Renewable responsive systems based on original click and polyurethane crosslinked architectures with advanced properties

Khantutta-Kim Tremblay-Parrado^[a], Luc Avérous^[a]

^[a]BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, Cedex 2, France

* Corresponding author: Prof. Luc Avérous, Phone: + 333 68852784, Fax: + 333 68852716, E-mail: luc.averous@unistra.fr

Abstract:

A new chemical architecture from oleic acid consisting of a diol structure containing pendent furan rings denoted the Furan Oligomer (FO) was synthesized and fully characterized. The FO was integrated into a linear rapeseed-based polyurethane (PU) backbone and crosslinked via Diels-Alder (DA) reaction using the pendent furan rings and a short polypropylene oxide based bismaleimide. This is the first time a thermo-reversible PU network based on vegetable oil is reported. The effects of varying proportions of FO in linear and crosslinked systems, by DA, were studied. These materials were analyzed by classic characterization techniques. The stability and recyclability of the crosslinked materials were shown by successive reprocessing cycles and reanalyzing the mechanical properties. Self-healing properties were macroscopically exhibited and by tensile tests of healed materials. The resulting crosslinked materials present a large range of properties such as tunable mechanical and thermo-responsive behavior, good thermal recyclability and self-healing abilities.

Keywords:

Renewable Resources, Oleic acid, Biobased polymers, Polyurethane, Diels-Alder Cycloaddition

Table of Content

Khantutta-Kim Tremblay-Parrado, Pr. Luc Avérous

Renewable responsive systems based on original click and polyurethane crosslinked architectures with advanced properties

Biobased Thermo-reversible Polyurethane: A new architecture from oleic acid consisting pendent furan rings denoted the Furan Oligomer (FO) was synthesized. The FO was integrated into a linear biobased polyurethane backbone and crosslinked via Diels-Alder reaction using a bismaleimide oligomer. The resulting networks present interesting properties such as tunable mechanical and thermos-responsive behavior, recyclability and a self-healing ability.

Introduction

Nowadays, developing biobased and environmentally friendly materials is not enough. Science has to face developing advanced materials with extending lifetimes and with a controlled end of life. Polymer materials with innovative architectures allowing for cutting-edge properties such as self-healing and reprocessability, do not only extend the life of end-user materials, but also allow for the reduction of energy use, resources and waste. Polyurethanes (PUs) are of particular interest to integrate these novel properties due to their global versatility. PUs are used for a wide range of applications such as adhesives, coatings, automotive and construction industry.^[1] Their production is ranked 6th amongst all polymers,^[2] with a planned production of approximately 23 million tons in 2019.^[3] Although the biobased PU market is expanding, limited work has explored the development biobased PUs with particular architectures to allow for dynamic and adaptable materials. Developing biobased materials and PUs is a starting point to a circular economy but by designing biobased PUs with dynamic architectures, this truly takes in to account the cradle-to-grave reasoning of materials to facilitate recyclability and the extension of material lifetime.

To develop renewable materials, vegetable oils have a particular importance, as they are abundantly available at rather low costs with attractive chemical structures for a rich chemistry.^[4] Soybean oil is the most abundantly produced vegetable oil and it has been particularly explored by academics and industrials for PU thermoset applications.^[4-5] Studies reporting the use of vegetable oils to synthesize diols for linear thermoplastic PUs (TPUs) include (i) the use of methyl oleate and ricinoleic acid through transesterification, epoxidation, ring-opening of epoxides and thiol-ene addition,^[6] (ii) methyl ester of rapeseed oil through transesterification and thiol-ene coupling,^[7] (iii) polyricinoleate diol by polycondensation^[8] and (iv) the dimerization of rapeseed oil fatty acids at high temperature by a Diels-Alder (DA) mechanism.^[9] Consequently, the use of vegetable oils for the development of biobased PUs is a favorable starting point. Nevertheless, there is an apparent lack, particularly at the industrial level, in the development of advanced biobased PUs materials with dynamic architectures for a well-thought out reflection of the extension of polymer material lifetimes.

In order to extend the lifetime of polymers, many efforts have been made to develop dynamic and reversible polymers. Such a behavior is based on the development of dynamic covalent bonds that can be formed and cleaved by exposure to an external stimulus or autonomously. Crosslinked polymers containing reversible covalent bonds are defined as Covalent Adaptive Networks (CANs)^[10] and can be further subdivide in two categories^[11], dissociative and associative systems.

1 Associative CANs consists of bond exchange between polymer chains, where the overall
2 crosslinking density is preserved as a new covalent bond can only be formed if another has been
3 broken, such as vitrimers,^[12] which can also be biobased.^[13] Dissociative CANs consist of chemical
4 bond exchanges where bonds are first broken and then formed again in another place. Reversible
5 covalent bonds such as the DA^[14] reaction or alkoxyamine^[15] chemistry can be used. As
6 highlighted by the work of Gandini and co-workers, the thermoreversible furan-maleimide [4+2]
7 cycloaddition DA reaction is the most extensively studied reversible covalent bond of dissociative
8 CANs used in the synthesis of macromolecular architectures.^[16] The DA reaction between a furan
9 and maleimide moiety is considered as a cycloaddition “click” reaction, generally occurring at
10 moderate temperature (below 90 °C) and the reversion reaction denoted as the retro-DA (r-DA)
11 reaction, occurs between 110 and 130 °C.^[17] The reactivity and reversibility of the DA and r-DA
12 reactions can be tuned significantly depending on the substituents located on a furan and
13 maleimide moiety.^[18] Several biobased CANs have been synthesized using the thermoreversible
14 DA reaction derived from lignins^[19], tannins^[20], alginate ^[21], chitosan^[22], starch^[23] or vegetable
15 oils.^[16a]

16 Using the DA reaction in PUs is of particular interest as it is believed that the shape memory
17 behavior of PUs facilitates the self-healing by DA reaction.^[24] Consequently, reversibly crosslinked
18 PUs have been studied through a multitude of different strategies.^[25] Nevertheless, only very few
19 studies explore the use of biobased PUs as a canvas to investigate reversibly crosslinked
20 polymers. Gu *et al.* synthesized a biobased TPU backbone using a renewable polylactide
21 copolymer diol and 2,5-furandimethanol as a soft segment and chain extender respectively. The
22 reversible covalent bonds were located in the hard segments (HS) where the DA reaction took
23 place between the furan ring of the chain extender and a bismaleimide.^[26] Wilson *et al.* synthesized
24 an original C₁₁ difuranic diol from furfural and 5-hydroxymethylfurfural, which they used to
25 synthesize polyesters and reversibly crosslinked polyurethanes networks with a bismaleimide.^[27]

26 In the present work, we produced reversibly crosslinked PUs based on vegetable oils using
27 thermally reversible furan-maleimide DA reaction. We synthesized a new chemical architecture
28 from oleic acid, consisting of a diol structure, containing pendent furan rings, which was thoroughly
29 characterized and denoted as the Furan Oligomer (FO). As depicted in Scheme 1, FO was
30 incorporated into the linear polymer backbone and further crosslinked with the use of a
31 bismaleimide based on polypropylene oxide (PPO BMI). The corresponding materials with varying
32 crosslinking contents were tested as remendable and self-healing PUs.

