Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry: Investigating polyester resins

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Summary

This thesis describes the novel research that has been performed in the field of bio-based recyclable thermoset materials. More in detail, in this work a bio-based structural analogue of bisphenol A that contains a furan moiety, namely diphenolic acid-furan (DPA-Fur), has been employed as a building block in the synthesis of epoxy and polyester resins.

In previous work, the focus has been on the synthesis of a long-chain polyester resin containing DPA-Fur as a bio-based building block. However, it was found that the high glass transition temperature of that polyester resulted in drawbacks concerning the processability and recyclability.

The focus of our work was the preparation of a (partially) bio-based short-chain polyester (PEST-Fur). This innovative polyester has been obtained through interfacial polycondensation, incorporating phenol as a chain stopper in the synthesis. A chain stopper was used in order to optimise the chain length of the polyester to obtain an optimal glass transition temperature.

Furthermore, the incorporated furan groups along the backbone of the polyester were able to form thermoreversible covalent networks (PEST-Fur/Bis) with various ratios of 1,1’-(Methylene-4,1-phenylene)bismaleimide through Diels-Alder (DA) chemistry. This thermoreversibility ultimately gives rise to improved recyclability and processability of polyester thermosets.

Several techniques have been employed to characterise both the polyester base-polymer, as well as the thermosetting polyester resin. These techniques include: Gel Permeation Chromatography (GPC), Thermographic analysis (TGA), Differential Scanning Calorimetry (DSC), ¹H-NMR and Dynamic Mechanical Thermal Analysis (DMTA).

It was found that short-chain polyester base-polymer (PEST-Fur) possesses a glass transition temperature of around 115 °C and a degradation temperature of 350 °C, creating a large temperature window in which the short-chain polyester can be processed and applied. The measured glass transition temperature is also a noticeable improved compared to previous work, resulting in better processability.

The reversibility of the Diels-Alder chemistry resulted in decrosslinking of the various polyester/bismaleimide resins (PEST-Fur/Bis) at temperatures above 130 °C through the retro-Diels-Alder (rDA) reaction.

Finally, excellent thermoreversibility and recyclability of the polyester resin have been shown through thermal and mechanical analysis. It was found that the change in thermal and mechanical properties of the resin is only marginal throughout the multiple reversible cycles, indicating a strong preservation of properties, which is essential for a sustainable recyclable thermoset.
Table of contents

Summary.................................................................................................................................................. i
Table of contents........................................................................................................................................ ii
Acknowledgements...................................................................................................................................... 1
List of abbreviations ................................................................................................................................... 2
List of Figures and Tables............................................................................................................................ 3
1. Introduction............................................................................................................................................. 4
  1.1. Recyclability ..................................................................................................................................... 4
  1.2. Diels-Alder thermoreversibility ......................................................................................................... 6
  1.3. Scope and aim of the work.................................................................................................................. 8

2. Furan functionalised monomer .............................................................................................................. 9
  2.1. Diphenolic acid ................................................................................................................................. 9
  2.2. Diphenolic acid-furan ....................................................................................................................... 9
  2.3. Experimental..................................................................................................................................... 10
    2.3.1. Materials and reagents ................................................................................................................ 10
    2.3.2. Characterisation .......................................................................................................................... 10
    2.3.3. Synthesis of DPA-Fur .................................................................................................................. 10

3. Furan functionalised polyesters ........................................................................................................... 11
  3.1. Polyester-furan .................................................................................................................................. 11
  3.2. Reaction mechanism ....................................................................................................................... 12
  3.3. Preparation of Polyester-Furan and Polyester-Furan/Bismaleimide networks ......................... 14
    3.3.1. Materials and reagents ................................................................................................................. 14
    3.3.2. Characterisation .......................................................................................................................... 14
    3.3.3. Synthesis of Polyester-Furan and Polyester-Furan/Bismaleimide networks ..................... 14

3.4. Results and discussion ....................................................................................................................... 16
  3.4.1. GPC............................................................................................................................................... 16
  3.4.2. Gelation Experiments .................................................................................................................. 17
  3.4.3. TGA .............................................................................................................................................. 18
  3.4.4. DSC ............................................................................................................................................. 19
  3.4.5. ¹H-NMR ..................................................................................................................................... 22
  3.4.6. DMTA.......................................................................................................................................... 23

3.5. Conclusions ...................................................................................................................................... 28

Appendix A: Furan functionalised polyepoxides ..................................................................................... 29
Appendix B: ¹H-NMR of Polyester-Furan ............................................................................................... 33
Appendix C: Synthesis and application of 1,12-Bis(maleimido)dodecane ......................................... 34
References.................................................................................................................................................. 36
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List of abbreviations

BADGE: Bisphenol A Diglycidyl Ether
BADGE-Fur: Bisphenol A Diglycidyl Ether-Furan
Bismaleimide: 1,1’-(Methylenedi-4,1-phenylene)bismaleimide
CDI: N,N’-carbonyldiimidazole
DA: Diels-Alder
DMF: Dimethylformamide
DMSO: Dimethyl sulfoxide
DMTA: Dynamic Mechanical Thermal Analysis
DPA: Diphenolic acid
DPA-Fur: Diphenolic acid - furan
DSC: Differential Scanning Calorimetry
GPC: Gel permeation chromatography
m-THF: 2-methylhydrofuran
NMR: Nuclear magnetic resonance
PEST-Fur-A:B: Polyester-furan-A:B (A:B denotes the theoretical ratio of repeating units and chain stopper (DPA-Fur + terephthaloyl vs. phenol respectively)
rDA: retro-Diels-Alder
TBAB: Tetra-n-butyrammonium bromide
TGA: Thermographic analysis
List of Figures and Tables

Figure 1: The recyclability of various petroleum-based and bio-based commercial polymers. .................................................5
Figure 2: Diels-Alder reaction ..................................................................................................................................................6
Figure 3: Endo and Exo formation of Diels-Alder adducts ........................................................................................................7
Figure 4: Synthesis of diphenolic acid from levulinic acid and phenol ......................................................................................9
Figure 5: Synthesis of DPA-Fur from DPA, CDI and furfurylamine .............................................................................................9
Figure 6: Synthesis of PEST from furan-functionalised diphenolic acid .....................................................................................11
Figure 7: Covalent bonding and debonding of furan and maleimide groups through the DA and rDA reactions. ……...12
Figure 8: Extended reaction mechanism for the synthesis of Polyester-Fur ..................................................................................13
Figure 9: GPC spectrum of multiple PEST-Fur batches .............................................................................................................16
Figure 10: GPC spectrum of PEST-Fur-2:2 and PEST-Fur-4:2 ....................................................................................................17
Figure 11: Gelation experiment of PEST-Fur-4:2/Bis-2:1 in DMSO ...........................................................................................18
Figure 12: TGA of (a) PEST-4:2. (b) PEST-Fur-4:2/Bis-2:1 ........................................................................................................18
Figure 13: DSC measurements of (a) PEST-Fur-4:2. (b) PEST-Fur-4:2/Bis-2:1. (c) PEST-Fur-4:2/Bis-4:1. (d) PEST-Fur-4:2/Bis-8:1 ...............20
Figure 14: DSC measurements of (a) PEST-Fur-2:2. (b) PEST-Fur-2:2/Bis-2:1 .................................................................................21
Figure 15: 1H-NMR spectra of PEST-Fur-4:2/Bis recorded at various moments before and after heating. ..............................22
Figure 16: Bars prepared from PEST-Fur/Bis (a) Hot-pressed PEST-Fur/Bis bars. (b) PEST-Fur/Bis bars after 4 DMTA Cycles. (c) Regrinded PEST-Fur/Bis bars after DMTA. (d) Recycled PEST-Fur/Bis bars. ..................24
Figure 17: DMTA of various ratios of PEST-Fur-4:2/Bis (a) Storage modulus E’. (b) Loss modulus E”. (c) Damping factor tan δ. (d) Recycled PEST-Fur-4:2/Bis-2:1. ...........................................................................25
Figure 18: DMTA of PEST-Fur-2:2/Bis-2:1 .....................................................................................................................................26
Figure 19: Synthesis of BADGE-Fur ...........................................................................................................................................29
Figure 20: 1H-NMR spectrum of DPA-Fur and the final product of the BADGE-Fur reaction .........................................................30
Figure 21: 1H-NMR spectrum of epichlorohydrin .........................................................................................................................31
Figure 22: Possible side-reactions during the synthesis of BADGE-Fur .......................................................................................31
Figure 23: 1H-NMR spectrum of PEST-Fur and DPA-Fur ...............................................................................................................33
Figure 24: Appearance of PEST-Fur-4:2 combined with 1,12-Bis(maleimido)dodecane ...................................................................34
Table 1: retro-Diels-Alder temperatures for various polyester-furan/bismaleimides .................................................................19
1. Introduction

In the last decade the focus in the field of polymeric products has shifted more and more towards bio-based and recyclable polymers. In the near future this will become even more important, due to the growing scarcity of petroleum as a feedstock for current conventional polymers. Since the amount of oil in the world is finite, the cost for the production of petroleum-based polymers will eventually outweigh the profit.

Also the ecological footprint is an important factor for the production of polymeric materials. The production of bio-based materials coincides with the principles of Green Chemistry and Engineering, which aim for the design, commercialisation, and use of processes and products that are technically and economically feasible while minimizing the generation of pollution at the source and the risk to human health and the environment\(^7\).

A popular usage of bio-based chemistry in the field of polymeric materials is for the so-called drop-in chemicals. Drop-in chemicals are bio-based substitutes for currently used chemicals derived from petrochemical sources. Various researchers in the field of polymers have been able to substitute petroleum-based components with bio-based analogues.

These substitute chemicals can be exact duplicates of the conventional chemicals, such as succinic acid, used amongst others for detergents, food and pharmaceuticals\(^3\). However, the drop-in chemicals can also be structural analogues of currently used petrochemicals, such as the use of phenolic compounds as a replacement for phenol in composite resins\(^4,5\).

