Biobased, thermoreversibly crosslinked polyesters

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Chapter 3
The effect of molecular weight on the (re)-processability and material properties of bio-based, thermoreversibly cross-linked polyesters

Submitted to polymer

3.1 Abstract

A (partially) bio-based short-chain polyester is prepared through interfacial polycondensation of furan-functionalized diphenolic acid with terepthalic chloride. The furan groups along the backbone of the obtained polyester are able to form a covalent network (PE-fur/Bism) with various ratios of 1,1′-(methylenedi-4,1-phenylene)bismaleimide via the thermoreversible Diels-Alder (DA) reaction. Several techniques have been employed to characterize the polyester network, including: ^{1}H-NMR, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The polyester base polymer displays a glass transition temperature of 115 ^{0}C while the temperatures at which the retro-Diels-Alder (rDA) reaction takes place lie above 130 ^{0}C for the various polyester/bismaleimide networks. Excellent thermoreversibility and recyclability of the polyester resin have been shown through DSC and DMTA measurements.

Keywords: polymers, bio-based, short-chain, polyester, furan, bismaleimide, thermoreversibility, Diels-Alder, recyclability.

3.2 Introduction

In the past 20 years the focus in the field of research on polymeric products has shifted towards the synthesis and application of polymers which are both bio-based and recyclable[1]. In the near future this will become even more important due to the growing scarcity of petroleum as a feedstock for current conventional polymeric products. Various publications describe the successful substitution of petroleum-based components with bio-based analogues[2-5]. However, to produce a sustainable product it is of vital importance not only to focus on the feedstock materials, but also to look at what is done with the product after utilization (i.e. the waste generated at end of life). It is well-known that recyclability of polymeric systems in general, and thermosets in particular, is often still a challenge[6,7]. The permanent shape and structure imparted by the covalent crosslinks severely limits the reusability of these polymers[8], which undergo degradation (as opposed to the desired softening or melting) upon heating.

There is no viable, straight-forward replacement for thermoset materials as the (densely) crosslinked networks of these materials impart superior barrier and mechanical properties compared to their (non-crosslinked) thermoplastic analogues. Due to this durable nature, thermosets are often used in a wide variety of applications such as composites, adhesives and coatings. The downside of these strong, (densely) crosslinked networks, however, is that thermosets do not possess the chain mobility that thermoplastics often do. This severely reduces their (re)processability and intrinsic capability to be repaired[9]. As a consequence, many thermoset resins cannot be recycled after usage and eventually end up in landfills. In recent years, the laws for waste management have become stricter, placing ever more emphasis on the production of recyclable products. Preventing waste at the source of manufacture is the most desired way to manage waste[10]. There are various ways of interpreting these goals. Enabling recyclability of previously unrecyclable materials reduces the demand for the production of new material, effectively preventing waste at the source. For polymer thermosets, one of the options to achieve this is to introduce thermoreversibility into the polymeric material, namely as characteristic feature of the crosslinking reaction. This thermoreversibility gives rise to the possibility of remolding and reshaping the thermoset material by applying heat, while optimally the mechanical properties of the material are retained.