Scheme 1. Illustration of the general synthesis of biobased thermoreversible polyurethane-based systems using Furan Oligomer

Results and Discussion

Analysis of the Synthesis of FO

The acid moiety and alkene site of octadec-9-enoic acid (**OA**) were used as reaction sites to yield an oligomer with a diol structure containing pendent furan rings, as depicted in Scheme 2. **OA** was esterified using furan-2-ylmethanol (FM) at ambient temperature to yield furan-2-ylmethyl-oleate (**FMO**). The advantage of this type of esterification reaction (Steglich esterification) is that no energy source is required, minimizing the global energy requirement, in agreement with one of the main principles for a green chemistry.^[28] Nevertheless, this esterification reaction can also be accomplished using *Candida Antarctica* lipase B, an enzymatic catalyst, with greener conditions as explored by Sengupta *et al.*^[29]. More recently, Muthusamy *et al.* used the same enzymatic catalyst to obtain furan based oligoesters.^[30] The use of enzymes as green catalysts for macromolecular synthesis has become prevalent in the recent years as highlighted by Kobayashi and co-workers.^[31] FTIR spectrum of **FMO** exhibits a predominant band at 1738 cm^{-1} , confirming the presence of an ester carbonyl group and the furan heterocycle bands at 1503, 1375, 1347, 1228, 1080, 920, 885, 739 and 599 cm^{-1} (Figure 1). The appearance of the resonances of the methylene protons of the ester moiety at 5.1 ppm and the furan ring protons at 6.36, 6.39 and 7.41 ppm on the ^1H NMR spectrum of **FMO** confirms the expected structure (Figure 2). The technical grade oleic acid received contains small amounts of ethyl ester impurities as the saponification of the

1 triglycerides takes place in ethanol. This is evidenced by the quartet signal associated the CH₂ of
 2 the ethyl ester at 4.21 ppm. The results of the analysis of ¹³C NMR of **FMO** agreed with the
 3 assigned structure as depicted in Figure S1 in the supplementary information (SI).

Scheme 2. Global reaction pathway of **FO**

1
2

Figure 1. FTIR spectra of (a) **OA** (b) **FMO** (c) **FMOO** and (d) **FO**

Thereafter, **FMO** underwent an *in situ* epoxidation with the use of acetic acid, hydrogen peroxide (H₂O₂) and acid catalyst in toluene to yield furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate (**FMOO**). The acetic acid is converted to the oxidizing agent, peroxyacetic acid and is regenerated. This type of epoxidation is nowadays routinely used on vegetable oils.^[32] When compared to conventional academic epoxidation based on *meta*-chloroperoxybenzoic acid (mCPBA) as an oxidizing agent in solvent,^[33] *in situ* epoxidation uses milder oxidizing agents and globally adheres better to green chemistry principles. The FTIR spectrum of **FMOO** (Figure 1c) shows the disappearance of the double bonds at 3009 cm⁻¹. By ¹H NMR analysis (Figure 2c) the structure is confirmed by the disappearance of the vinyl and allyl protons at 5.35 and 1.99 ppm respectively, and by the appearance of the epoxide and protons alpha to the epoxides at 2.90 and 1.45 ppm respectively. The results of the analysis of ¹³C NMR of **FMOO** agreed with the assigned structure as depicted in Figure S2 in SI.

Figure 2. ^1H NMR spectra (a) of **OA** (b) **FMO** (c) **FMOO** and (d) **FO**

An oligomer polyether diol was finally obtained by the acid-catalyzed ring-opening polymerization (ROP) of **FMOO** and denoted as Furan Oligomer (**FO**). This cationic polymerization was accomplished using fluoroantimonic acid, HSbF_6 , as it predominantly achieved oligoether species.^[34] It was observed that 1.5 w.t. % of initiator was required to achieve complete oligomerization. The reaction was performed in bulk and followed by ^1H NMR analysis. The FTIR spectrum (Figure 1d) exhibits the broad stretch of the hydroxyl groups at 3440 cm^{-1} . The **FO** structure was further confirmed by ^1H NMR analysis (Figure 2d) by the disappearance of the epoxide protons and protons in alpha to the epoxides at 2.90 and 1.45 ppm, respectively, and the appearance of the formed polyether backbone between 3.00-3.60 ppm (for detailed integration see Figure S3). By ^{13}C NMR and ^{13}C NMR DEPT 135, as seen in Figure S4 and Figure S5 in the SI respectively, carbons associated to the polyether backbone corresponding to ether and carbon containing secondary hydroxyl groups clearly appear. Concurring with Lligadas *et al.*, water was introduced in the oligomerization synthesis to suppress the occurrence of macrocyclization. This

allowed for the nucleophilic attack of water to compete with intramolecular attacks, consequently favoring the proportion of linear species. Three different oligomers architectures were synthesized. As highlighted in Table 1, introducing higher water equivalents limits the oligomerization and yields overall higher hydroxyl values (HV) of the synthesized oligomers. The oligomer hydroxyl functionality was determined by using the M_n and HV and remains very close to two for all oligomers synthesized. This was further confirmed by the MALDI-TOF MS analysis of Oligomer Sample B as seen in Figure S6 and Figure S7 in SI, where the repeating units, n , varied from 2 to 9. The most intense peaks belonging to the series of oligomers with n values of 3-5. The HV was determined using ^{31}P -NMR and quantification results can be found in Figure S8 and Table S2 in SI.^[35] Quantitative ^1H NMR was used to determine the furan content (mmol furan/g) of **FO** and quantification results are available in Figure S9 and Table S3 in SI. Oligomer B was then used for the PU synthesis.

Table 1. Synthesis and properties of different **FO** obtained by cationic ROP of **FMO**

Oligomer Sample	Initiator HSbF_6 (w.t. %)	H_2O (mol %)	Hydroxyl Value by ^{31}P NMR (mg KOH/g)	Equivalent Weight (g/equiv) ^[a]	M_n (SEC; g/mol)	$\bar{D}$ ^[b]	Functionality (M_n/EW) ^[c]	Furan Content by ^1H NMR (mmol/g)
A	1.5	80	60	935	1179	1.75	1.90	1.89
B	1.5	70	55	1020	1983	1.69	1.94	1.89
C	1.5	60	49	1145	2222	1.94	1.94	1.74

[a] Equivalent weight calculated from the hydroxyl value, EW. [b] Dispersity = M_w/M_n [c] Obtained by the division of the experimental molar mass (M_n) by the EW.

Analysis of DA of **FO** and *N*-Methylmaleimide

FO was reacted with monofunctional *N*-methylmaleimide in DMSO at 65 °C, to study the DA adduct formation by ^1H NMR in absence of gelation. ^1H NMR attests the formation of the DA adduct (Figure 3a). Proton assignment was achieved using the ^1H NMR of initial compounds and comparison to the literature.^[19b, 36] To quantify the conversion, proton signals, f_1 and f_4 (in the furan) and m_2 (in the maleimide) and f_1' , f_4' and m_2' (in the adduct) were used as they are free from overlap with other signals (Figure 3a). The conversion was calculated in accordance with Equation 1 for proton set f_1 and f_1' as follows; where Int_{f_1} and $\text{Int}_{f_1'}$ represent the integral values of their respective protons:

1

$$X (\%) = \frac{Int_{f_1'}}{Int_{f_1} + Int_{f_1'}} * 100 \quad (1)$$

2 Similar results could be obtained with proton sets f_4 , f_4' and m_2 , m_2' . The evolution of the conversion
3 with respect to time at 65 °C is depicted on Figure 3b. An equilibrium conversion of 65% was
4 attained after 121 hours of reaction time, as similarly reported in literature.^[37] Furthermore, proton
5 signals, f_1' and m_2' , were used to quantify the evolution of two diastereomers of the DA adduct
6 (*endo* and *exo*) with respect to time (Figure 3b), as the chemical shift differs slightly for each
7 diastereomer. The *endo* adduct which is kinetically favored,^[36] is first formed at 62%. As the
8 reaction time progresses, the thermodynamically stable *exo* diastereomer becomes the
9 predominant entity (91 w.t. %) after 121 hours of reaction time.

Figure 3. (a) ^1H NMR spectra of mixture of FO and *N*-methylmaleimide after 0 and 24h, (b) conversion and percentage of endo structure with respect to time at 65 °C.