Another reason to replace conventional chemicals with structural analogues is the impact of those chemicals not only on the climate and environment, but also on health and safety. An example of a widely used conventional chemical that poses a risk to health and safety is styrene. Ever since the commercial production of styrene first began in the 1930s, styrene has been used in numerous applications such as styrene incorporated resins, rubbers and latex, unsaturated polyester resins and other plastic applications\(^6\); more recent applications include the possible use of styrene incorporated foam in the footwear industry\(^7\). The hazards of exposure to styrene have intensively been studied. It was found that the main metabolite product in the human body after absorption of styrene is phenylethylene oxide (styrene oxide), a chemical that has been reported as mutagenic and carcinogenic\(^8,9\).

Exposure to styrene happens in monomer styrene production plants as well as in polymerisation plants, but also during the production of plastic products containing styrene, especially in the reinforced plastics industry\(^6,10\).

A third reason for the usage of bio-based derived chemicals is that only a limited amount of different platform chemicals can be produced from oil, such as ethylene, propylene, benzene and alkyl benzenes\(^11\). Due to the seemingly limitless diversity found in nature, the usage of bio-mass derived chemicals would open up a whole new world of possibilities with respect to chemical products.

1.1. Recyclability

However, to produce a sustainable product it is of vital importance not only to focus on the feedstock materials, but to also look at what becomes of the product after utilisation. Figure 1 shows different commercial polymers that are currently used in our society.

Various rubbers and resins exist which are (generally) derived from fossil sources and that cannot be recycled after usage, these products eventually often end up in landfills. There are also other petroleum-based polymeric products which are recyclable; these include everyday products such as plastic drink bottles, plastic bags and egg boxes. Various examples also exist of polymers that are subtracted from natural sources and can again be recycled or even bio-degraded after usage.
The fourth category is of particular interest and is the focus of this report. This category contains polymers that can be produced from natural resources, but are not (yet) recyclable. As mentioned before, for a product to be sustainable it’s not only important to produce a bio-based product, but to also make sure that the product is recyclable. Hence, the phrase “going green is not good enough” is often used. If recyclability is not taken into account, then only the problem of decreasing fossil resources is countered, the waste disposal problem will still exist!

Even in the case of recyclable polymers, it is still very difficult to recover the polymers or corresponding monomers from polymer-containing waste in a real process. That is why an optimal sustainable polymer incorporates easy recycling, use of renewable resources, mild synthetic reaction conditions and even biodegradability.

![Figure 1: The recyclability of various petroleum-based and bio-based commercial polymers.](image)

It is understood that recyclability of especially thermosets is often still an issue. The permanent shape and structure determined by the covalent crosslinks severely limits the reusability of these polymers. Thermosets often do not possess the chain mobility that thermoplastics do, severely reducing the processability and intrinsic repairability.

The densely crosslinked networks of thermoset materials possess superior barrier and mechanical properties compared to their linear thermoplastic analogues. Due to their durable nature they are often used in a wide variety of applications like composites, adhesives and coatings. Thermoset composites are often used in the automotive industry and in construction. This includes the use of polyester resins combined with glass fibers and fillers, to produce moulding compounds for applications that don’t require high mechanical properties. Other examples include carbon fibres and epoxy resins required for high strength materials used in the aerospace industry.

Thermoset resins can often not be reshaped or remoulded like thermoplastics, since heating of the material often leads to degradation and decomposition. Most common thermosets, such as polyesters and polyepoxide resins, also can’t readily be converted back to their monomers. However, this is not true for all thermosets; since some thermoset polymers such as polyurethanes can relatively easily be transformed back to their original monomeric building blocks.
For thermoset composites another problem arises concerning recyclability; composites can consist of various components including a thermoset polymer for strength, fillers, flame retardants, fibre reinforcements, etc. This poses another problem as it is often difficult to separate the various components, let alone recycle the thermoset polymer.

In the last few years waste management has become a high global priority. Within the European Union there exist a clear hierarchy of waste management, which are in decreasing order of desirability:

- Prevent waste at source of manufacture
- Reuse a product
- Recycle the material
- Incinerate waste with material and energy recovery
- Incinerate waste with energy recovery
- Incinerate waste without energy recovery
- Landfill

In the past most thermosets were ultimately disposed as landfill. In recent years, the laws for waste management have become stricter, forcing product manufacturers to produce products that are more and more recyclable. As stated in the above hierarchy of waste management, preventing waste at the source of manufacture is the most desired way to prevent waste. As for polymer thermosets, one of those ways is to introduce thermoreversibility into the polymeric material. This thermoreversibility gives rise to the possibility of remoulding and reshaping the thermoset material by applying heat, while optimally the mechanical properties of the resin are retained. The focus in this report is on thermoreversible systems that employ Diels-Alder chemistry.

### 1.2. Diels-Alder thermoreversibility

The Diels-Alder (DA) reaction is named after its discoverers, Otto Diels and Kurt Alder\(^{19}\). The discovery was already made in 1928, for which the two scientists received the Noble Prize in Chemistry in 1950\(^{20}\). The DA reaction is seen as one of the most powerful transformations in organic synthesis\(^{21}\).

The general Diels-Alder mechanism consists of a \((4\pi + 2\pi)\) cycloaddition reaction between a conjugated diene and an alkene as dienophile to form a substituted cyclohexene system\(^{20,22,23}\). The reaction between the diene and dienophile functional groups leads to the formation of covalent bonds at lower temperatures (around 50 \(^{\circ}\)C) through the DA reaction, while at higher temperatures (approximately 120 \(^{\circ}\)C and above) the covalent bonds break and the original diene and dienophile groups are again obtained through the retro-Diels-Alder (rDA) reaction\(^{24}\). The temperatures at which the diene and dienophile groups couple and respectively decouple are influenced by the structure of the diene and dienophile. The general Diels-Alder reaction is given in Figure 2.

![Figure 2: Diels-Alder reaction.](image)

One way to solve the issues regarding recyclability of thermoset polymers is to introduce Diels-Alder capable moieties into the crosslinking system of the polymeric network. If this mechanism would be used as a crosslinking system in thermoset polymers, it would greatly increase the mobility of the chains at higher temperatures. When the temperature at which the crosslinks debond lies below the degradation
temperature of the material or in general the temperature at which side-reactions occur, the polymeric system is regarded as fully reversible.

An important element in the concept of thermoreversible crosslinking is that often a few percent of crosslinking is enough to create a rigid polymer network, while not all the crosslinks have to be broken for the system to be recyclable, as long as the extent of bond breakage results in a flowable polymer melt\(^25\).

The first preparation of thermally reversible polymers employing DA chemistry is reported by Craven \textit{et al.}\(^{13, 26}\). A description is made of a furan incorporated polymer, which forms thermally reversible networks with multiple maleimides.

These thermoreversible systems employing Diels-Alder chemistry give rise not only to improved processability and recyclability, but also to applications such as self-healing/remendable polymers\(^{13, 24, 27, 32}\), shape-memory materials\(^{14, 33}\), probe-based lithographic and data-storage applications\(^{34}\), removable foams for electronic encapsulation\(^{35}\), thermally reversible gels\(^{36, 37}\), polymeric encapsulants\(^{39}\) and thermally removable adhesives\(^{38}\). Another advantage of a thermoreversible DA system is that it does not need a third chemical such as a catalyst to function\(^{25, 27, 39}\).

### 1.2.1. Stereoselectivity

The Diels-Alder reaction of cyclic dienes with cyclic dienophiles can in principle follow two pathways regarding stereoselectivity\(^{40}\). The dissociation of Diels-Alder adducts upon heating and the reconnection of these adducts upon cooling introduce an extra parameter in the stereoselectivity of the reaction. This thermoreversibility results in that if two stereoisomeric products are formed (endo and exo), the repeated dissociation and recombination may result in the formation of the thermodynamically more stable adduct rather than the formation of the kinetically favoured stereoisomer\(^{23}\).

\[
\begin{align*}
&\text{O} &\text{N-R}_2 \\
&\text{R}_1 &\longrightarrow \\
&\text{O} &\text{N-R}_2 \\
&\text{R}_1 &\text{H}
\end{align*}
\]

**Figure 3: Endo and Exo formation of Diels-Alder adducts.**

It is well known that the DA reaction of furan and maleimide leads to a stereoisomeric mixture\(^{41}\), this is shown schematically in Figure 3. Rulišek \textit{et al.}\(^{42}\) report that the endo conformation only has a very small kinetic preference over the exo stereoisomer, and that on a macroscopic scale the exo adduct mainly is observed. Initially the endo adduct is favourably formed, though at higher temperatures the exo conformation is thermodynamically more stable adduct rather than the formation of the kinetically favoured stereoisomer\(^{23}\).

Hence, after heating the material above the rDA temperature, the more stable exo adduct will mainly be formed upon cooling down from a high temperature starting point. Fine-tuning of the reaction temperature is an important tool in controlling the stereoselectivity of the DA reaction and can be very useful to exploit when either the endo or exo conformation is required for use in applications\(^{47}\).

Though generally no catalysts are required for the DA reaction to occur, through the use of Lewis acid catalysts enhanced stereoselectivity can be induced. Lewis acid catalysts decrease the activation energy needed for the cycloaddition. However, the endo formation benefits more from the decrease in activation energy than does the exo formation, which results in an increased ratio of endo/exo\(^{48}\).
1.3. Scope and aim of the work

The goal of this project is to research the preparation and properties of (partially) bio-based polyester thermosetting networks that employ the DA reaction as a thermoreversible crosslinking mechanism. This incorporated thermoreversibility gives way to possibilities concerning the recycling of thermosets.

The base-polymer for the thermoreversible networks examined consists of linear polymer chains containing pendant functional furan groups; the functional building block of this linear polymer being diphenolic acid-furan (DPA-Fur), which synthesis and properties are described in chapter 2.

An attempt was made to prepare a (partially) bio-based epoxy resin employing the DA and rDA thermoreversible system. Theoretically, the reaction between DPA-Fur and epichlorohydrin could yield a furan functionalised equivalent of the classical bisphenol A diglycidyl ether (BADGE-Fur). However, because of the low and impure yield due to possible side-reactions, it was concluded that at this stage it is not possible to obtain an epoxy resin containing DPA-Fur as a functional monomer. More about this part of the research can be found in Appendix A.

