced materials. (5 to 10 mg of the samples was encapsulated in 40µL aluminum sample cups. The samples were first submitted to a heating (I) from 25 °C to 150 °C, (II) cooled to -60 °C and (III) heated to 150 °C using cooling and heating rates of 10 °C/min under a nitrogen atmosphere.

Rheological measurements. Measurements were carried out on a TA Instruments (New Castle, DE, USA) Discovery Hybrid 2 (DHR2) rheometer, using disposable aluminum parallel plate geometries (ø = 8 mm) with a gap of 300 µm. Curing experiments were carried out at 130 °C in an environmental test chamber (ETC) with a nitrogen gas inlet, using oscillatory time sweeps at 1 Hz. After curing, the samples were cooled to 25 °C and analyzed with frequency sweeps from 0.01 to 100 Hz at a displacement of 0.01 mm. Amplitude sweeps at 1 Hz were carried out to confirm that measurements were within the linear viscoelastic region (LVR).

Adhesion test. We used a modified version of a JKR instrument[11] that enable continuous motion of the probe towards the sample surface. A stiff hemispherical cap of fused silica (R=5 mm) was approached and separated with continuous speed (100 µm/s) towards the elastic films of the polymer network to be tested spread on a flat glass slide. The force during the approach / retraction cycle is captured as a function of time and position.

Results and discussion

Lipase catalysis for synthesis of monomers

In order to form fully-biobased and biodegradable soft polymer networks for PSA applications, four different monomeric structures were prepared (Figure 1) e.g. S-4E, S-E6 etc. Two different variables were contemplated in the design of the monomers, *i.e.* epoxide content and hydroxyl content. The introduction of hydroxyl groups with the sugar was envisaged to have a tackifying effect on the final polymer constructs. The epoxide content was used to discern effect of using 4 or 6 functional monomers for step wise polymerization.

Transesterification reactions were performed using an initial feed of 2 equivalents fatty acid per sugar unit, with a catalytic loading of 10% (w/w) Novozyme 435. Reaction temperatures ranging from 100 to 110 °C were varied depending on the melting point of the reactants. The final reaction conversion was assessed through ^1H NMR and calculated as the conversion of the fatty acid methyl ester ($-CH_3$ δ: 3.6 ppm). Lower reaction temperatures resulted in the decrease of the reaction conversion. Control reactions without enzyme showed that no condensation reactions were taking place. Showing the importance for the use of the catalyst in the production of the different monomers, the catalysts were removed by filtration.

One of the objectives of the study was to demonstrate this robust synthesis route with no work-up except removal of the catalyst by filtration. Considering the scope of this work, the accuracy level in degree of substitution was considered to be sufficient to proceed with materials evaluation and formation polymer networks.