Analysis of DA and r-DA Reactions between FO and a Bismaleimide

To test and simulate the formation of DA adducts between PU chains, the **FO** was reacted with PPO BMI. DSC was used to monitor the formation of the DA adducts and the r-DA reaction. A stoichiometric mixture of **FO** and PPO BMI was heated from -30 to 175 °C. As controls, **FO** and PPO BMI were separately investigated under the same conditions. As seen in the thermograms reported in Figure 4a, no thermodynamic phenomena take place for each separate entity. However, in the thermogram of the mixture (orange), an exothermic peak begins to appear between 50 to 60 °C, indicating the DA reaction. Two endothermic peaks, corresponding to the r-DA, follow the exothermic peak. The first one, between 90-120 °C, corresponds to the r-DA of the *endo* diastereomer, while the second one refers to the r-DA of the *exo* diastereomer, between 120-150 °C.^[36]

The thermoreversibility of the network formed between the **FO** and the BMI was further qualitatively studied by dissolving the mixture in DMSO and exposing it to different heating cycles. As depicted in Figure 4b-i, the mixture is first completely soluble in DMSO. Once exposed to 60 °C for 24 hours, a gel is formed by cross-linkage (Figure 4b-ii). The mixture was then exposed to 120 °C for 1h, causing the disassembly of the network due to the r-DA reaction (Figure 4b-iii). When repeating the heating cycle, the same phenomenon took place (Figure 4b-iv). To further evidence the DA reaction, the mixture was studied prior and after gel formation by FTIR. Before crosslinking, the FTIR spectrum of the mixture contains signals of free furan (739 and 1503 cm⁻¹) and maleimide rings (695 and 826 cm⁻¹) (Figure 4c). After gel formation, the FTIR spectrum exposes a complete disappearance of the respective free furan and maleimide ring signals. To quantitatively study the DA reaction and r-DA between **FO** and BMI, the rheological behavior of gel formation between the two entities was evaluated by a dynamic experiment. As seen in Figure S10, the gelation reaction was analyzed by a time sweep test at 60 °C at 1% strain and 1 Hz, while recording the variation of the two dynamic moduli. Gelation occurs when the moduli cross over at 1740 s (29 mins, ($G' \sim G'' \sim 650$ Pa). Thereafter, heating steps were imposed to evaluate the thermoreversibility of the gel, 60 °C for the DA and 120 °C for r-DA. During the r-DA heating steps, the gel would disassemble and the two moduli shoot back to zero. The gel was reassembled two more times, each time leading to quicker gelation times. This thus proves the thermoreversibility of the crosslinking points of the PU materials made using these two building blocks.

Figure 4. (a) DSC thermograms of PPO BMI, FO and the mixture of both, from 0 to 170 °C, (b) i – Initial mixture of FO and PPO BMI, ii – mixture after 24h at 60 °C, iii – mixture after additional 1h at 120 °C, iv - mixture after additional 24h at 60 °C, (c) FTIR spectra of initial mixture (green) and final dried crosslinked gel (orange).

Analysis of the Synthesis of Biobased Crosslinked PU containing FO and BMI

The synthesis of crosslinked biobased PUs containing thermoreversible DA adducts was obtained by using **FO** and PPO BMI. Scheme 1 illustrates the route for the preparation of the control (linear PUs – reaction 1) systems and crosslinked PUs (reactions 1 and 2). Different types of PUs were prepared by varying the proportion of **FO** in a PU system by the polyaddition between the biobased polyester polyol (chemical structure found in Figure 5) and hexamethylene di-isocyanate (HDI). The **FO** content in the PU systems was varied from 0 to 30% of the total hydroxyl moles required to synthesize PUs with a final NCO:OH ratio of 1.05. PUs were obtained without HS (segments synthesized with short diols and di-isocyanates) to study the effect of the **FO** on a model, a simple system. The nomenclature of all PU systems synthesized is summarized in Table 2. The different control PU systems, with varying amounts of **FO** content were denoted as PU-FO-0, PU-FO-10,

1 PU-FO-20, and PU-FO-30. Thermoreversible crosslinked PU systems were obtained by dissolving
2 the corresponding linear PU in dry DMF, adding the required amount of PPO BMI and letting the
3 solution stir overnight at 70 °C, to allow the DA reaction to take place. These solutions then
4 underwent solvent casting in a PTFE square mold for 48 h at 70 °C followed by 24 h under vacuum
5 at 70 °C to yield a crosslinked PU. Crosslinked PUs containing the required PPO BMI mass to
6 yield a 1:1 furan to maleimide ratio were denoted as PU-FO-10XL, PU-FO-20XL and PU-FO-
7 30XL. Two additional crosslinked PUs were synthesized using the linear PU-FO-20 but with 1: 0.7
8 and 1: 0.5 furan and maleimide ratios and denoted as PU-FO-20XL-0.7BMI and PU-FO-20XL-
9 0.5BMI, respectively.

Figure 5. Chemical structure of the biobased polyester polyol supplied by the provider. Polyol based on dimeric fatty acids from rapeseed oil.

Table 2. Linear PU (control) and crosslinked systems: nomenclature and corresponding formulations.

PU System Nomenclature	Type of System	Furan Oligomer (FO) Content ^[a] (%)	Rapeseed Polyol Content ^[a] (%)	PPO BMI Equivalents ^[b]
PU-FO-0	Linear	0	100	0
PU-FO-10	Linear	10	90	0
PU-FO-10XL	Crosslink	10	90	1
PU-FO-20	Linear	20	80	0
PU-FO-20XL	Crosslink	20	80	1
PU-FO-20-0.7BMI	Crosslink	20	80	0.7
PU-FO-20-0.5BMI	Crosslink	20	80	0.5
PU-FO-30	Linear	30	70	0
PU-FO-30XL	Crosslink	30	70	1

1

2 All PU systems post curing (linear and crosslinked) were insoluble in conventional solvents

3 (CHCl_3 , DMSO, THF, DMF) and thus were examined by FTIR. It has been shown that symmetrical

4 di-isocyanates such as HDI increase the crystallinity and hard segment packing of polyurethanes

5 which may account for the lack of solubility that occurs in the presented networks.^[38] A comparison

6 of the FTIR spectra of **FO**, biobased polyester rapeseed polyol, PU-FO-30, PU-FO-30-XL and

7 PPO BMI is displayed in Figure 6. In Figure 6c of the FTIR spectrum PU-FO-30, the disappearance

8 the hydroxyl stretches (approximately at 3440 cm^{-1}) associated to the hydroxyls of **FO** and

9 rapeseed polyol is observed. Consequently, the appearance of vibrations at 3380 and 1550 cm^{-1}

10 corresponding to -N-H stretching and bending respectively of urethane group, whereas the ester

11 urethane stretch present itself at a shouldering located at 1700 cm^{-1} . The FTIR spectrum of PU-

12 FO-30XL (Figure 6d) displays a similar spectrum than that of PU-FO-30. However, the addition of

13 PPO BMI to yield a crosslinked system results in the appearance of the carbonyls of the

14 maleimides at 1705 cm^{-1} . Moreover, as the PU-FO-30XL is crosslinked via DA reaction, the

disappearance of furan heterocycle and C-H bending of maleimide ring (826 and 692 cm^{-1}) is observed.

Figure 6. FTIR spectra of (a) **FO** (b) Rapeseed Polyol (c) PU-FO-30 (d) PU-FO-30XL (e) PPO BMI

Characterization of Biobased Crosslinked PUs

The thermal stability of all PU materials was evaluated by TGA. Detailed TGA results are found in Figure S11 in SI. As exhibited in Table 3, the initial thermal degradation ($T_{5\%}$) for all materials begins at temperatures above that of the r-DA reaction. This is indicative that reprocessing and disassembly of crosslinked points is thus possible without thermal degradation, although the introduction of the **FO** seems to decrease the $T_{5\%}$ (from 337 to 230 $^{\circ}\text{C}$ for PU-FO-0 to PU-FO-30). Furthermore, the respective crosslinked material have lower $T_{5\%}$, with except of PU-FO-10XL. The glass transition temperatures (T_g) were measured by DSC and results are summarized in Table 3. The T_g of crosslinked materials were recorded using a single heating ramp, from -80 $^{\circ}\text{C}$ to 175 $^{\circ}\text{C}$ in order to avoid any significant degradation as indicated by TGA results. When comparing a control PU-FO-30 with its respective crosslinked PU counterpart (PU-FO-30XL), the T_g increases due to a high level of crosslinking. Furthermore, as seen in Figure 7, the thermograms of crosslinked PUs exhibit the presence of an endothermic peak between 90 and 150 $^{\circ}\text{C}$ corresponding to the r-DA reaction, whereas, their control PU counterparts are flat-lined as no BMI is present. Materials containing increased amounts of **FO**, (and consequently increased

crosslinking density) logically exhibit a more prominent endothermic r-DA peak between 90 and 150 °C. A slight endothermic peak seems to appear in all crosslinked materials of Figure 7 between 30 to 60 °C. As previously mentioned, crosslinked materials are evaluated by a single heating ramp from -80 to 175 °C. These endothermic peaks were present as well in linear material upon first heating but disappeared upon the second heating when as the thermal history of the material has been erased. Thus, these slight endothermic peaks appear to be associated the thermal history of the material. Detailed DSC results are found in Figure S12.