One way to introduce thermoreversible crosslinking into a polymeric system is to incorporate moieties that are capable of undergoing (reversible) Diels-Alder interactions. Once incorporated into the polymer matrix these moieties can act as crosslinking points. 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[11-13]. This cycloaddition leads to the formation of covalent bonds at lower temperatures (generally around 50 ^{0}C and below) through the Diels-Alder (DA) reaction, while, the reaction being an equilibrium, at higher temperatures (approximately 120 ^{0}C and above) the covalent bonds break and the original diene and dienophile groups are obtained through the retro-Diels-Alder (rDA) reaction[14]. The first preparation of thermally reversibly crosslinked polymers employing DA chemistry was reported by Craven *et al.*[6,15]. A furan-functionalized polymer is described, which forms thermally reversible networks with multiple maleimides. A large number of diene and dienophile couples can be used in DA chemistry, where electron-pushing and electron-withdrawing substituents in the diene and dienophile greatly influence the reactivity[16]. The furan ring is one of the most important dienes used in DA reactions, due to the exceptional dienic character of the furan ring, which makes it specifically suitable in terms of kinetics and yields[17]. On top of that, furan compounds are often obtained from renewable sources. Furthermore, maleimides are commonly used as dienophilic counterparts because of their highly reactive nature due to electron-withdrawing substituents adjacent to the double bond[17]. The coupling (DA) and decoupling (RDA) temperatures for the furan maleimide pair (~50°C and 150°C respectively) make this couple very suited for this application. Finally, the Diels-Alder reaction can be performed without solvent and does not need a third chemical such as a catalyst to function[18-20]. 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. (i.e. above the RDA temperature) When the rDA temperature is below the degradation temperature of the material or in general the temperature at which side-reactions occur, the polymeric system is regarded as fully thermoreversible. An important element in the concept of thermoreversible crosslinking is that often 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[18]. Thermoreversible systems employing Diels-Alder cross-linking chemistry give rise not only to improved processability and recyclability, but also to very specific and novel, unique applications such as self-healing/remendable polymers[6,14,20-25], shape-memory materials[7,26], probe-based lithographic and data-storage applications[27], removable foams for electronic encapsulation[28], thermally reversible gels[29,30], polymeric encapsulants[22] and thermally removable adhesives[31].

In this work, the preparation and characterization of a (partially) bio-based thermoreversible polyester resin is discussed. One of the main building blocks of this polyester is diphenolic acid, which can be derived from the bio-based building block levulinic acid[32]. Diphenolic acid is an acid-functionalized structural analogue of bisphenol A (BPA), which is widely used for commercial polycarbonate, epoxy and polyester resins[33,34]. The acid functionality of diphenolic acid is further functionalized with a furan group, introducing a Diels-Alder capable moiety. Finally, a polyester base-polymer is obtained via interfacial polycondensation of the furan modified diphenolic acid and terephtaloyl chloride, using phenol as a chain stopper (PE-fur, Figure 1). The addition of chain stopper should lower the average chain length of the polymer obtained, which in turn should reduce the glass transition temperature (T_g) of the material. This reduction is needed because it has been demonstrated that the T_g of PE-fur (without chain stopper) is too high for processing (e.g. the required processing temperature in order to assure proper polymer flow is too close to the degradation temperature)[35]. Phenol is of particular interest since it conserves aromaticity, readily takes part in the condensation synthesis and shares a structural similarity with diphenolic acid. Furthermore, it can be obtained from bio-based sources[36,37].

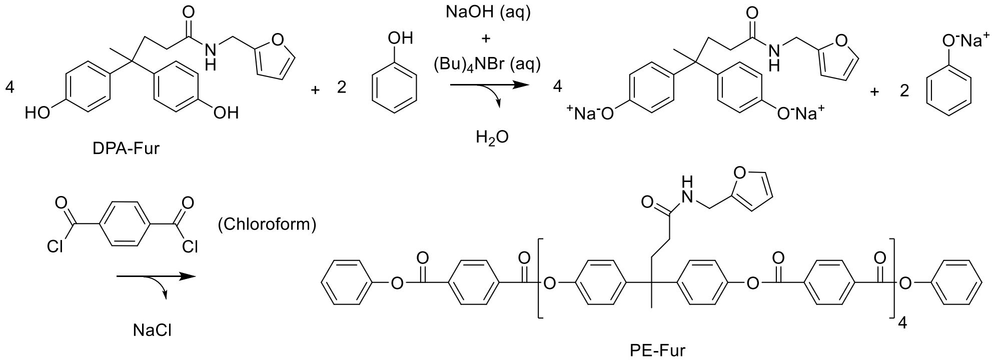


Figure 1: Synthesis of PE-fur from furan-functionalized diphenolic acid

3.3 Experimental section

3.3.1 Materials and reagents

Phenol (≥99%, Sigma-Aldrich), tetra-n-butylammonium bromide (≥98%, TBAB, Fluka), terephthaloyl chloride (99+%, Acros), NaOH (97%, Sigma-Aldrich), methanol (practical grade, Interchema), chloroform (anhydrous, ≥99% Lab-Scan), and 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (95%, Bismaleimide, Sigma-Aldrich) were used as received. DPA-fur was prepared following a reported procedure [1].