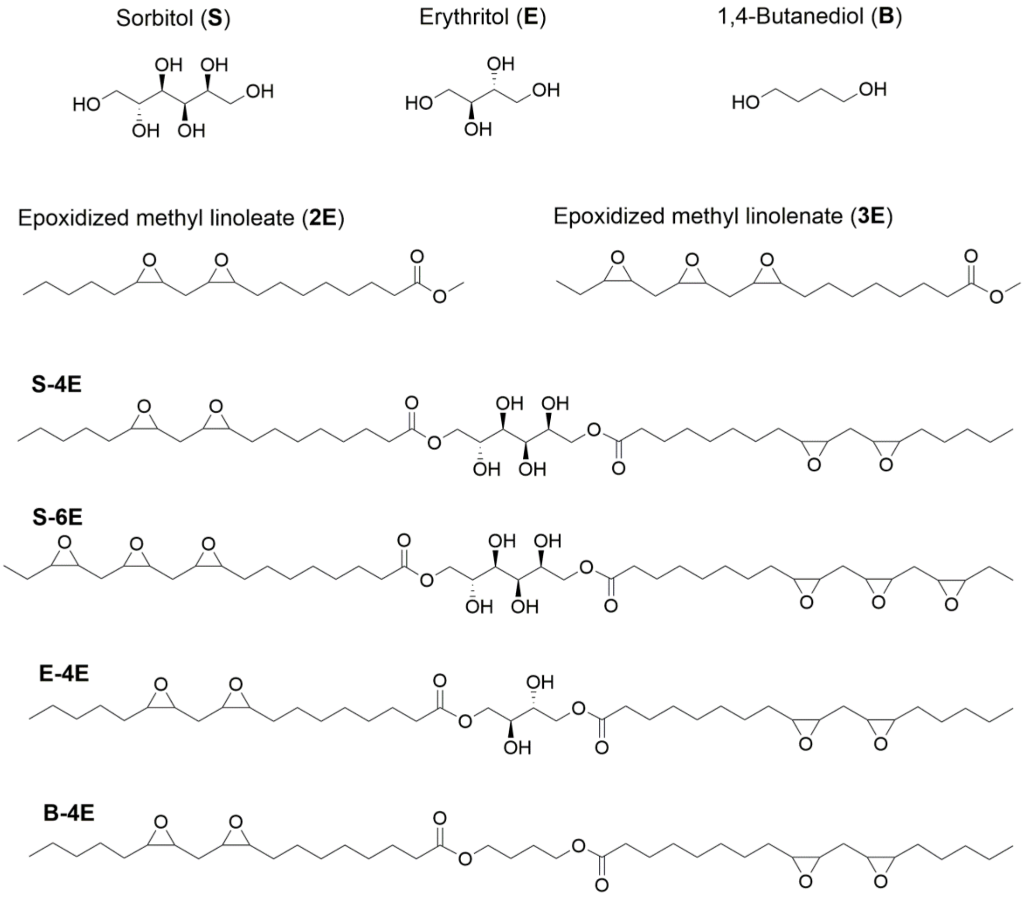

Figure 1. Summary of the sugars and fatty acid methyl esters used as reactants together with the homologous molecule without OH groups, i.e. 1,4-butanediol, used for comparison. Depicted in the bottom of the figure are the major products synthesized.

Crosslinking reaction using catalytic amounts of DBU

In order to better understand the impact of adding sugar to fatty acid based networks on the viscoelastic and adhesive properties, networks with varying crosslink density and hydroxyl content were aimed for through polymerization of the epoxides. Due to the short length of the segments and the high degree of functionality, the monomers were combined with a commercially available bio-based fatty acid dimer (Pripol 1009) containing 2 carboxylic acids. This was selected to avoid formation of high T_g materials[10] that is not suitable for the selected PSA application.

Ring opening of epoxides with a carboxyl to form an ester bond proceed in a step wise manner via a nucleophilic attack on the epoxide, however, there are other background reactions that can occur simultaneously. In order to minimize the two main side reactions; *i.e.* (i) condensation between acids and free OH groups, and (ii) etherification between epoxides and hydroxyls, different reaction conditions were tested and evaluated through FTIR spectroscopy (see Figure 2 and Figure 3).

It was observed that an increase from 1 wt% to 4 wt% DBU further promoted the reaction between the epoxides and acids, confirmed by the disappearance of the acid peak (1713 cm^{-1}), and a decrease in the reaction times from 2h to 1h, respectively. The quick decrease of the epoxy peak (815 cm^{-1}) parallel to the decrease of the acid peak (1713 cm^{-1}) indicated that the epoxy-acid esterification was the primary reaction taking place. Polymerization of the monomer from 1,4-butane diol (**B4E**) without any pendant hydroxyls gave the exact same shifts as the sugar-based analogue (**E4E**).