Table 3. Characterizations of synthesized biobased polyurethanes.

PU System	TGA T _{5%} (°C)	DSC T _g (°C)	Young's Modulus E (MPa)	Tensile Strength σ (Mpa)	Elongation ε (%)	Swelling Ratio in DMF (%)	Insoluble Fraction (%)
PU-FO-0	337	-50	0.39 ± 0.03	0.58 ± 0.02	563 ± 36	36.9 ± 1.8	96.4 ± 0.3
PU-FO-10	327	-51	0.14 ± 0.01	0.36 ± 0.02	368 ± 27	51.6 ± 2.3	94.4 ± 0.6
PU-FO-10XL	333	-51	0.32 ± 0.01	0.51 ± 0.03	409 ± 54	44.3 ± 0.6	95.0 ± 0.9
PU-FO-20	298	-51	0.11 ± 0.01	0.38 ± 0.03	288 ± 4	58.5 ± 3.4	92.9 ± 0.6
PU-FO-20XL	267	-50	0.32 ± 0.01	0.50 ± 0.01	232 ± 2	46.9 ± 0.1	95.2 ± 2.9
PU-FO-20- 0.7BMI	287	-51	0.30 ± 0.01	0.40 ± 0.02	208 ± 2	48.2 ± 6.3	92.0 ± 2.9
PU-FO-20- 0.5BMI	293	-50	0.26 ± 0.01	0.32 ± 0.01	232 ± 11	55.7 ± 3.0	90.6 ± 1.2
PU-FO-30	250	-55	NA	NA	NA	146.1 ± 7.4	77.5 ± 0.8
PU-FO-30XL	234	-51	0.57 ± 0.09	0.49 ± 0.04	107 ± 9	70.4 ± 2.7	92.5 ± 0.6

2 **Figure 7.** Thermograms of four PUs: PU-FO-10, PU-FO-10XL, PU-FO-20XL and PU-FO-30XL from 0 to
3 175 °C.

4 The mechanical properties of the PUs were evaluated by uniaxial tensile tests at room
5 temperature. The sticky-like and weak behavior of control PU, PU-FO-30, rendered the material
6 non-testable because it was non-processable for dumbbell shaping, as molding these samples
7 was impossible. When examining Table 3 and more specifically control PUs results, the
8 incorporation of **FO** into the PU structure weakens the material as there is an apparent decrease
9 in tensile strength and Young's modulus of PU-FO10, PU-FO-20 in comparison to PU-FO-0.
10 Furthermore, the addition of **FO** also reduces the elasticity of the material as the elongation of PU-
11 FO-10, PU-FO-20 is decreased with respect to PU-FO-0. Nevertheless, when examining the
12 mechanical properties of crosslinked PUs: PU-FO-10XL, PU-FO-20XL and PU-FO-30XL, the
13 crosslinking by DA improves the tensile strength of the materials, but most notably the Young's
14 modulus.

15 From Figure 8, which exhibits the stress-strain curves of PU-FO-0, PU-FO-10XL, PU-FO-20XL
16 and PU-FO-30XL, it can be deduced that by increasing the portion of **FO** in the PU structure and
17 crosslinking by PPO BMI, the material properties vary from a thermoplastic elastomer (PU-FO-0)
18 to a thermoset material (PU-FO-30XL). Furthermore, it was evidenced that mechanical properties

can be further tuned by varying the equivalents of PPO BMI introduced into the material. This is evidenced by the mechanical properties of PU-FO-20XL-0.7BMI and PU-FO-20XL-0.5BMI, whereby varying the equivalents of PPO BMI between 0.7 and 0.5 to furan equivalents resulted in tensile strengths and Young's modulus in an intermediate range between PU-FO-20 and PU-FO-20XL (Table 3).

Figure 8. Stress-strain curves of PU-FO-0, PU-FO-10XL, PU-FO-20XL and PU-FO-30XL.

All PU materials were lastly characterized by swelling test in DMF. As seen in Table 3, when first examining linear materials PU-FO-0, PU-FO10, PU-FO-20, and PU-FO-30, it can be observed that the polymer networks experience higher swelling when increasing the amount of **FO** in the polymer architecture. Contrastingly, due the crosslinking by DA reaction, the results of crosslinked PUs yield considerably lower swelling ratios in comparison to their respective control PU. The most considerable effect of DA crosslinking is seen for the highest crosslinked content, between PU-FO-30 to PU-FO-30XL, where the swelling ratio decreased from 146 to 70%, respectively, and the insoluble fraction increases from 78 to 93%, respectively. Except PU-FO-30, all PU material were relatively insoluble. Furthermore, the swelling ratio of PU material PU-FO-20XL-0.7BMI and

1 PU-FO-20XL-0.5BMI yields intermediate results between the crosslinked material, PU-FO-20XL
2 and the linear control PU, PU-FO-20. This is a testament of tunable properties when varying not
3 only the **FO** content but as well the PPO BMI concentration.

4 **Thermoreversibility of Biobased Crosslinked PU leading to Remendable and Self-healing** 5 **Behaviors**

6 Preamble studies conducted to prove the thermoreversible between **FO** and the monofunctional
7 *N*-methylmaleimide or PPO BMI permitted to test and simulate the thermoreversibility of
8 crosslinked PU by the DA and r-DA reaction. To first evaluate the thermoreversibility of crosslinked
9 marterials, PU-FO-20XL was examined by FTIR after exposing the material to different heating
10 cycles. As depicted in Figure 9, when heating the material for 2h at 120 °C, free maleimide ring
11 peaks appear prevalent at 692 and 825 cm⁻¹ due the occurrence the r-DA reaction. These free
12 maleimide ring peaks disappear once the DA reaction takes place, when the material is re-
13 exposed to 70 °C for 20h. This heating cycle was repeated and yields the same result, as seen in
14 Figure 9. This indicates that the materials crosslinked by DA have the potential of being
15 reprocessable and could be self-healing.

16
17 **Figure 9.** FTIR spectra of original PU-FO-20XL followed by: PU-FO-20XL heated for 2h at 120 °C, PU-
18 FO-20XL heated for 20h at 60 °C and PU-FO-20XL heated for 2h at 120 °C.

Reprocessability was also studied on PU-FO-30XL. It was first processed by solvent casting and then characterized (Table 4). This material was then reprocessed by compression molding at 150 °C for 25 minutes. The material was cured at 60 °C in the oven for 48 hours and post cured for 24 hours at room temperature. The uniaxial tensile test and T_g were studied for this material labeled PU-FO-30XL-RP1. The material was then reprocessed, re-evaluated, and labeled PU-FO-30XL-RP2. The results are summarized in Table 4 and are conclusive that the material can indeed be reprocessed without significant material degradation. The T_g of the reprocessed material is stable, as is the Young's modulus. Nevertheless, reprocessing does induce only some light decrease in the material performances as the tensile strength and elongation at break slightly decreases.

Table 4. Characterization of biobased PU, PU-FO-30XL reprocessed several times.