Furthermore, the synthesis, characterisation and optimisation of a novel (partially) bio-based polyester network are described in chapter 3. Especially the glass transition temperature ($T_g$) of the base-polymer was a critical factor during the research, since it has a big influence on both the industrial processability as well as on the final application. In our previous work\(^1\) we describe the synthesis of a long-chain polyester incorporating furan moieties, which was prepared without the use of a chain stopper. However, it was concluded that the $T_g$ of the long-chain polyester is rather high, resulting in issues regarding the processing and recycling of the polyester.

For processing and recyclability purposes it is important that the glass transition of the base-polymer occurs at an appropriate temperature. A suitable $T_g$ of the material is needed to process the polyester resin through techniques such as melt-moulding. For melt-moulding purposes, it is a necessity to have a low enough glass transition temperature without the occurrence of the rDA reaction\(^{12}\). If the $T_g$ of the base-polymer is located below the rDA temperature of the polymer network, the material will undergo a phase change from an elastomer to a viscous liquid\(^49\). The aim is to synthesise a short-chain polyester using a chain stopper, in order to impart a desirable glass transition temperature.

The ultimate objective is to obtain a bio-based polymer thermoset that is recyclable through the DA crosslinking mechanism and that retains the same mechanical properties after each thermoreversible cycle. The research focussing on this is also reported on in chapter 3. The reported polymer thermosetting network consists of a furan functionalised polyester which is crosslinked by an aromatic bismaleimide. Optimally, this polymer thermoset also possesses properties which makes it suitable for both processing on large scale, as well as for industrial and commercial application.
2. Furan functionalised monomer

2.1. Diphenolic acid

One of the main building blocks used for the preparation of the polymers described in this report is derived from diphenolic acid. Diphenolic acid is an aromatic compound bearing a carboxyl group, it can be considered as an acid-functionalised equivalent of bisphenol A, which is widely used for commercial polycarbonate, epoxy and polyester resins. Diphenolic acid can even be considered as a possible replacement for bisphenol A, since it can be employed in many of the same applications. Several applications can make use of diphenolic acid, such as lubricants, adhesives and paints.

The reason that the use of diphenolic acid is of particular interest is that it can be synthesised from bio-based platform chemicals. The synthesis of diphenolic acid consists of a condensation reaction between levulinic acid and two equivalents of phenol, as shown in Figure 4. This reaction can be catalysed by strong Brønsted mineral acids or polyoxometalates.

![Figure 4: Synthesis of diphenolic acid from levulinic acid and phenol.](image)

As mentioned before, the reactants for the synthesis of diphenolic acid can be obtained from green sources. Levulinic acid can be produced from lignin by acid hydrolysis of 6-carbon sugars. There are various reports on the production of phenolic compounds from biological sources, though often the compounds are complex and separation costs high.

2.2. Diphenolic acid-furan

The first reaction in which diphenolic acid is converted to DPA-Fur was, to the best of our knowledge, described in our previous work. The first step consists of the reaction in which diphenolic acid reacts with N,N'-carbonyldiimidazole to form an intermediate structure. N,N'-carbonyldiimidazole is a common compound used for various syntheses ranging from the preparation of esters, amides and peptides to being used for the activation of carboxylic acids, glycosidation and dehydration. It can be synthesised from mixing phosgene with four equivalents of imidazole in benzene. Due to its reactive nature it is often kept sealed to protect it from reacting with moisture from the air.

![Figure 5: Synthesis of DPA-Fur from DPA, CDI and furfurylamine.](image)

The second step in the reaction peptide bond formation between the intermediate structure and furfurylamine. Furfurylamine can be produced from furfural, a bio-based platform product which can be prepared from various agricultural by-products including corncobs, wheat and lignin.
2-Methylhydrofuran was used as a solvent during the synthesis, mostly due to its immiscibility with water. This results in easy purification and separation steps when employing acidic and basic aqueous solutions for washing. The reaction mechanism for the synthesis of DPA-Fur is given in Figure 5.

2.3. Experimental

2.3.1. Materials and reagents
Diphenolic acid (DPA, Sigma-Aldrich), 2-methylhydrofuran (m-THF, Acros), N,N'-carbonyldiimidazole (CDI, Acros), NaOH (97%, Sigma-Aldrich) and ethanol (99.9% pure, Merck) were used as received. Furfurylamine (Acros) was purified through distillation before use. 1M HCL, 0.1M NaOH and a Brine-solution were prepared.

2.3.2. Characterisation
$^1$H-NMR spectra were taken on a Varian Mercury Plus NMR-300 using DMSO-d$_6$ as a solvent.

2.3.3. Synthesis of DPA-Fur
A three-neck round bottomed flask and a condenser were dried in an oven at 105 °C and brought under N$_2$-atmosphere afterwards. 5 g (17.5 mmol) DPA, 30 mL m-THF and 3.398 g (21 mmol, 1:1.2 molratio) CDI were added to the round bottomed flask. Subsequently, the reaction was stirred at 90 °C for 2 hours. 1.85 mL (21 mmol, 1:1.2 molratio) furfurylamine was added to the mixture and the reaction was stirred for 5 hours at 90 °C.

The reaction was then cooled and diluted with 45 mL m-THF, subsequently a brown-yellowish liquid was obtained. Furthermore, the mixture was washed with 2 x 37 mL 1M HCL, 2 x 47 mL 0.1M NaOH and finally with 1 x 15 mL Brine. Rotary evaporation (350 mbar, 40 °C) of the organic layer by yields a clear yellow oil. Recrystallization from ethanol gives a white-yellowish solid (DPA-Fur, yield 65%).

$^1$H-NMR (300 MHz, DMSO-d$_6$): δ = 9.18 (s, 2H, OH), 8.2 (t, 1H, NH), 7.53 (s, 1H, fur-p), 6.93 (d, 4H, benzene-o), 6.66 (d, 4H, benzene-m), 6.36 (t, 1H, fur-m), 6.19 (d, 1H, fur-o), 4.21 (d, 2H, N-CH$_2$), 2.21 (t, 2H, -CH$_2$-), 1.90 (t, 2H, -CH$_2$-), 1.46 (s, 3H, -CH$_3$).


3. Furan functionalised polyesters

3.1. Polyester-furan

Polyester resins are used for a wide range of applications ranging from decorative coatings to composite materials for structures such as tanks, boats, automobile parts and so on\textsuperscript{62}.

Generally, a polyester resin is derived from an unsaturated polyester prepared through the polycondensation of a polyol and a polyvalent acid or acid anhydride. These unsaturated polyesters are then subjected to radical or thermal reactions in the presence of unsaturated comonomers, such as styrene, to form a polyester resin\textsuperscript{18}. Industrially, polyester resins are often produced by dissolving unsaturated polyesters in styrene, forming a crosslinked thermoset with the help of a catalyst and an accelerator. However, during this crosslinking process approximately 10-15\% of the used styrene is released into the air\textsuperscript{10}.

Polyester resins can be produced from various polyesters including both aliphatic and aromatic ones, the properties of course depending on the type and structure of the polyester chains. Polysters are often prepared from bisphenolic compounds to impart aromaticity\textsuperscript{63}.

Our aim is to synthesise a (partially) bio-based polyester thermoset through interfacial polycondensation, employing DPA-Fur as a building block to introduce thermoreversibility into the polyester system. To achieve a desirable glass transition temperature of the base-polymer, phenol is used as a chain stopper to yield polyester chains of shorter lengths. Phenol is of particular interest since it conserves aromaticity and readily takes part in the condensation synthesis. The synthesis for base-polyester, polyester-furan (PEST-Fur), is shown in Figure 6; the full reaction mechanism for this interfacial polycondensation is reported later on.

![Figure 6: Synthesis of PEST-Fur from furan-functionalised diphenolic acid.](image)

The combination of the base-polymer PEST-Fur and an aromatic bismaleimide crosslinker would in theory yield a covalent thermosetting network at temperatures around room temperature, due to the formation of crosslinks via the DA reaction, as shown in Figure 7. At higher temperatures the equilibrium shifts to the side of the diene and dienophile, resulting in an increase in flow properties. The thermoreversible nature of the DA reaction would give rise to recyclability of this polyester thermoset system. In addition, this system of thermoset crosslinking eliminates the use of styrene for the preparation of a polyester resin.
3.2. Reaction mechanism

The short-chain polyester-furan was prepared through interfacial polycondensation. In the 1950s normal polycondensations were generally considered as slow reactions, often performed using high temperatures and reduced pressure. Consequently, there was need for a fast polymerisation procedure, which can be performed with common laboratory equipment under atmospheric reaction conditions. Furthermore, other techniques used to prepare polyesters, such as the direct reaction of a di-basic acid and glycol, ester exchange and the melt reaction between an acid chloride and glycol are not suitable for the synthesis of aromatic polyphenyl esters. Pioneering work on interfacial polycondensation has been done by Morgan et al.

More recently, interfacial polycondensation reactions have been combined with stabilisers to yield nanoparticles through techniques such as nanoprecipitation, salting-out and emulsification-evaporation. Nowadays, microencapsulation, responsive and catalytic films and membrane technology are highly successful applications that are prepared through interfacial polycondensation.

Interfacial polycondensations can be employed to yield various types of polymers. Specifically, the polyesters described in this report were prepared through interfacial polycondensations between a carboxylic acid chloride in a water-immiscible organic solvent (chloroform) and a bisphenolic compound in water. Bisphenols are specifically well-suited for interfacial polycondensation, due to their acidic character, which favours the formation of a bisphenoxide ion.

The choice of organic solvent used in the interfacial polycondensation is of great importance, since it will have an impact on not only multiple polymerisation parameters such as potential partition of the reactants between the two phases, the diffusion of reactants and reaction rate; it will also have an effect on the final polymer in terms of solubility, swelling, permeability and molecular weight. The formation of most condensation polymers occurs in the organic phase, the primary function of the aqueous phase is to dissolve, amongst others, the bisphenolic compound. Often the addition of an inorganic base is necessary in order to dissolve the bisphenol in the aqueous phase, resulting in a bisphenoxide compound.