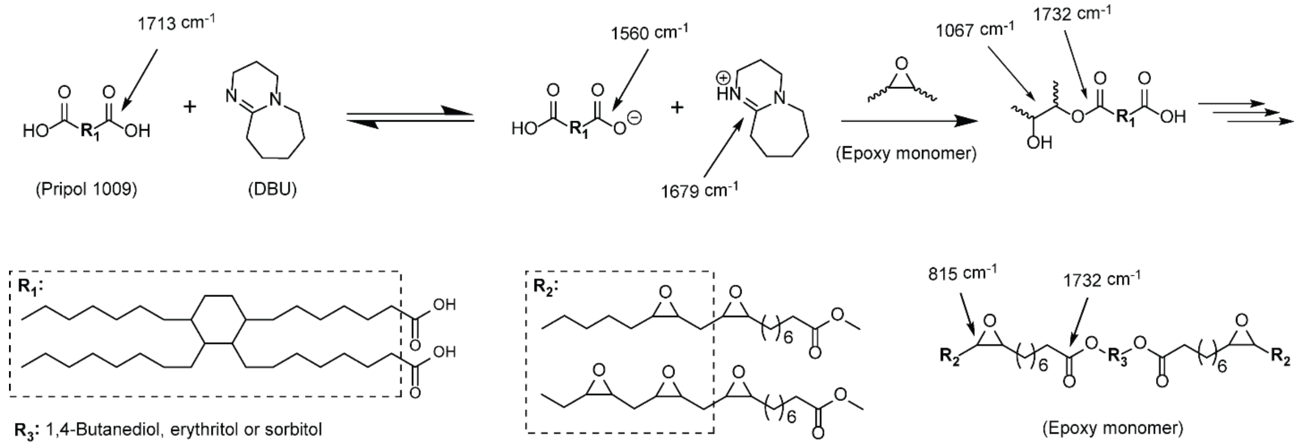

Figure 2. Mechanism for the formation of polymer networks catalyzed by DBU. With arrows indicating FTIR absorption bands of the different functional groups.

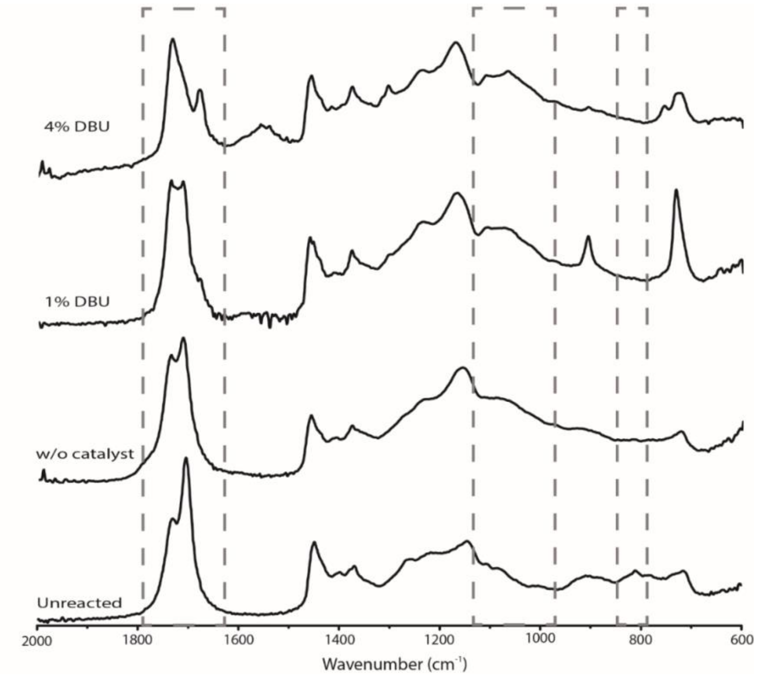

Figure 3. FTIR spectra of the different reaction conditions attempted for the polymerization of S-6E-6A.

By measuring rheological properties, it was observed that the *G'* of the formed networks, and thus the viscoelastic properties, could easily be tailored by adjusting the stoichiometry of epoxy monomer to di-acid (see Table 2). In all cases, increasing amount of acid resulted in the decrease of *G'* which allowed tailoring the networks towards suitable PSA properties[12]. When using an excess of acid, the amount of dangling chain ends and distance between crosslinks increase, along with greater probability for intramolecular reactions, *i.e.* formation of loops. As a consequence of the higher fatty acid content, the T_g of the networks is also lowered, a prerequisite for good PSA properties. However, large excess of acid content (>50 mol%) failed to reach a gelation point. When the acid content was decreased to substoichimetric amounts, higher *G'* values were observed, meaning that an optimal network formation is achieved with an excess of epoxides.

Table 2. Summary of the properties of formed networks

Diol	**CODE**	**Epoxy:acid ratio**	**Tg (°C)** [a]	**G' (kPa) at 25°C**[b]	**G' (kPa) at 130°C**[c]
Erythritol	E-4E-4A	4:4	-6	51.4	56.1
	E-4E-5A	4:5	-20	13.7	25.2
Sorbitol	S-4E-4A	4:4	-4	188.8	138.6
	S-6E-6A	6:6	4	184.1	233.5
	S-4E-5A	4:5	-14	9.8	54.1
	S-6E-7A	6:7	-11	73.4	111.7
1,4-butandiol	B-4E-4A	4:4	-21	95.9	93.4
	B-4E-5A	4:5	-26	36.9	47.4