PU System	DSC T_g (°C)	Young's Modulus E (MPa)	Tensile Strength σ (MPa)	Elongation (%)
PU-FO-30XL	-51	0.57 ± 0.09	0.49 ± 0.04	107 ± 9
PU-FO-30XL-RP1	-50	0.62 ± 0.03	0.47 ± 0.04	83 ± 5
PU-FO-30XL-RP2	-50	0.58 ± 0.02	0.40 ± 0.03	74 ± 6

As depicted in Figure 10a, self-healing was studied by cutting a dumbbell sample of PU-FO-30XL in half and exposing it to 1 hour at 120 °C and 2 days at 60 °C and denoted PU-FO-30XL-HL1. By utilizing the thermo-reversibility of the DA bonds, the breaking and reforming of the crosslinks allows a severed dumbbell sample to be healed when exposed to such heating cycles. The initial heating at 120 °C for 1 hour allows to break the crosslinks, thus enhancing network mobility. Consequently, the polymer chains can locally flow giving rise to adhesion to the two severed pieces. The final heating step at 60 °C for 2 days allows the network to be reformed by the DA reaction. As seen Figure 10b, the healed materials show a novel integrity and recovery in terms of Young's modulus with around 0.5 MPa, a value equivalent to the initial material. Only at high elongation, a decrease of the performances is visible. This behavior is largely indicative that the thermoreversible DA crosslinking of PUs allows the material to have self-healing properties.

Figure 10. Self-healing evaluation. (a) (i) Photo of PU-FO-30XL dumbbell sample cut in half, (ii) healed dumbbell sample of PU-FO-30XL after heating 1 hour at 120 °C and 2 days at 60 °C, (iii) lifted healed dumbbell with zoom on healed section (b) Stress-strain curves of PU-FO-30XL and PU-FO-30XL-HL1

Conclusion

Thermo-reversible and self-healing crosslinked biobased systems based on urethane groups and clickable functions were successfully synthesized using vegetable oil derivatives and utilizing Diels-Alder reaction to control the design of their macromolecular architectures. A new biobased building block has been designed. The Furan Oligomer was developed from oleic acid in a sustainable way, largely in agreement with different green chemistry principles. As a general trend, crosslinked systems had characteristically higher T_g , insoluble ratio and enhanced stiffness and strength and lower swelling ratio when compared to their control PU counterparts. The crosslinked materials exhibit modular mechanical properties with respect to Furan Oligomer content. These biobased materials present a large range of behavior, from a typical thermoplastic elastomer-like material (least crosslinked material) to a thermoset (most crosslinked material). Reprocessing cycles were successfully performed and exhibited stable material properties. The systems also present self-healing properties. Dumbbell samples were cut in half, healed by joining the pieces together and exposing them to 120 °C, and cured at 60 °C. Both parts were able to recombine and considerably mend the material. To this end, this work is a stepping-stone in developing vegetable oil-based architectures with integrated dynamicity for evolution of high-performance and advanced biobased materials.

1 Future efforts will be dedicated to develop a greener chemistry with e.g. the reduction of the
2 solvent consumption and the use of more sustainable solvents. In the near future, similar
3 crosslinked vegetable oil based polyurethane formulation varying HS content can be studied for
4 material application such as adhesives and coatings thus providing exciting perspectives for a
5 greener future with advanced behavior to decrease the global impact of these materials, with a
6 controlled end of life.

Experimental Section

Reagents and Materials

Octadec-9-enoic acid (OA) from sunflower oil was kindly supplied by ITERG. It is a technical grade fatty acid with an acid value of 185 mg KOH/g. Furfuryl alcohol (FA, 98%), 4-dimethylaminopyridine (DMAP, 99%), hydrogen peroxide (H₂O₂, 30% w/v aqueous solution), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (CL-TDP, 95%), chromium (III) acetylacetonate (99.99%), cholesterol (>99%), dimethyl sulfoxide-d₆ (DMSO, 100%, 99.96% atom D) were purchased from Sigma Aldrich; *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), polyether catalysis HSbF₆ (65% w/w aqueous solution) were purchased from Alfa Aesar; hexamethylenediisocyanate (HDI, 99%), chloroform-d (CDCl₃, 100%, 99.96% atom D) were purchased from Acros Organics; dichloromethane dried over molecular sieve (DCM, >99%, stabilized with amylene), diethyl ether (stabilized with BHT) were purchased from Carlo Erba; toluene (100%,) was purchased from VWR Chemicals; glacial acetic acid (GAA, >99%), *N,N*-dimethylformamide (DMF, 99.8%) was purchased from Fisher Scientific and amberlite IR-120 H from Fluka Chemicals. Biobased polyester polyol was purchased from Oleon is derived from dimeric fatty acids from rapeseed oil with purity greater than 98% and weight average molar mass (M_w) around 3 000 g/mol. Hydroxyl and acid values were 33 and 0.253 mg/g KOH, respectively. The poly(propylene oxide) based bismaleimide (DP = 3) cross-linker was purchased from Specific Polymers (Castries, France). 2,3,4,5,6-pentafluorobenzaldehyde (PFB,98%) was purchased from fluorochem.

Syntheses and Material Processing

Esterification of Furan-2-ylmethanol and Octadec-9-enoic Acid from Sunflower Oil

The esterification of Octadec-9-enoic acid (OA) was adapted from Vilela *et al.* and Rauf *et al.*,^[28, 39] for an esterification conducted under mild conditions. A solution included one molar equivalent of OA, *N,N'*-dicyclohexylcarbodiimide (DCC, 1.1 mol eq.), 4-dimethylaminopyridine (DMAP, 0.1 mol eq) in 25 w/v % of dried dichloromethane (DCM) was stirred magnetically for one hour in a two-necked round bottom flask at room temperature. Furfuryl Alcohol (FA, 1.1 mol eq) was then added dropwise through a dropping funnel. The reaction mixture was left stirring overnight at room temperature and under nitrogen. The *N,N'*-dicyclohexylurea (DCU) formed during the reaction precipitated and was filtered off. The filtrate was washed twice with water, twice with 5% acetic acid solution and finally again with water until a neutral pH was attained. The organic phase was dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure. The ester formed, Furan-2-ylmethyl-octadec-9-enoate (**FMO**) was then further purified over a silica gel plug using petroleum ether/diethyl ether (95:5, vol/vol) as eluents to remove remnants of DCU. FMO was dried under vacuum overnight vacuum, at 50 °C.

Furan-2-ylmethyl-octadec-9-enoate (FMO) - ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 7.41 (1H, dd, 5-H of 2-furan), 6.39 (1H, d, 3-H of 2-furan), 6.36 (1H, dd, 4-H of 2-furan), 5.34 (2H, m, $\text{CH}=\text{CH}$), 5.06 (2H, s, OCH_2), 2.32 (2H, t, $\text{CH}_2\text{C}(=\text{O})$), 1.99 (2H, m, $\text{CH}=\text{CHCH}_2$), 1.62 (2H, m, $\text{CH}_2\text{CH}_2\text{C}(=\text{O})$), 1.37-1.18 (20H, m, aliphatic CH_2), 0.88 (3H, t, CH_3). ^{13}C NMR (500 MHz, CDCl_3 , δ (ppm)): 1734 ($\text{C}=\text{O}$), 150 (C-2 of 2-furan), 143 (C-5 of 2-furan), 130 ($\text{CH}=\text{CH}$), 130 ($\text{CH}=\text{CH}$), 111 (C-3 of 2-furan), 111 (C-4 of 2-furan), 57.9 (OCH_2 -2-furan), 34.2 (CH_2 - $\text{C}(=\text{O})$), 31.9-22.7 (aliphatic CH_2), 14.1 (CH_3)

Epoxidation of Furan-2-ylmethyl-octadec-9-enoate

The epoxidation of FMO was conducted by the in-situ formation of peracetic acid from glacial acetic acid and H_2O_2 , and was adapted from Arbenz *et al.* In a two-necked round bottom flask, equipped with a magnetic stirrer and a dropping funnel, FMO (1 mol eq of unsaturations), amberlite IR-120 H (25 wt% of FMO), glacial acetic acid (0.2 mol eq) was inserted into the flask and dissolved in 12.5 wt% (m:v) of toluene. The solution was stirred to 70 °C and then 1.2 mol eq. of H_2O_2 was added dropwise. The mixture was stirred at 70°C for 7 hours. In comparison to current literature ^[32, 40], a lower acetic acid and H_2O_2 but increased toluene content is required to yield a high conversion of the alkene bond into an epoxy moiety, all the while minimizing the hydrolysis of the newly formed ester bond. The optimization trials of reactional components stoichiometry can be found in SI Table S1. Amberlite IR-120 H was filtered off and the solution was washed with distilled water until a neutral pH was attained. The organic phase was dried with anhydrous sodium sulphate and then filtered. The solvent was evaporated under reduced pressure. Epoxidized FMO (EFMO) was dried under vacuum overnight, at 50 °C. The reaction product, Furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate (**FMOO**), was clear yellow oil.

Furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate (FMOO) - ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 7.41 (1H, dd, 5-H of 2-furan), 6.39 (1H, d, 3-H of 2-furan), 6.36 (1H, dd, 4-H of 2-furan), 5.06 (2H, s, OCH_2), 2.90 (2H, m, CHOCH), 2.32 (2H, t, $\text{CH}_2\text{C}(=\text{O})$), 1.62 (2H, m, $\text{CH}_2\text{CH}_2\text{C}(=\text{O})$), 1.37-1.18 (24H, m, aliphatic CH_2), 0.88 (3H, t, CH_3). ^{13}C NMR (500 MHz, CDCl_3 , δ (ppm)): 174 ($\text{C}=\text{O}$), 150 (C-2 of 2-furan), 143 (C-5 of 2-furan), 111 (C-3 of 2-furan), 111 (C-4 of 2-furan), 57.9 (OCH_2 -2-furan), 57.2 ($\text{HC}-\text{O}-\text{CH}$), 34.2 (CH_2 - $\text{C}(=\text{O})$), 31.9-22.7 (aliphatic CH_2), 14.1 (CH_3)

Oligomerization of Epoxidized Furan-2-ylmethyl-octadec-9-enoate (FMOO)

For a molar equivalent of FMOO, H_2O (0.7 mol eq) was added in a two-necked round bottom flask and stirred mechanically. A cationic initiator, HSbF_6 (1.5 wt% of FMOO) was added dropwise. The mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of water and dissolved in diethyl ether. The organic solution was washed with a 5% sodium bicarbonate solution and distilled water until a neutral pH was attained. The solution was dried over anhydrous sodium

sulfate, and filtered. The solvent was evaporated under reduced pressure and the oligomer was dried under vacuum overnight, at 50 °C. The oligomerization resulted in an orange clear viscous oil.

Furan Oligomer: ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 7.41 (1H, dd, 5-H of 2-furan), 6.39 (1H, d, 3-H of 2-furan), 6.36 (1H, dd, 4-H of 2-furan), 5.06 (2H, s, OCH_2), 3.80 - 2.82 (m, polyether backbone), 2.32 (2H, t, $\text{CH}_2\text{C}(=\text{O})$), 1.62 (2H, m, $\text{CH}_2\text{CH}_2\text{C}(=\text{O})$), 1.37-1.18 (24H, m, aliphatic CH_2), 0.88 (3H, t, CH_3). ^{13}C NMR (500 MHz, CDCl_3 , δ (ppm)): 174 ($\text{C}=\text{O}$), 150 (C-2 of 2-furan), 143 (C-5 of 2-furan), 111 (C-3 of 2-furan), 111 (C-4 of 2-furan), 85.0-70.0 Polyether backbone($\text{C}-\text{O}-\text{C}$), 57.9 (OCH_2 -2-furan), 34.2 ($\text{CH}_2-\text{C}(=\text{O})$), 31.9-22.7 (aliphatic CH_2), 14.1 (CH_3)

Model Reaction between FO and N-methylmaleimide

200 mg of **FO** (0.378 mmol of furan) was dissolved in 2 mL of $\text{DMSO}-d_6$ in a 10 mL round bottom flask. *N*-methylmaleimide (0.378 mmol of maleimide) was added to obtain a furan to maleimide ratio of 1:1 (mol/mol). The solution was placed in an oil bath regulated to 65 °C and samples of 200 μL were taken at regular intervals over 5 days. The samples were further diluted to 650 μL and analyzed by ^1H NMR to determine the reaction conversion and *endo/exo* ratio of the DA adducts.

Diels-Alder and Retro-Diels-Alder Reaction between FO and a Bismaleimide

FO and a PPO-based BMI were mixed together in a small flask at a 1:1 furan to maleimide ratio (mol/mol) and dissolved in DMSO at 40 wt% concentration. The sample was heated in an oven at 60 °C without stirring. Once gelation occurred (typically after 24 hours), samples were heated to 120 °C for 1 hour in an oven to perform the r-DA reaction and the mixture returned to a liquid state. The sample was underwent the same cycle one more time. After crosslinking in solution, the gel was washed with water and dried in an oven at 40 °C under vacuum. The gel was analyzed by FTIR compared to the initial mixture of **FO** and BMI.

Synthesis of Polyurethanes containing FO

All glassware and reactants were previously dried. Four different kinds of polyurethanes films were prepared with varying amounts of **FO** (0%, 10%, 20% and 30% of total the hydroxyl value was derived from the **FO**, for example for **FO**-20%, 2.96 mmol OH from **FO**). Under nitrogen, in a three-necked round bottom flask, biobased rapeseed polyester polyol (11.8 mmol OH) and **FO** (2.96 mmol OH) was added to hexamethylene di-isocyanate (HDI, 15.5 mmol NCO) and the mixture was mechanically stirred at 70 °C for 3-4 h. The ratio $-\text{NCO}/-\text{OH}$ functional groups were fixed to 1.05 in all cases.

Crosslinking of Polyurethanes containing of FO

The polyurethane was dissolved in dry DMF. To this, BMI was added in a 1:1 furan to maleimide ratio (mol/mol). The reaction mixture was stirred at 70 °C for 12 h to allow for the DA adducts to form. The

solution was poured into a polytetrafluoroethylene mold and put into the oven to evaporate the solvent (70 °C, 48 h). Solvent traces were removed placing material under vacuum at 70 °C for 24h.

Material Reprocessing of Crosslinked Polyurethanes

Polyurethane films are reprocessed by compression molded in tile mold (10 cm x 10 cm x 1 mm) at 150 °C in LabTech Scientific press hot press. First, the films were cut in several small pieces and placed in the center of the tile and left to undergo a 10 minutes preheating cycle to soften the material. This was followed by several venting steps and the material was pressed with a constant applied force of 16 MPa between the two plates. The square materials were then cured at 60 °C in the oven for 48 hours and post cured for 24 hours at room temperature.

Study of the Self-Healing Behavior

The macroscopic self-healing ability of material PU-FO30XL was determined by observing how a dumbbell-shaped sample cut in half healed. To accomplish this, a dumbbell-shaped sample was cut in half in the middle and subsequently healed by placing the halves in contact for 1 hour at 120 °C, followed by 60 °C overnight and 24 h at room temperature.

Methods

Acid Value

Acid value (AV) was determined according to ISO 660. Approximately 0.1 g of OA was dissolved in 50 mL of a 50:50 ethanol and diethyl ether solution. One drop of phenolphthalein solution used as an indicator was added to the solution. Then titration is performed with 0.1M potassium hydroxide (KOH) aqueous solution. AV is expressed in mg of KOH.g⁻¹ according to Equation 2.

$$AV = \frac{(V_{eq} * C) * 56.1}{W_s} \quad (2)$$

Where V_{eq} (mL) is the titration equivalent volume, C (mol.L⁻¹) is the KOH solution concentration and W_s (g) is the OA weight.