Stirring can be used to increase the surface area of the interface, and thus increasing the diffusion of the bisphenoxide compound to the organic phase. Though stirring is not mandatory for the interfacial condensation, it is advisable in order to obtain high yields. In general, the final polymer should be 5 % wt or less in respect to the combined weights of the water and organic phases. At too high concentrations the solvents might be absorbed by the swollen polymer, resulting in a mixture which cannot be stirred. This yields incomplete polymerisation and low molecular weight.
For the interfacial polycondensation of a bisphenolic compound it is necessary to first form a bisphenoxide ion, otherwise the reaction rate will be very slow and the bisphenol will have trouble dissolving in the aqueous phase\textsuperscript{67}, as mentioned before. In the described synthesis sodium hydroxide was employed to yield bisphenoxide ions.

The obtained sodium bisphenoxide is highly soluble in the aqueous phase, but has low solubility in the organic phase. This is why quaternary ammonium salts were employed to assist the polymerisation. The assistance is in the form of the formation of organic soluble bisphenoxides and transport of the chloride ion to the aqueous phase as the quaternary ammonium salt\textsuperscript{67}. The specific ammonium salt that was used for the described polyester synthesis is tetra-n-butylammonium bromide.

Since one of the research goals is to prepare a short-chain polyester, phenol was employed as a chain stopper during the interfacial polycondensation reactions. The complete reaction mechanism is schematically shown in Figure 8; this is an adaption of interfacial condensation mechanisms described by other authors\textsuperscript{54, 71}.

**Figure 8: Extended reaction mechanism for the synthesis of Polyester-Fur.**
3.3. Preparation of Polyester-Furan and Polyester-Furan/Bismaleimide networks

3.3.1. Materials and reagents
Phenol (Sigma-Aldrich), tetra-n-butylammonium bromide (TBAB, Fluka), terephthaloyl chloride (99%, Acros), NaOH (97%, Sigma-Aldrich), methanol (practical grade, Interchema), chloroform (Lab-Scan) and 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (bismaleimide, Sigma-Aldrich) were used as received. DPA-Fur was prepared as described earlier.

3.3.2. Characterisation
$^1$H-NMR spectra were taken on a Varian Mercury Plus NMR-300 and a Varian Mercury Plus NMR-400 using DMSO-$d_6$ as a solvent. GPC spectra were taken on a PSS HPLC/GPC using THF as an eluent. DSC data was recorded on a Perkin Elmer DSC Pyris 1 from 20 ⁰C to 180 ⁰C at rates of 2 ⁰C/min or 10 ⁰C/min. TGA data was recorded on a Mettler Toledo TGA. Gelation experiments were performed using a prepared solution of 10 %wt PEST-Fur/bismaleimide in DMSO.

DMTA measurements were performed on a Rheometrics scientific solid analyser (RSA II) under air environment using a dual cantilever at an oscillation frequency of 1 Hz and a heating rate of 2 ⁰C/min. The data was measured during four cycles in a temperature range of 20 ⁰C to 160 ⁰C.

3.3.3. Synthesis of Polyester-Furan and Polyester-Furan/Bismaleimide networks
PEST-Fur-4:2
The reaction of the DPA-Fur monomer with terephthaloyl chloride resulted in a polyester containing pendant furan groups. The ratio of monomer/chain stopper added in this reaction was set at 4:2 to yield an average theoretical chain length of four monomeric repeating units, end-capped by two chain stoppers. 5 g (13.68 mmol, 4 eq) DPA-Fur, 0.435 g TBAB (8.7 %wt of DPA-Fur), 0.644 g (6.841 mmol, 2 eq) phenol, 1.411 (34.2 mmol) NaOH and 120 mL water were added to a 500 mL round bottomed flask. Subsequently, the reaction was stirred for 2 hours at room temperature.

After 2 hours the water-soluble components of the mixture were dissolved, while the water-insoluble components were still present in the reaction mixture as solid flakes. Continuously, 3.125 g (15.39 mmol) terephthaloyl chloride partially dissolved in 120 mL chloroform was added to the mixture. The reaction mixture was then stirred overnight at room temperature.

Finally, the polymer was precipitated in a large beaker containing 2 L methanol. The precipitation yielded a solid precipitate on the bottom of the beaker, as well as a suspension of small particles in the methanol phase.

The methanol phase containing small solid particles was centrifuged in 50 mL cups at 4500 rpm for 15 minutes. Furthermore, the precipitate obtained in the centrifuge cups was filtered over a Büchner funnel and washed with water. Additionally, the solid precipitate on the bottom of the beaker was also filtered over a Büchner funnel and washed with water.

Finally, all the solid products obtained were combined and dried in an oven at 70 ⁰C for a couple of hours to yield a white-yellowish solid (PEST-Fur-4:2, best yield achieved 74%).

$^1$H-NMR (300 MHz, DMSO-$d_6$): δ = 8.32-8.10 (m, 7H, aromatic not next to ester), 7.55 (s, 1H, fur-p), 7.49 (d, 1H, NH), 7.4-7.2 (m, 8H, aromatic next to ester), 6.37 (s, 1H, fur-m), 6.22 (s, 1H, fur-o), 4.23 (d, 2H, N-CH2), 2.43 (s, 2H, -CH2-), 1.98 (s, 2H, -CH2-), 1.66 (s, 3H, -CH3).
**PEST-Fur-2:2**
The synthesis of the PEST-Fur with ratio 2:2 followed the same procedure as for PEST-Fur-4:2, described earlier. The only difference is the ratio of reactants that were added, a ratio of 2:2 monomer/chain stopper instead of the previous ratio 4:2.

The amount of phenol that was used was doubled from 0.644 g to 1.288 g (13.68 mmol), while 1.7621 g (42.73 mmol) NaOH was added instead of 1.411 g. The amounts of therephthaloyl chloride and DPA-Fur employed were held constant.

The final product was obtained as a white-yellowish solid (PEST-Fur-2:2, best yield achieved 17%).

\[ \text{H-NMR (300 MHz, DMSO-d}_6\text{): } \delta = 8.32-8.10 \text{ (m, 7H, aromatic not next to ester), 7.55 (s, 1H, fur-p), 7.49 (d, 1H, NH), 7.4-7.2 (m, 8H, aromatic next to ester), 6.37 (s, 1H, fur-m), 6.22 (s, 1H, fur-o), 4.23 (d, 2H, N-CH}2\text{), 2.43 (s, 2H, -CH}2\text{), 1.98 (s, 2H, -CH}2\text{), 1.66 (s, 3H, -CH}_3\text{).} \]

**PEST-Fur-4:2/Bis and PEST-Fur-2:2/Bis**
The PEST-Fur/Bis networks were prepared through a general method. An amount of PEST-Fur-4:2 or PEST-Fur-2:2 (1 eq. mol) was added to a single-neck round-bottomed flask. The molar amount of furan groups was estimated by assuming that the polymer consists only out of monomeric repeating units with a molecular weight of 496.53 g/mol (1 DPA-Fur group and 1 therephthaloyl group, see Figure 6). This was assumed in order to calculate the molar amount of maleimide groups needed.

Subsequently the proper amount of \(1,1^\prime\)-(Methylene-4,1-phenylene)bismaleimide was added, different ratios were used to create different networks (0.5 eq. mol, 0.25 eq. mol and 0.125 eq. mol bismaleimide for PEST-Fur-4:2; 0.5 eq. mol bismaleimide for PEST-Fur-2:2). While the mixture was stirred at 60 °C, just enough chloroform was added to dissolve the PEST-Fur and bismaleimide in order to create a homogeneous mixture.

The chloroform was then partially removed by rotary evaporation to yield a dark-brown rubbery substance. Completely removing the solvent by rotary evaporation results in a hard yellowish/brown product, which is hard to remove from the glassware.

The dark-brown rubbery substance was ground using a motorised hand grinder, and subsequently dried in a vacuum oven (vacuum, 45 °C). Finally, the resulting product was ground in liquid N\(_2\) with a motorised hand grinder to yield a fine light-yellow powder (PEST-Fur/Bis).

**Preparation of DMTA specimens**
DMTA specimens were obtained by pressing a mixture of PEST-Fur-4:2/Bis or PEST-Fur-2:2/Bis into bars with dimensions of 54x6x1 mm (length, width, height). The pressing sequence consisted of first cold pressing the polymer in the mould for 2 minutes at room temperature and 10 MPa. Subsequently, the polymer was pressed in a pre-heated press for 2 hours at 150 °C and 10 MPa. The press was then slowly cooled down to 50 °C, after which the DMTA bars were treated at 50 °C for 24 hours.

Specimens from different molar ratios of furan/bismaileimide have been prepared: 2:1, 4:1 and 8:1. However, during the production of test-specimen from PEST-Fur-4:2/Bis-8:1 some practical problems arose. The polyester resin bars were subject to crack formation during the cooling down after the hot compression-moulding, something which was not observed with moulding of specimens from different ratios. This is the reason no proper test-specimens were obtained for the ratio 8:1 (polyester/crosslinker).
3.4. Results and discussion

3.4.1. GPC
Gel permeation chromatography was employed to examine the size and the molecular weight of the prepared base-polymers PEST-Fur-4:2 and PEST-Fur-2:2. However, the GPC column that was used was calibrated for polystyrene standard. That is why no absolute values can be extracted from the data, though a qualitative analysis can still be carried out.

![Figure 9: GPC spectrum of multiple PEST-Fur batches.](image)

The GPC spectra of multiple PEST-Fur-4:2 batches are shown in Figure 9. The first thing to notice is the existence of multiple peaks, instead of a single smooth curve. This is also observed by Kricheldorf et al.\(^{72,73,74}\) for the synthesis of cyclic polycarbonates from various bisphenol analogues. The existence of multiple peaks indicates relative small polymers consisting of relative large monomeric repeating units.