[a] Measured with DSC

[b] Measured from rheological frequency sweeps at $\gamma = 0.01$ and $\omega = 2\pi$ rad s^{-1}

[c] Measured from rheological time sweeps at $\gamma = 0.01$ and $\omega = 2\pi$ rad s^{-1}

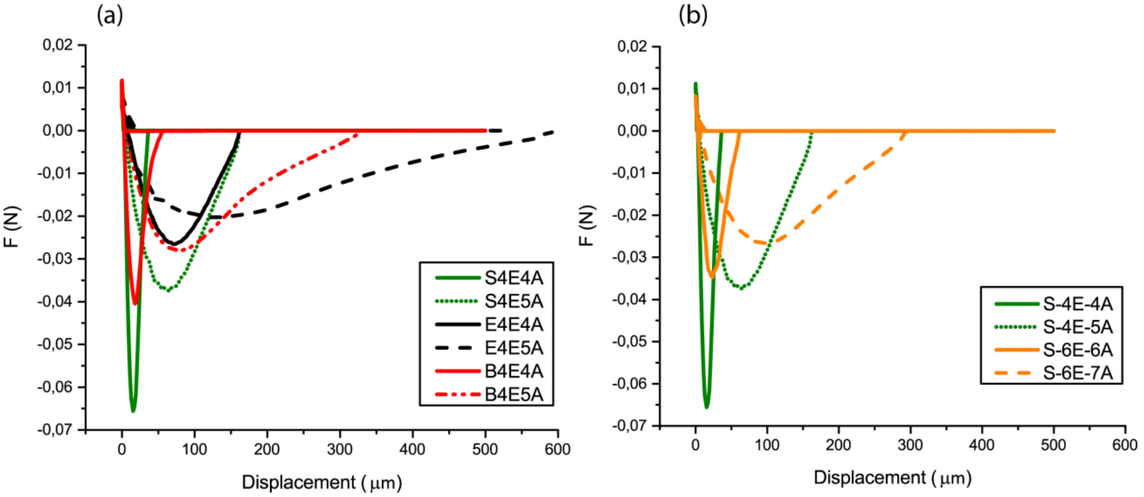

Figure 4. Debonding curves from adhesion measurements, stoichiometric ratios (epoxide:acid) 1:1 represented by solid lines and excess acid by dashed lines. (a) Networks formed from monomers containing 4 epoxides. (b) Networks containing sorbitol and 4 or 6 epoxides.

Adhesive properties of the networks

In order to evaluate the adhesive properties of the polymer networks, JKR-based axisymmetric adhesion experiments were performed. This experiment measures the adhesion force on withdrawal of compressive bonding stress, *i.e.* debonding process between the adhesive and a hemispherical probe of fused silica. During the detachment from the probe the applied stress is dissipated through the sample until cohesive or adhesive failure is produced. As can be observed in Figure 4, two differentiated trends were observed during the debonding process. Materials with predominant elastic behavior (high *G'*), *e.g.* S-4E-4A, exhibited short displacement until complete detachment from the probe, caused by the material's hampered ability to dissipate energy. These materials can be classified as solid-like PSA and are characterized by their higher force capacity resulting from higher cohesive strength. The other type of materials, liquid-like PSA, are characterized by their better ability for dissipating energy due to their more pronounced viscous character (high G''). These types of materials present visible viscous filaments during debonding resulting from cohesive failure.

Conclusion

By combining selections of different fatty acids and different sugars the final macromolecular structure could be fine-tuned. This resulted in formation of monomeric structures with varying hydroxyl content and different amount of epoxy functionalities without need for extra work-up except filtering of the catalyst. The following selective coupling of the epoxides with bio-based diacid allowed the formation of polyester network via step-growth polymerization. Control of the final mechanical properties was achieved through variations in the epoxy-content on the monomers and the epoxy to diacid ratio. In both cases, steric effects arising from the increasing acid content resulted in softer networks due to lower cross-linking density.

Hence, polymer networks with tailored elastic modulus were prepared through variation of type of fatty acids that finally controls the macromolecular structure. Rheological and adhesion studies elucidated strong variations in the viscoelastic properties resulting from the incorporation of sugar in the monomer backbone. A more extended version of the work presented in this paper was recently published as a research article.[13]

Citations

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