Iodine Value

Iodine value (IV), known as the measure of the double bond content, was determined using the Wijs method. This result is expressed in g of iodine (I₂) per 100 g of sample. A 0.5g sample was dissolved in 20 mL of 50:50 mixture of cyclohexane and glacial acetic acid. Then, 25 mL of the Wijs solution (0.1M) composed of iodine chloride in glacial acetic acid solution was added; the corresponding solution was stirred for 1 h in the dark. Then, 20 mL of a 10 wt% potassium iodide aqueous solution and 150 mL of water was added to quench the reaction. The solution was then titrated with a 0.1 M

sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution using starch solution as indicator. IV in I_2 g/100 g was determinate according to Equation 3:

$$IV = \frac{(V_{blank} - V_s) * C * 126.9}{W_s} * 100 \quad (3)$$

V_{blank} (mL) and V_s (mL) are the volumes of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for blank and sample titrations, respectively. C (mol L^{-1}) is the $\text{Na}_2\text{S}_2\text{O}_3$ solution concentration and W_s (g) is the sample weight. It is important to note that Wijs method does not react with the conjugated double bonds of the furan ring.

NMR Spectroscopies

All NMR spectra were recorded on a Bruker Ascend™ 400 or 500 MHz spectrometer. Sample were dissolved in deuterated chloroform (CDCl_3) or deuterated dimethyl sulfoxide (DMSO-d_6) with concentrations varying between 8-10 and 20-30 mg/mL for ^1H -NMR and ^{13}C -NMR, respectively. The number of scans was set to 128 for ^1H -NMR and 2048 for ^{13}C -NMR. The calibration of ^1H - and ^{13}C -NMR spectra was performed using the chloroform peak at 7.26 and 77.16 ppm, respectively and DMSO peak at 2.50.

^{31}P NMR analysis was performed on **FO** and polyester polyol samples phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Cholesterol was used as an internal standard, as described in standard protocols.^[35a] 128 scans were recorded with a 15s delay and a spectral width of 80 ppm (180-100 ppm).

For quantitative ^1H NMR analysis, about 20 mg of **FO** were dissolved in 0.5 mL of DMSO-d_6 before the addition of 100 μL of a standard solution of pentafluorobenzaldehyde in DMSO-d_6 , 32 scans were collected 10 s delay.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy was performed using a Fourier transformed infrared spectrometer, Nicolet 380 used in reflection mode equipped with an ATR diamond module (FTIR-ATR). An atmospheric background was collected before each sample analysis (32 scans, resolution 4 cm^{-1}).

Mass Spectroscopy – MALDI-TOF

Mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-TOF-TOF Autoflex Speed LRF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$). An external multi-point calibration was carried out before each measurement. Scan accumulation and data processing were performed with FlexAnalysis 3.0 software. 2,5-dihydroxybenzoic acid (DHB) was obtained from Sigma-Aldrich. Matrix solutions was freshly prepared: DHB was dissolved to saturation

1 in a H₂O/CH₃CN/HCOOH (50/50,1%) solution. Typically, 0.5μL of a mixture containing the sample
2 solution and the matrix (1/1) was deposited on the stainless-steel plate.

3 **Rheological Measurements**

4 Time required to form a gel between **FO** and BMI at 60 °C (gelation time, t_{gel}) was determined by
5 dynamic oscillatory rheology measurements performed on a TA Instruments Discovery HR-3 using
6 ETC parallel 25 mm plate geometry upper plate and 60mm lower plate. The viscometer was equipped
7 with a Peltier system for temperature control. The evolution of storage (G') and loss (G'') modulus was
8 measured at 60 °C at a constant shear strain (1%) and at 1Hz. The gel point was considered as the
9 time where the curves of storage and loss modulus crossover at a fixed temperature and frequency.

10 **Thermal Gravimetric Analysis (TGA)**

11 Thermogravimetric analysis (TGA) was performed using a TA Instrument Hi-Res TGA Q5000 at a
12 heating rate of 10 °C/min from room temperature to 700 °C under nitrogen atmosphere (flow rate 25
13 mL/min). Sample weighed between 1-3 mg.

14 **Differential Scanning Calorimetry (DSC)**

15 Differential scanning calorimetry (DSC) was performed using a TA Instrument Q200 under nitrogen
16 flow (50 mL/min). Samples of 1-3 mg were sealed in standard aluminum pans. Depending on the
17 information to be acquired, different heating runs were performed. For the qualitative studies on the
18 DA adduct and r-DA, the **FO** and PPO-based BMI mixtures were heated up from -30 °C to 175 °C with
19 a heating ramp of 2.5 °C/min. The glass transition temperature (T_g) of crosslinked materials were
20 recorded using a single heating ramp, from -80 °C to 175 °C at 10 °C/min. The T_g of the non-crosslinked
21 materials were recorded using cyclic procedure involving a heating ramp from -80 °C to 175 °C at 10
22 °C/min, followed by a cooling ramp down to -80 °C at 5 °C/min and finally a second heating to 175 °C
23 at 10 °C/min. The temperature was kept constant for 2 minutes at the end of each temperature ramp.

24 **Uniaxial Tensile Tests**

25 Tensile properties of materials were determined with an Instron tensile testing machine (model 5567
26 H, USA), at a rate of 20 mm/min, using dumbbell specimens (dimensions: 30 X 5 X 1 mm³). For each
27 formulation at least five dumbbell samples were tested.

28 **Swelling Index and Gel Content Determination**

29 Swelling measurements of the polymer network were carried out in DMF. The swelling percentage was
30 determined using the weight difference between dried and swollen samples. The sample (written mi
31 and ranging from 10 to 20 mg) was immersed in 15 mL of solvent. After 24h, the sample was removed
32 from the solution, the surfaces were dried superficially using a filter paper, and the weight was recorded

1 (ms). Three repetitions were conducted for each material and each respective solvent. For each
2 sample, a swelling ratio (SR) was calculated according to the Equation 4:

3
$$SR = \frac{m_s - m_i}{m_i} * 100 \text{ (4)}$$

4 The sample was then dried in a vacuum oven at 40 °C during 1 day. The resulting weight was recorded
5 (m_i) and the insoluble fraction (IF) was calculated according to the Equation 5:

6
$$IF = \frac{m_f}{m_i} * 100 \text{ (5)}$$

7

Acknowledgements

The authors would like to thank BPI-France for the funding of Trans'Alg Project and the corresponding consortium. Iterg for kindly providing technical grade oleic acid. The authors would like to thank Dr. Antoine Duval for his input, the R&D Team of Soprema (France) and Sophie Wendels for help with rheological measurements.