It is seen that the difference in molar mass between the various peaks is more or less the same, ranging from 2300 g/mol to 2700 g/mol difference between neighbouring peaks. Both the high and narrow appearance of the peaks, as well as the more or less constant difference in molar mass between the peaks are a strong indication of short-chain polyesters with each peak varying one monomeric repeating unit from its neighbour.

When the comparison between the spectrum of the long-chain polyester and PEST-Fur-4:2 (as seen in Figure 9) is made, it is indeed seen that the molar mass distribution for the short-chain PEST-Fur-4:2 yields relative shorter chains than the distribution for the long-chain polyester. Furthermore, it must be noted that the GPC column employed is only able to handle molar masses up to 200,000 g/mol. This restriction results in the possible existence of even longer chains than visible in the spectrum, also indicated by the large peak in the spectrum at 200,000 g/mol. It is also observed that the employment of phenol as a chain stopper yields a narrower molar mass distribution than is obtained without the use of a chain stopper.

The comparison between the lengths of PEST-Fur-4:2 and different batches of PEST-Fur-2:2 is given in Figure 10. It is observed that the peaks which belong to PEST-Fur-2:2 have been shifted towards lower molar masses compared to those of PEST-Fur-4:2, indeed indicating slightly shorter chains.
The differences in molar mass between the neighbouring peaks of PEST-Fur-2:2 are in the range of 2300 g/mol to 2600 g/mol, the same range as seen for PEST-Fur-4:2. This implies that also for PEST-Fur-2:2 the spectrum indicates the synthesis of short polyester chains with each peak varying a couple of monomeric repeating units from its neighbouring peak.

![Figure 10: GPC spectrum of PEST-Fur-2:2 and PEST-Fur-4:2.](image)

Furthermore, according to the theoretical ratio of monomer and chain stopper incorporated in the synthesis (2:2), it would be expected that the average chain length is around half of the chain length of the PEST-Fur-4:2 chains. However, it is seen in Figure 10 that this is not the case. It is also seen that the molar mass distribution of PEST-Fur-2:2 appears narrower than that of PEST-Fur-4:2.

An explanation for these phenomena might be that a practical minimum is reached in respect to the shortening of the polyester chains. Below this practical minimum a part of the polyester chains is too small to be precipitated and thus stays in solution, yielding a GPC spectrum that only contains the polyester chains large enough to precipitate; hence the narrower spectrum with expected peaks missing in the lower molar mass region. This theory is supported by the extremely low yield of the PEST-Fur-2:2 synthesis in comparison to that of PEST-Fur-4:2 (17% against 74% respectively).

### 3.4.2. Gelation Experiments

To validate that the polyester/bismaleimide system is indeed capable of forming covalent bonds through crosslinking, gelation experiments were employed. It is seen that the parameters of gel formation are closely linked to temperature and solvent. For the particular gelation experiment described here DMSO was used as a solvent. A solution of 10 %wt of a PEST-Fur-4:2/Bis mixture in DMSO was prepared at room temperature while stirring.

Initially no crosslinking reaction occurred. However, after keeping the mixture at room temperature overnight, it was seen that a gel had been formed (Figure 11). This is proof that the polyester/bismaleimide system is able to form crosslinks, since for systems that are capable of crosslinking gelation occurs. When a single macromolecule first spans the sample, then the appearance of the mixture changes from a liquid solution to a solid gel.

Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry

February, 2014
Furthermore, the thermoreversibility of the crosslinks can also be examined. The gelated sample was heated at 120 °C for 45 minutes. Hereafter it was seen that the gel had become a liquid again, also a shift in colour from yellow to red has been observed (Figure 11). The liquefaction of the gel indicates that the crosslinks formed at room temperature are again broken at 120 °C, a first indication of thermoreversibility of the polymer network. After cooling down to room temperature the sample returned to its gelated state, the red colour however remained. The colour change might be caused by small impurities present in the sample as well as oxidation reactions, even though the corresponding oxidation products are not detected by NMR. One of the possible reactions is the oxidation of the furan ring present in the base-polymer. The possible oxidation reactions can be suppressed by the use of antioxidants.

### 3.4.3. TGA

Thermographic analysis was employed in order to examine the temperature window in which both the base-polymer as well as the polyester resin are stable. The results for PEST-Fur-4:2 and PEST-Fur-4:2/Bis-2:1 can be seen in Figure 12a and b respectively. It is observed that the degradation of the single polyester chains start around 350 °C, which is well above the T_g of 115 °C. This yields a large temperature window in which the polymer can be processed.

![Figure 11: Gelation experiment of PEST-Fur-4:2/Bis-2:1 in DMSO.](image)

![Figure 12: TGA of (a) PEST-Fur-4:2. (b) PEST-Fur-4:2/Bis-2:1.](image)
However, a decrease in mass of PEST-Fur-4:2/Bis-2:1 is observed at lower temperatures, around 150 °C. There exist various possible explanations for this phenomenon. One likely explanation is that during the preparation of the polyester resin an amount of solvent chloroform was trapped in the polymeric network, which now evaporates when subjected to temperatures above 150 °C.

Another explanation could be that the incorporation of the bismaleimide introduces a lower thermal stability, this lower thermal stability of furan/bismaleimide networks in respect to the clean polymer chains is also observed by Goiti et al.\textsuperscript{77,78} An altering of the thermal stability might be due to the occurrence of free-radical reactions or aromatisation concerning the DA adduct, which can happen at higher temperatures\textsuperscript{79}. In case of aromatisation of the DA adduct water is produced as a by-product, and will evaporate at higher temperatures.

Also, free maleimide groups obtained after the rDA reaction are able to homopolymerise at higher temperatures, also seen for an epoxy resin employing Diels-Alder chemistry by Liu et al.\textsuperscript{29}. Homopolymerisation of maleimide moieties is also reported by other authors\textsuperscript{28,80}. Generally, free-radical homopolymerisation reactions and aromatisation of the DA adduct yield a more thermal stable product\textsuperscript{79,81}.

3.4.4. DSC

Differential Scanning Calorimetry was used to research the processability of the polyester as well as the thermal reversibility of the polyester/bismaleimide networks.

It is seen in Figure 13a that the glass transition temperature of PEST-Fur-4:2 lies around 115 °C. This is lower compared to the determined T\textsubscript{g} of the earlier prepared long-chain polyester, which is around 125 °C\textsuperscript{1}. This decrease of the glass transition temperature makes way for improved recyclability and processability compared to the long-chain polyester.

A decrease in T\textsubscript{g} for decreasing chain lengths is also seen with other linear bisphenolic polymers\textsuperscript{82,83}. Decrease in the glass transition temperature can primarily be ascribed to the loss of entanglements due to the shortening of chains. Examples of aromatic polyesters from literature include a bisphenolic polyester possessing a T\textsubscript{g} of 105-120 °C by Apicella et al.\textsuperscript{84} and an aromatic copolyester possessing a T\textsubscript{g} of 88-120 °C by Turner et al.\textsuperscript{85}.

### Table 1: retro-Diels-Alder temperatures for various polyester-furan/bismaleimides.

<table>
<thead>
<tr>
<th>Ratio furan/ chain stopper</th>
<th>Molratio furan/bismaleimide</th>
<th>rDA\textsuperscript{DSC, a)} (°C)</th>
<th>rDA\textsuperscript{DMTA, b)} (°C)</th>
<th>rDA\textsuperscript{DMTA, c)} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEST-Fur/Bis</td>
<td>4:2</td>
<td>151</td>
<td>132</td>
<td>146</td>
</tr>
<tr>
<td>PEST-Fur/Bis (Recycled)</td>
<td>4:2</td>
<td>2:1</td>
<td>150</td>
<td>146</td>
</tr>
<tr>
<td>PEST-Fur/Bis</td>
<td>4:2</td>
<td>4:1</td>
<td>152</td>
<td>114</td>
</tr>
<tr>
<td>PEST-Fur/Bis</td>
<td>4:2</td>
<td>8:1</td>
<td>144</td>
<td>-</td>
</tr>
<tr>
<td>PEST-Fur/Bis</td>
<td>2:2</td>
<td>2:1</td>
<td>151</td>
<td>135</td>
</tr>
</tbody>
</table>

a) Estimated from DSC by taking the peak temperature of the first cycle.

b) Estimated from DMTA at the onset of the decrease in E' during the first cycle.

c) Estimated from DMTA by taking the lowest value for E' (also point of maximum decrease) during first cycle.

The DSC measurements for the multiple ratios of PEST-Fur-4:2/Bis resins are shown in Figure 13b, c and d. These measurements consist of 7 subsequent cycles in a temperature range of 20-180 °C. It is shown that when the temperature ascends above 130 °C a transition takes place, which corresponds to the rDA reaction\textsuperscript{14,17,29}; this is seen for all of the three different resins. Subsequently, during cooling down an exothermic peak is shown in the same region, indicating the DA reaction\textsuperscript{29}. The temperatures at which the said rDA reaction occurs for the multiple polyester-furan/bismaleimide networks are also seen in Table 1, showing the combined results from the DSC and DMTA measurements.
It is seen that the endothermic peak of the first cycle appears to differ from the subsequent cycles (most clearly observed in Figure 13b and d). This phenomenon is also described by Toncelli et al.33 for furan/maleimide polyketone networks and by Tian et al.86,30 for thermoreversible epoxy resins. The shift of the endothermic peak to higher temperatures might be explained by the transition of DA adducts from the endo to the exo conformation87. The enhanced thermodynamic stability of the exo adduct explains the shift of the peak towards higher temperatures after the first cycles33. The stereoselectivity of the DA reaction for the PEST-Fur/Bis resin is examined later on via 1H-NMR analysis.

The next cycles appear to be more or less the same, though a slight decrease in integral value might possibly be due to the fact that the system does not have enough time to fully recover all the DA bonds15,33. The equality of the subsequent thermal cycles indicates a strong thermoreversibility.

![Figure 13: DSC measurements of (a) PEST-Fur-4:2, (b) PEST-Fur-4:2/Bis-2:1, (c) PEST-Fur-4:2/Bis-4:1, (d) PEST-Fur-4:2/Bis-8:1.](image)

When comparing the different composition ratios for the polyester resin, it is seen that the integral of the curve for the rDA reaction decreases in the line of PEST-Fur-4:2/Bis-2:1 > 4:1 > 8:1, also seen for other systems with fixed furan content and lower crosslinking concentrations33. Subsequently, it is also seen that the peaks for the rDA reaction become broader for decreasing crosslinking concentrations.
Furthermore, the temperature at which the rDA reaction occurs merely differs for the composition ratios of 2:1 and 4:1, also seen by Toncelli et al.\textsuperscript{33} The rDA temperature does however change significantly for the ratio polyester/bismaleimide 8:1, compared to 4:1 and 2:1.

Since the equilibrium between the DA and rDA reaction is dependent on the concentration of the reacting materials\textsuperscript{43}, the second-order DA and first-order rDA reactions would imply that the de-crosslinking temperature increases with increasing concentrations of reacting materials\textsuperscript{14}. This is also reported by Okhay et al.\textsuperscript{88} for their maleimide-functionalised urethane polymers. An explanation for the weak dependency of the rDA temperature on the polyester/bismaleimide ratio might be that during the cycles there is not enough time for all the DA bonds to fully recover, due to the DA-rDA kinetics. Subsequently, in that case the final amount of bonds that is formed during the limited time in each cycle only slightly differs for different ratios of polymer and crosslinker. This could explain why the rDA temperature seems only slightly influenced by the polyester/bismaleimide ratio.

![Figure 14: DSC measurements of (a) PEST-Fur-2:2. (b) PEST-Fur-2:2/Bis-2:1.](image)

The results from the DSC measurements of PEST-Fur-2:2 are given in Figure 14. The same scanning methods were used when obtaining the DSC spectra of PEST-Fur-4:2 and the PEST-Fur-4:2/Bis networks.

It is observed that the glass transition temperature of the linear PEST-Fur-2:2 lies around 115 °C (Figure 14a), which is practically the same value as the measured \( T_g \) for PEST-Fur-4:2. As seen in the GPC spectrum (Figure 10) the molar mass distribution only differs slightly for PEST-Fur-2:2 compared to PEST-Fur-4:2. Apparently the practical minimum concerning the shortening of the polyester chains also results in a minimum in terms of lowering the glass transition temperature. Furthermore, an optimum of the influence of chain length on chain mobility for short polymer chains does not seem unlogical, since the difference between a chain with two repeating units and one with four repeating units is only marginal on a polymeric scale.

Figure 14b shows the DSC data obtained for PEST-Fur-2:2/Bis-2:1. Also for this polyester/bismaleimide network two transitions upon heating and cooling are observed, corresponding to the rDA and DA reactions respectively.

The temperature at which the rDA occurs for PEST-Fur-2:2/Bis-2:1 lies in the same range as for the PEST-Fur-4:2/Bis networks. A shift of the endothermic rDA peak to higher temperature after multiple cycles and a decrease in integral value are phenomena which were observed earlier for the PEST-Fur-4:2/Bis resins; these phenomena are also seen in the spectrum of PEST-Fur-2:2/Bis-2:1.
This is not surprising, since it already was established that the $T_g$ of the linear PEST-Fur-2:2 material is practically the same as that of PEST-Fur-4:2. Consequently, the PEST-Fur-2:2/Bis-2:1 network possesses a comparable strong thermoreversibility as the PEST-Fur-4:2/Bis networks do.

3.4.5. $^1$H-NMR

Proton-NMR was employed to give more insight into the stereoselectivity of the DA and rDA reactions. It is known that two possible stereo-adducts can be formed during the Diels-Alder reaction, as described in chapter 1. The DSC results indicate that after multiple heating cycles the conformation of the formed adducts gradually shifts from endo to exo, resulting in a higher thermal stability of the adducts.

Besides the fact that the shift of adduct conformation from endo to exo at higher temperatures is confirmed by multiple sources, the stereoselective favourability was also examined by $^1$H-NMR. The stereoselectivity is monitored by NMR through a series of events, the results are given in Figure 15.

![Figure 15: $^1$H-NMR spectra of PEST-Fur-4:2/Bis recorded at various moments before and after heating.](image)

A sequence of DA and rDA reactions has been monitored by $^1$H-NMR. First, a 10 %wt amount of PEST-Fur and bismaleimide was dissolved in DMSO-d$_6$ in a Teflon capped NMR-tube. The first spectrum was recorded right after mixing, which is shown in Figure 15, denoted as Pre(-heating), $t = 0$. Continuously, the NMR tube was kept at room temperature for 24 hours; hereafter a gel had been formed, indicating crosslink formation via the DA reaction. The NMR-spectrum recorded after 24 hours at room temperature is also shown in Figure 15, denoted as Pre(-heating), $t = 24$ h. Subsequently, the $^1$H-NMR tube containing the sample was heated at 120 °C for 30 minutes in a NMR-tube oven, after which the oven was switched off.
The sample was kept in the oven for 24 hours, in order to slowly cool down the sample to room temperature. The third spectrum seen in Figure 15 shows the sample after heating at 120 °C and cooling down for 24 hours and it denoted as Post-(heating), t = 24 h.

Finally, the last spectrum was recorded after keeping the sample at room temperature for another 24 hours, denoted in Figure 15 as Post-(heating), t = 48 h.

Multiple peaks of the Diels-Alder adduct can be observed in 1H-NMR spectra, though the peaks belonging to the proton that is adjacent to the adduct bridge are most clearly differentiated from the others. It is known from literature that the peaks around 5.2 and 5.3 ppm belong to the adjacent bridge proton and correspond to the exo and endo conformations respectively\textsuperscript{13, 79, 89}

It is seen that at t = 0 h no adduct protons are observed, showing that the DA reaction has not yet taken place. After 24 hours at room temperature adduct formation is indicated by existence of multiple peaks (peaks 1-5) corresponding to the DA adduct\textsuperscript{13, 24, 89}. It is seen that the peak at 5.33 ppm (3), corresponding to the endo conformation, has got a much larger integral than the peak at 5.20 ppm (3), corresponding to the exo conformation. The relative existence of endo/exo conformations after 24 hours at room temperature is 77%/23% respectively.

It is observed that also after heating at 120 °C and cooling down for respectively 24 and 48 hours 1H-NMR peaks are observed that correspond to the DA adduct. However, in contrary to the first spectrum, it is seen that the integral of the exo peak is larger than the peak corresponding to the endo conformation; the relative existence of endo/exo after 24 and 48 hours post-heating is 32%/68% respectively.

Firstly, the equality of the spectra recorded after 24 and 48 hours post-heating indicate that an equilibrium in DA adduct formation has been reached already after 24 hours. It is worth noting that at temperatures close to the rDA temperature multiple reactions can take place. Adduct formation through the DA reaction, adduct breakage through the rDA reaction and changes in the structural conformation of the DA adducts can simultaneously occur. That is why one must be careful with drawing conclusions about the stereoselectivity solely from the given 1H-NMR results. One of the conclusions that however can be made, is that the shift from endo to exo after a heating cycle indicates that the exo conformation is favoured at higher temperatures. This indication can also explain the phenomena observed in the DSC spectra.

To the best of our knowledge, this is one of the first times, together with our previous work\textsuperscript{1}, that stereoselectivity of the Diels-Alder reaction is shown by 1H-NMR analysis of a polymer network, rather than a model compound. Additionally, it is also to the best our knowledge the first time that exo favourability of the Diels-Alder reaction at higher temperatures is shown by 1H-NMR analysis of a polymer network.

As stated by Canadell \textit{et al.}\textsuperscript{87}, differences in thermal reversibility due to the influence of either endo or exo adducts can have an important impact on the material properties of especially thermoreversible polymers and networks. The influence of stereoselectivity on the mechanical properties of the prepared polyester resin are examined and discussed later on.

### 3.4.6. DMTA

According to the thermal analysis both the $T_g$ of the short-chain polyester as well as the rDA temperature of the PEST-Fur/Bis resins allow the formation of bars, which are able to be produced beneath the temperature limit where degradation starts to occur. Hence, polyester resin bars were produced as described earlier and Dynamic Mechanical Thermal Analysis was employed to examine the mechanical properties.

A first indication of thermoreversible crosslinking is in fact the ability to produce test-specimen using hot compression-moulding, from material that already was crosslinked in solution. With material containing non-reversible crosslinks, this would not have been possible\textsuperscript{33}. 

Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry
February, 2014
Figure 16 shows the life-cycle of the test-specimens prepared from PEST-Fur/Bis. Figure 16a shows newly pressed bars prepared to the described method. After a four cycle DMTA experiment (20°C-160°C-20°C) a change in the appearance of the bars was visible (Figure 16b). It is seen that the test-specimens have buckled under the force exerted during the DMTA measurement. Furthermore, a change in colour is observed, which changed from dark yellow before the DMTA to brown afterwards. Again, this colour change might be caused by possible oxidation of the material, which can be countered by using antioxidants.

![Figure 16: Bars prepared from PEST-Fur/Bis (a) Hot-pressed PEST-Fur/Bis bars. (b) PEST-Fur/Bis bars after 4 DMTA Cycles. (c) Regrinded PEST-Fur/Bis bars after DMTA. (d) Recycled PEST-Fur/Bis bars.](image)

Continuously, the bars were regrinded into powder with a motorised hand-grinder (Figure 16c). Ultimately, the regrinded powder was again processed to polyester resin test-specimens according to the general pressing method, as shown in Figure 16d. These recycled PEST-Fur/Bis bars appear in an even darker brown colour in comparison to the dark-yellow and light-brown colours seen in Figure 16a and b respectively. This life-cycle sequence of PEST-Fur/Bis test-specimens shows the ultimate goal in terms of thermoreversibility: recycling polyester resin material after usage.
Mechanical data obtained from multiple DMTA cycles of various PEST-Fur-4:2/Bis networks is shown in Figure 17. For all graphs shown one should take into account that only the heating part of the DMTA cycles is displayed.

Firstly, it is observed that during the first cycle a temporarily decrease in mechanical properties occurs at elevated temperatures (most clearly seen for ratio 2:1). This is due to the buckling of the bars as a result of the forces exerted by the DMTA-machine.