References

- [1] J. T. Haponiuk, K. Formela, in *Polyurethane Polymers* (Eds.: S. Thomas, J. Datta, J. T. Haponiuk, A. Reghunadhan), Elsevier, Amsterdam, **2017**, pp. 1-20.
- [2] C. Carré, Y. Ecohard, S. Caillol, L. Averous, *ChemSusChem* **2019**, *12*.
- [3] J. Akindoyo, M. Beg, S. Ghazali, M. Islam, N. Jeyaratnam, Y. Ar, *Polyurethane types, synthesis and applications-a review*, Vol. 6, **2016**.
- [4] G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, *Mater. Today* **2013**, *16*, 337-343.
- [5] aM. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chemical Society Reviews* **2007**, *36*, 1788-1802; bM. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, *Polymer Reviews* **2012**, *52*, 38-79.
- [6] D. V. Palaskar, A. Boyer, E. Cloutet, J.-F. Le Meins, B. Gadenne, C. Alfes, C. Farcet, H. Cramail, *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 1766-1782.
- [7] M. Desroches, S. Caillol, R. Auvergne, B. Boutevin, *European Journal of Lipid Science and Technology* **2012**, *114*, 84-91.
- [8] aZ. S. Petrović, I. Cvetković, D. Hong, X. Wan, W. Zhang, T. Abraham, J. Malsam, *Journal of Applied Polymer Science* **2008**, *108*, 1184-1190; bY. J. Xu, Z. Petrovic, S. Das, G. L. Wilkes, *Polymer* **2008**, *49*, 4248-4258.
- [9] M. Ionescu, *Chemistry and Technology of Polyols for Polyurethanes*, **2005**.
- [10] C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman, *Macromolecules* **2010**, *43*, 2643-2653.
- [11] W. Denissen, J. M. Winne, F. E. Du Prez, *Chemical Science* **2016**, *7*, 30-38.
- [12] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965-968.
- [13] S. Dhers, G. Vantomme, L. Avérous, *Green Chemistry* **2019**, *21*, 1596-1601.
- [14] A. Sanyal, *Macromolecular Chemistry and Physics* **2010**, *211*, 1417-1425.
- [15] H. Otsuka, K. Aotani, Y. Higaki, Y. Amamoto, A. Takahara, *Macromolecules* **2007**, *40*, 1429-1434.
- [16] aA. Gandini, A. J. F. Carvalho, E. Trovatti, R. K. Kramer, T. M. Lacerda, *European Journal of Lipid Science and Technology* **2018**, *120*, 1700091-n/a; bA. Gandini, T. M. Lacerda, A. J. F. Carvalho, E. Trovatti, *Chemical Reviews* **2016**, *116*, 1637-1669; cT. M. Lacerda, A. Gandini, *Journal of Renewable Materials* **2014**, *2*, 2-12; dA. Gandini, *Progress in Polymer Science* **2013**, *38*, 1-29.
- [17] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698-1702.
- [18] R. C. Boutelle, B. H. Northrop, *The Journal of Organic Chemistry* **2011**, *76*, 7994-8002.
- [19] aA. Duval, H. Lange, M. Lawoko, C. Crestini, *Green Chemistry* **2015**, *17*, 4991-5000; bP. Buono, A. Duval, L. Averous, Y. Habibi, *Polymer* **2017**.
- [20] A. Duval, G. Couture, S. Caillol, L. Averous, *Acs Sustainable Chemistry & Engineering* **2017**, *5*, 1199-1207.
- [21] C. García-Astrain, L. Avérous, *Carbohydrate Polymers* **2018**, *190*, 271-280.
- [22] aC. García Astrain, R. Hernandez, O. Guaresti, L. Fruk, C. Mijangos, A. Eceiza, N. Gabilondo, *Click Crosslinked Chitosan/Gold Nanocomposite Hydrogels*, Vol. 301, **2016**; bO. Guaresti, C. García-Astrain, R. H. Aguirresarobe, A. Eceiza, N. Gabilondo, *Carbohydrate Polymers* **2018**, *183*, 278-286; cO. Guaresti, C. García Astrain, L. Urbina, A. Eceiza, N. Gabilondo, *Reversible swelling behaviour of Diels-Alder clicked chitosan hydrogels in response to pH changes*, Vol. 13, **2018**.
- [23] K. González, C. García-Astrain, A. Santamaria-Echart, L. Ugarte, L. Avérous, A. Eceiza, N. Gabilondo, *Carbohydrate Polymers* **2018**, *202*, 372-381.
- [24] Y. Heo, H. A. Sodano, *Advanced Functional Materials* **2014**, *24*, 5261-5268.
- [25] aT. T. Truong, H. T. Nguyen, M. N. Phan, L.-T. T. Nguyen, *Journal of Polymer Science Part A: Polymer Chemistry* **2018**, *56*, 1806-1814; bT. T. Truong, S. H. Thai, H. T. Nguyen, D. T. T. Phung, L. T. Nguyen, H. Q. Pham, L.-T. T. Nguyen, *Chemistry of Materials* **2019**, *31*, 2347-2357; cB. Willocq, F. Khelifa, J. Brancart, G. Van Assche, P. Dubois, J. M. Raquez, *RSC Advances* **2017**, *7*, 48047-48053; dL. Irusta, M. J. Fernandez-Berridi, J. Aizpurua, *Journal of Applied Polymer Science* **2017**, *134*, 9; eE. Dolci, G. Michaud, F. Simon, B. Boutevin, S. Fouquay, S. Caillol, *Polymer Chemistry* **2015**, *6*, 7851-7861; fE. Dolci, V. Froidevaux, G. Michaud, F. Simon, R. Auvergne, S. Fouquay, S. Caillol, *Journal of Applied Polymer Science* **2017**, *134*, 11; gC. Lakatos, K. Czifrak, J. Karger-Kocsis, L. Daroczi, M. Zsuga, S. Keki, *Journal of Applied Polymer Science* **2016**, *133*; hP. F. Du, H. Y. Jia, Q. H. Chen, Z. Zheng, X. L. Wang, D. L. Chen, *Journal of Applied Polymer Science* **2016**, *133*; iG. Rivero, L.-T. T. Nguyen, X. K. D. Hillewaere, F. E. Du Prez, *Macromolecules* **2014**, *47*, 2010-2018.
- [26] L. Gu, Q. Y. Wu, *Journal of Applied Polymer Science* **2018**, *135*, 46272.
- [27] J. F. Wilson, E. Y. X. Chen, *ACS Sustainable Chemistry & Engineering* **2019**, *7*, 7035-7046.
- [28] C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, *Macromolecular Rapid Communications* **2011**, *32*, 1319-1323.

- 1 [29] A. Sengupta, T. Dey, M. Ghosh, J. Ghosh, S. J. J. o. T. I. o. E. S. E. Ghosh, **2012**, 93, 31-36.
- 2 [30] K. Muthusamy, K. Lalitha, Y. S. Prasad, A. Thamizhanban, V. Sridharan, C. U. Maheswari, S. Nagarajan, **2018**, 11, 2453-
- 3 2463.
- 4 [31] S.-i. Shoda, H. Uyama, J.-i. Kadokawa, S. Kimura, S. Kobayashi, *Chemical Reviews* **2016**, 116, 2307-2413.
- 5 [32] Z. S. Petrović, A. Zlatanić, C. C. Lava, S. Sinadinović-Fišer, *European Journal of Lipid Science and Technology* **2002**, 104,
- 6 293-299.
- 7 [33] C. Kim, T. G. Traylor, C. L. Perrin, *Journal of the American Chemical Society* **1998**, 120, 9513-9516.
- 8 [34] G. Lligadas, J. C. Ronda, M. Galià, U. Biermann, J. O. Metzger, *Journal of Polymer Science Part A: Polymer Chemistry*
- 9 **2006**, 44, 634-645.
- 10 [35] aA. Spyros, *Journal of Applied Polymer Science* **2002**, 83, 1635-1642; bP. Korntner, I. Sumerskii, M. Bacher, T. Rosenau,
- 11 A. Potthast, *Holzforschung* **2015**, 69, 807-814.
- 12 [36] V. Froidevaux, M. Borne, E. Laborbe, R. Auvergne, A. Gandini, B. Boutevin, *RSC Advances* **2015**, 5, 37742-37754.
- 13 [37] aB. J. Adzima, H. A. Aguirre, C. J. Kloxin, T. F. Scott, C. N. Bowman, *Macromolecules* **2008**, 41, 9112-9117; bG. Scheltjens,
- 14 M. M. Diaz, J. Brancart, G. Van Assche, B. Mele, *A self-healing polymer network based on reversible covalent bonding, Vol.*
- 15 *73*, **2013**.
- 16 [38] S. Das, D. F. Cox, G. L. Wilkes, D. B. Klinedinst, I. Yilgor, E. Yilgor, F. L. Beyer, *Journal of Macromolecular Science, Part B*
- 17 **2007**, 46, 853-875.
- 18 [39] A. Rauf, H. Parveen, *European Journal of Lipid Science and Technology* **2004**, 106, 97-100.
- 19 [40] A. Arbenz, R. Perrin, L. Avérous, *Journal of Polymers and the Environment* **2017**, 26, 254-262.