![Figure 17](image-url)

**Figure 17:** DMTA of various ratios of PEST-Fur-4:2/Bis (a) Storage modulus $E'$. (b) Loss modulus $E''$. (c) Damping factor $\tan \delta$. (d) Recycled PEST-Fur-4:2/Bis-2:1.

Figure 17a, b and c display the mechanical properties of different ratios of polyester and crosslinker. It is seen that at certain temperatures above 100 °C a large decrease in moduli is observed, it is also in this region that $\tan \delta$ tends to reach higher values. The loss of mechanical properties is due to the rDA reaction, causing a softening point at elevated temperatures after which the polymer exhibits a viscous behaviour, rather than elastic. The temperatures at which the rDA reaction takes place are also shown in Table 1 for several PEST-Fur/Bis networks.
During the multiple DMTA-cycles the mechanical properties remain the same in the glassy region, while the temperature of the softening point slightly shifts to higher values after each cycle. This might again be due to the change in conformation of the DA adduct from endo to exo, as also seen in the DSC results and shown with $^1$H-NMR analysis. Since the exo adduct is more thermally stable, a shift of the softening point to higher temperatures seems logical. The change in softening temperature implies that the rDA reaction becomes more difficult after multiple heating cycles. This shift of the softening point is also seen by Tian et al., though they assign it to the increase in cross-link density. However, the increase in the softening point temperature is only minor.

It is seen that mechanical properties are more or less preserved after the subsequent thermal cycles. This is a noticeable improvement compared to our previous work, where a substantial decrease in mechanical properties was observed after multiple thermal cycles.

When the mechanical properties for different ratios polyester/crosslinker are examined, it is observed that the storage modulus ($E'$) decreases slightly for the ratio of 4:1 (polyester/bismaleimide) in comparison to 2:1. Tan $\delta$ also slightly shifts to a lower temperature. A shift in the decrease of storage modulus and a shift of tan $\delta$ to lower temperatures are also seen by Zhang et al. and Toncelli et al., in the case of higher furan/maleimide ratios. A general trend is seen in the literature that the stiffness of the polymer decreases for lower crosslink densities. The loss moduli for the various ratios are more or less similar at lower temperatures, though here also a ratio dependent softening temperature is observed.

The change in mechanical properties for various ratios of polymer/bismaleimide is caused by the difference in cross-linking density and therefore the number of formed DA adducts.

Figure 17d shows the mechanical properties of a new prepared test-specimen against the properties for a recycled polyester resin bar. In contrast to the virgin PEST-Fur-4:2/Bis-2:1 material, it is seen that the recycled material exhibits a lower storage modulus and a lower loss modulus, indicating less mechanical strength. The same phenomenon as described earlier (the shift of the softening point to higher temperatures after each cycle) is also observed for the recycled polyester resin. In the glassy region, the mechanical properties are more or less similar after each cycle.

Secondly, when comparing the softening temperatures of the newly prepared test-specimens with those of the recycled ones, it is seen that the decrease in mechanical properties occurs at higher temperatures for the recycled specimens. Again, this might be the result of increasing difficulty for the rDA reaction to occur after multiple heating cycles.

Mechanical data obtained from multiple DMTA cycles of the PEST-Fur-2:2/Bis-2:1 network is shown in Figure 18. The temporarily decrease in mechanical properties due to buckling of the test-specimen is also observed for PEST-Fur-2:2/Bis-2:1, as was for the PEST-Fur-4:2/Bis networks.
Furthermore, at elevated temperatures softening points are seen resulting from the rDA reactions. When comparing the DMTA results for PEST-Fur-2:2/Bis-2:1 to the results for PEST-Fur-4:2/Bis-2:1 (Figure 17), it is seen that the storage modulus, the loss modulus, the damping factor and their variations throughout the temperature range are pretty much identical. It was already established from GPC and DSC results that the small difference in molar mass between PEST-Fur-4:2 and PEST-Fur-2:2 has little to no influence on the glass transition temperature. Furthermore, the influence of the small difference in molar mass is also negligible when it comes to mechanical properties.
3.5. Conclusions

Diphenolic acid-furan was successfully employed as a bio-based building block in the synthesis of a novel (partially) bio-based short-chain polyester incorporating Diels-Alder capable moieties, namely PEST-Fur.

One of the aims of this work was to prepare a short-chain polyester in such a way that the polymer chains possess a lower glass transition temperature than the long-chain polyester prepared in our previous work, optimally resulting in improved processability and applicability.

A practical minimum has been found concerning the shortening of the polyester-furan chains using phenol as a chain stopper. Employing phenol as a chain stopper in the interfacial polycondensation of polyester-furan resulted in a short-chain polymer containing relatively large repeating units, as is indicated by the GPC results.

Upon examining the glass transition of the short-chain polyester-furan it was found that the $T_g$ of the polyester lies at 115 °C, which is indeed lower than the $T_g$ of the long-chain polyester, estimated at 125 °C\(^1\). This lowering of the glass transition temperature results in both improved processability of the base-polymer, as well as in improved recyclability of the polyester resin. It is also shown that the short-chain polyester base-polymer possesses a high degradation temperature of 350 °C, creating a large temperature window for processing and application of the polyester.

Furthermore, the short-chain polyester has been reacted with various ratios of an aromatic bismaleimide crosslinker to yield thermoreversible thermosetting networks through the Diels-Alder reaction. Moreover, the use of styrene to prepare a polyester resin was completely eliminated.

Thermoreversibility has furthermore been proved by cyclic DSC measurements showing transitions during heating and cooling corresponding to the rDA and DA reactions respectively. The small variations between subsequent cycles can be explained by the conformational transition of the DA adducts from the endo to the exo conformation at higher temperatures, yielding a thermally more stable material. The structural shift from endo to exo at higher temperatures has also been shown by \(^1\)H-NMR experiments, which proves the favourability of the exo adduct at higher temperatures. This is to the best of our knowledge the first time that favourable formation of the exo adduct during the Diels-Alder reaction at higher temperatures is shown by \(^1\)H-NMR analysis of a polymer network, rather than a model compound.

DMTA measurements also show thermoreversibility of the polyester resin during multiple cycles. A decrease in mechanical properties for higher ratios of polyester/bismaleimide is observed, indicating a less rigid network for lower amounts of crosslinker. Minor variations between subsequent DMTA cycles of the polyester/bismaleimide resins can also likely be explained by the endo/exo conformational shift, resulting in increased thermomechanical stability of the adducts during multiple heating cycles.

The preservation of mechanical properties during thermal cycles is a noticeable improvement on our previous work\(^1\), where a substantial decrease in mechanical properties was observed.

Ultimate recyclability has been shown by remoulding used DMTA-specimens into new test-specimens. These specimens showed a slight decrease in moduli and an increase in softening point temperature compared to the original material. Furthermore, thermoreversibility of the recycled material has been shown during cyclic DMTA measurements.

From the various results obtained through experimental research it can be concluded that the novel polyester resin prepared in this work gives new insights in the field of recyclable thermoset materials. The near perfect recyclability together with the excellent preservation of material properties of the polyester resin shown in this work is a next step in the direction of commercially recycling thermoset materials. The additional bio-based nature of the resin shows that it is in fact possible to produce a fully sustainable polymer thermoset.
Appendix A: Furan functionalised polyepoxides

Bisphenol A diglycidyl ether-furan

The class of epoxy resins is an important group of thermosetting materials that possesses excellent properties such as adhesion ability to various materials, superb chemical and corrosion resistance, thermal stability, electrical insulation, superior mechanical properties and low shrinkage during curing. Hence, epoxy resins are widely used as structural adhesives, matrices of composites and material for electronics encapsulation. Generally, the covalent crosslinks and hydrogen bonding inherent in epoxy resins result in insoluble, unprocessable thermosets.

Polyepoxides can consist of aliphatic, cyclo-aliphatic or aromatic hydrocarbon chains. Epoxy resins based on bisphenol A are widely used since they are commercially available and possess good thermal and mechanical properties. Around 20% of the commercially available bisphenol A is used for the production of epoxy resins.

A widely used and important class of commercial epoxy resins is the epoxy formed by the condensation reaction of bisphenol A and epichlorohydrin in the presence of sodium hydroxide, which yields bisphenol A diglycidyl ether (BADGE), sometimes known as diglycidyl ether of bisphenol A (DGEBA). In this research bisphenol A is replaced by our furan functionalised DPA-Fur.

Our aim is to prepare bisphenol A diglycidyl ether-furan (BADGE-Fur) through a condensation reaction with epichlorohydrin to yield a (partially) bio-based epoxide which can be used to synthesise thermoreversible epoxy resins. Figure 19 displays the synthesis reaction of BADGE-Fur.

![Figure 19: Synthesis of BADGE-Fur.](image)

Ultimately, the introduced thermoreversibility gives rise to improved recyclability of epoxy resins. Besides the improvement in recyclability, the thermoreversible epoxy resin can also be used as a protection coating in the electronics industry, when subsequent removal of the coating is required for component repair, modification or quality control.

Experimental

Materials and reagents
KOH (Merck), acetonitrile (Lab-Scan), epichlorohydrin (Sigma-Aldrich) and ethanol (99.9% pure, Merck) were used as received. DPA-Fur was prepared as described earlier (chapter 2).

Characterisation

$^1$H-NMR spectra were taken on a Varian Mercury Plus NMR-300 using DMSO-d$_6$ as a solvent.

Synthesis of BADGE-Fur

This synthesis uses the prepared DPA-Fur to synthesise Bisphenol A Diglycidyl Ether-Furan (BADGE-Fur). This preparation is an adaption of the synthesis of deuterated BADGE by Coulier et al.

1.6 g (4.38 mmol) DPA-Fur, 0.65 g (11.58 mmol) KOH and 60 mL ethanol were charged to a single-neck round bottomed flask. The mixture was stirred at room temperature to give a potassium DPA-Fur salt.

The solvent was evaporated using rotary evaporation (150 mbar, 60 °C) and vacuum drying overnight (60 °C). A hard yellow-brownish solid structure was obtained.
30 mL of water-free acetonitrile (prepared by 50 g Na₂SO₄ + 200 ml acetonitrile) and 9 mL (115 mmol) epichlorohydrin were added to the salt. The reaction mixture was stirred at room temperature for 1 hour, 30 min at 50 °C and then finally refluxed for 10 min.

The mixture was cooled down and filtered using a Büchner funnel, the residue was then extracted with 2 x 30 mL water-free acetonitrile. The resulting solution was collected and dried using rotary evaporation (150 mbar, 60 °C) to yield a dark red/brown oil (very low yield).

**Results and discussion**

As mentioned earlier, the synthesis of BADGE-Fur is an adaption of a synthesis described by Coulier *et al.* Other synthesis routes have been examined, but these routes gave even less promising results. The reaction has been carried out multiple times, with a comparable final result each time; the reaction yielded an extremely low amount of a dark red/brown oil.

¹H-NMR spectroscopy was employed to characterise the structure that was prepared according to the BADGE-Fur synthesis. Figure 20 shows the ¹H-NMR spectrum of both DPA-Fur as the starting material and the final product, which theoretically should be BADGE-Fur.

The two peaks which are visual in both spectra at 3.33 and 2.50 ppm correspond to residual H₂O and solvent DMSO respectively. It is seen that peak 1 (9.2 ppm) which corresponds to the terminal alcohol groups of DPA-Fur does not exist in the spectrum of BADGE-Fur. It is also shown that the peak which corresponds to the proton of the amide group of DPA-Fur (2; 8.2 ppm) is seen in both the spectra.

![Figure 20: ¹H-NMR spectrum of DPA-Fur and the final product of the BADGE-Fur reaction.](image-url)
There also exist some peaks (1’-6’) in the spectrum of BADGE-Fur which are not seen in the $^1$H-NMR spectrum of DPA-Fur. Peaks 2’ and 4’-6’ (3.9, 3.55, 2.85 and 2.7 ppm respectively) correspond to one of the starting materials, namely epichlorohydrin (see Figure 21).

![Figure 21: $^1$H-NMR spectrum of epichlorohydrin](image)

![Figure 22: Possible side-reactions during the synthesis of BADGE-Fur.](image)
Peaks 1’ and 3’ indicate the occurrence of possible side reactions. A few examples of these possible side reactions include the reactions of the –OH groups of DPA-Fur or the –NH groups of DPA-Fur or BADGE-Fur with a newly formed epoxide group. Another possibility would be the reaction of residual H₂O with the epoxide group to form a glycol group\textsuperscript{103}. The possible occurring side reactions are shown schematically in Figure 22.

**Conclusions**

As seen in the \textsuperscript{1}H-NMR spectrum of the final product, the peak which corresponds to the terminal alcohol groups of DPA-Fur completely disappeared. This shows that at least one or more reactions have been taking place, and that nearly all of the terminal alcohol groups reacted. Furthermore, the existence of the amide peak in the spectrum of the final product shows that the amide bond is still intact. However, this does not completely eliminate the possibility that a small portion of amide groups has participated in unwanted side reactions.

The occurrence of side reactions is furthermore supported by the fact that there exist multiple \textsuperscript{1}H-NMR peaks (1’ and 3’) that are not expected in the spectrum of BADGE-Fur. Secondly, several peaks that should be expected in the spectrum of BADGE-Fur do not show up at all in the measured spectrum, or are almost negligible small\textsuperscript{101,103}. Examples of the possible side reactions are mentioned earlier.

It can be concluded that it is not possible to employ diphenolic acid-furan as a building block in the synthesis of bisphenol A diglycidyl ether-furan via the synthesis routes examined in this report. The synthesis yields a very low and impure amount of product, mainly as a result of the possible side-reactions occurring during the reaction.
Appendix B: \(^1\)H-NMR of Polyester-Furan

Proton-NMR was employed to characterise the polyester that was obtained according to the synthesis of PEST-Fur. Figure 23 shows the \(^1\)H-NMR spectrum of both DPA-Fur as the starting monomer, as well as the final product, PEST-Fur. In both spectra two peaks at 2.50 ppm and 3.33 ppm can be observed; these peaks correspond to solvent DMSO and residual H\(_2\)O respectively\(^{102}\).

It is seen that the peak 1 (9.2 ppm), which corresponds to the terminal alcohol group of DPA-Fur, is no longer visible in the spectrum of PEST-Fur. Furthermore, it is seen that all of the other peaks present in the spectrum of DPA-Fur are also observed in the spectrum of PEST-Fur. However, some peaks have shifted towards a higher or lower frequency and/or seem to overlap with other peaks (1’, 3’, 4’, 8’, 9’, and 10’).

As mentioned before, the peak which corresponds to the terminal alcohol group of DPA-Fur (peak 1) is not visible in the spectrum of PEST-Fur; this is an indication that merely all of the alcohol groups of DPA-Fur reacted. Furthermore, it is seen that the peak corresponding to the amide group is visible in both spectra (peak 2 and 3’). This shows that after the polymerisation reaction the amide bond is still intact, and has not been prone to degradation through hydrolysis\(^{104}\). This is of great importance, since the DA functionality of the polymer is depending on the furan groups connected to the polymer chain through the amide bonds.
Appendix C: Synthesis and application of 1,12-Bis(maleimido)dodecane

Though it was outside the scope of this research, an additional side experiment has been performed employing an aliphatic bismaleimide crosslinker rather than an aromatic one in the formation of a polyester resin network. 1,12-Bis(maleimido)dodecane has been reacted with PEST-Fur-4:2 to yield a rigid structure, shown in Figure 24. Due to time limitations, no further research was performed on this polymer network.

![Figure 24: Appearance of PEST-Fur-4:2 combined with 1,12-Bis(maleimido)dodecane.](image)

Synthesis of 1,12-Bis(maleimido)dodecane

**Materials and reagents**

1,12-diaminododecane (Sigma-Aldrich), maleic anhydride (Fluka), acetic anhydride (Sigma-Aldrich), nickel(II)acetate (Sigma-Aldrich), triethylamine (Sigma-Aldrich), acetone (Lab-Scan) and active charcoal (Merck) were used as received. Dimethylformamide (Sigma-Aldrich) was purified through distillation before use.

**Characterisation**

$^1$H-NMR spectra were taken on a Varian Mercury Plus NMR-400 using DMSO-d$_6$ as a solvent.

**1,12-Bis(maleimido)dodecane**

The synthesis reaction of 1,12-Bis(maleimido)dodecane is an adaption of the synthesis described by Kossmehl et al.$^{105}$

50.1 g (0.25 mol) 1,12-diaminododecane was added to a stirred mixture of 49.0 g (0.5 mol) maleic anhydride in 150 mL freshly distilled dimethylformamide (DMF). The mixture was then stirred for one hour at 90 °C, during that time the visual appearance of the mixture changed from opaque white to clear yellow.

Subsequently, 102.0 g (1.0 mol) acetic anhydride, 0.5 g nickel(II)-acetate and 10.0 g triethylamine were added to the solution, thereafter the mixture turned to dark brown. The reaction mixture was continuously stirred at 90 °C for one hour. The solution was cooled down to 40 °C, after which it was precipitated for 10 minutes under stirring in 2 L of ice-water.
The resulting brown precipitate was filtered off by suction, after which it was washed twice with 1 L of water, stirred for one hour with 2 L of water, again filtered off by suction and finally washed again twice with 1 L of water. Subsequently, the brown solid was dissolved in 700 mL acetone under reflux conditions, during which it was dried with sodium sulfate. The mixture was filtered, after which the solution was refluxed for one hour with 25 g active charcoal and finally filtered again.

The solvent acetone of the solution was evaporated just enough to yield good crystallisation conditions. After obtaining the product via recrystallisation, the crystals were washed with small amounts of an aqueous solution of NaOH with pH 8.5. Finally, after drying the product a white powder was obtained (1,12-Bis(maleimido)dodecane).

\[ ^1H-NMR \text{ (400 MHz, CDCl}_3\text{): } \delta = 6.4 \text{ (s, 4H, olefinic), } 3.25 \text{ (t, 4H, N-CH}_2\text{), } 1.30 \text{ (m, 4H, CH}_2\text{), } 1.00 \text{ (d, 16H, CH}_2\text{).} \]

**PEST-Fur-4:2/lineair bismaleimide**

PEST-Fur-4:2 (1 eq. mol) was added to a single-neck round-bottomed flask. The molar amount of furan groups was estimated by assuming that the polymer consists only out of monomeric repeating units with a molecular weight of 496.53 g/mol (1 DPA-Fur group and 1 therephthaloyl group), this was assumed in order to calculate the molar amount of maleimide groups needed.

Subsequently the proper amount of 1,12-bis(maleimido)dodecane was added to prepare a 2:1 molar mixture (polyester:bismaleimide). While the mixture was stirred at 60 °C, just enough chloroform was added to dissolve the PEST-Fur and the lineair bismaleimide in order to create a homogeneous mixture.

The chloroform was then partially removed by rotary evaporation to yield a dark-brown rubbery substance. Completely removing the solvent by rotary evaporation results in a hard yellowish/brown product, which is hard to remove from the glassware.

The dark-brown rubbery substance was grinded using a motorised hand grinder, and subsequently dried in a vacuum oven (vacuum, 45 °C) to yield the product (PEST-Fur-4:2/lineair bismaleimide).
Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry

February, 2014

References


5. Wang, M.; Xu, C. (.; Leitch, M. Biore sour Technol 2009, 100, 2305.


20. Gujral, S. S.; Popli, A.


25. Picchioni, F.


Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry

February, 2014


46. Watanabe, M.; Yoshie, N. Polymer 2006, 47, 4946.


53. Hayes, D. J.; Fitzpatrick, S.; Hayes, M. H.; Ross, J. R. Biorefineries 2006, 1, 139.


Recycling bio-based thermosets through thermoreversible Diels-Alder chemistry

February, 2014


86. Tian, Q.; Rong, M. Z.; Zhang, M. Q.; Yuan, Y. C. Polym Int 2010, 59, 1339.