3.3.2 Characterization

^{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 measurements were performed on a HP1100 equipped with three 300x7.5 mm PLgel 3µm MIXED-E columns in series using a GBC LC 1240 RI detector. Average molecular weight calculations were performed with the PSS WinGPC Unity software from Polymer Standards Service. The following conditions were used: THF as eluent at a flow rate of 1 ml min^{-1}; 140 bar, a column temperature of 42 °C, 20 µl injection volume and a 10 mg mL^{-1} sample concentration. Toluene was used as a flow marker and polystyrene samples with different molecular weights were used as calibration standard. DSC data was recorded on a Perkin Elmer DSC Pyris 1 from 20 ^{0}C to 180 ^{0}C at rates of 2 ^{0}C/min or 10 ^{0}C/min. TGA data was recorded on a Mettler Toledo TGA. DMTA measurements were performed on a Rheometrics scientific solid analyzer (RSA II) under air environment using a dual cantilever at an oscillation frequency of 1 Hz and a heating rate of 2 ^{0}C/min. The data was measured during four cycles in a temperature range of 20 ^{0}C to 160 ^{0}C.

3.3.3 Synthesis of polyester-furan

The reaction of the DPA-fur monomer with terephthaloyl chloride results 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.

5.00 g (13.8 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 g (34.2 mmol) NaOH and 120 mL water were added to a 500 mL round bottomed flask. Subsequently, the reaction was stirred for 2 h at room temperature. Afterwards, 3.125 g (15.39 mmol) terephthaloyl chloride 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 min. Furthermore, the precipitate obtained in the centrifuge cups was filtered over a Büchner funnel and washed with 50 mL of 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 ^{0}C for a couple of hours to yield a white-yellowish solid (PE-fur, 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, -CH_2-), 1.98 (s, 2H, -CH_2-), 1.66 (s, 3H, -CH_3).

3.3.4 Preparation of polyester-furan/bismaleimide networks

The PE-fur/Bism networks were prepared via a general method. An amount of PE-fur (1.00 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 terephthaloyl group, see Figure 1). This was assumed in order to calculate the molar amount of maleimide groups needed.

Subsequently the proper amount of bismaleimide was added, different ratios were used to create different networks (0.50 eq. mol, 0.25 eq. mol and 0.125 eq. mol bismaleimide with respect to the furan content). While the mixture was stirred at 60 ^{0}C, just enough chloroform was added to dissolve the PE-fur and bismaleimide in order to create a homogeneous mixture. The chloroform was then partially removed by rotary evaporation (40 °C, 800 mbar) to yield a dark-brown rubbery substance. Completely removing the solvent by rotary evaporation is not recommended as this results in a hard yellowish/brown product, which is hard to remove from the glassware.

The dark-brown rubbery substance was ground using a motorized hand grinder, and subsequently dried in a vacuum oven (10 mbar, 45 ^{0}C). Finally, the resulting product was ground in liquid N_2 with a motorized hand grinder to yield a fine light-yellow powder (PE-fur/Bism) in quantitative yield.

3.3.5 Preparation of DMTA specimens

DMTA specimens were obtained by hot compression-molding of a mixture of PE-fur/Bism into bars with dimensions of 54x6x1 mm (length, width, height). The pressing sequence consisted of first cold pressing the polymer in the mold for 2 minutes at room temperature and 10 MPa. Subsequently, the polymer was pressed in a pre-heated press for 2 h at 150 ^{0}C and 10 MPa. The press was then slowly cooled down to 50 ^{0}C, after which the DMTA bars were treated at 50 ^{0}C for 24 h. Specimens from different molar ratios of furan/bismaleimide have been prepared: 2:1, 4:1 and 8:1.

3.4 Results and Discussions

The addition of a chain stopper appears to have little effect on the polymerization reaction kinetics. The reaction still proceeds readily as is evident from comparable yields in identical reaction conditions. There is, however, a small negative impact on total yield: the precipitation step does not yield all the polymer as the molecular weight of the shortest fractions is limited and as such they are still soluble in methanol. Furthermore, there is a very clear effect on chain length as shown in GPC elugraphs. A significantly shorter polymer is obtained when comparing the obtained PE-fur with the long chain PE-fur described before [1] (Figure 2).

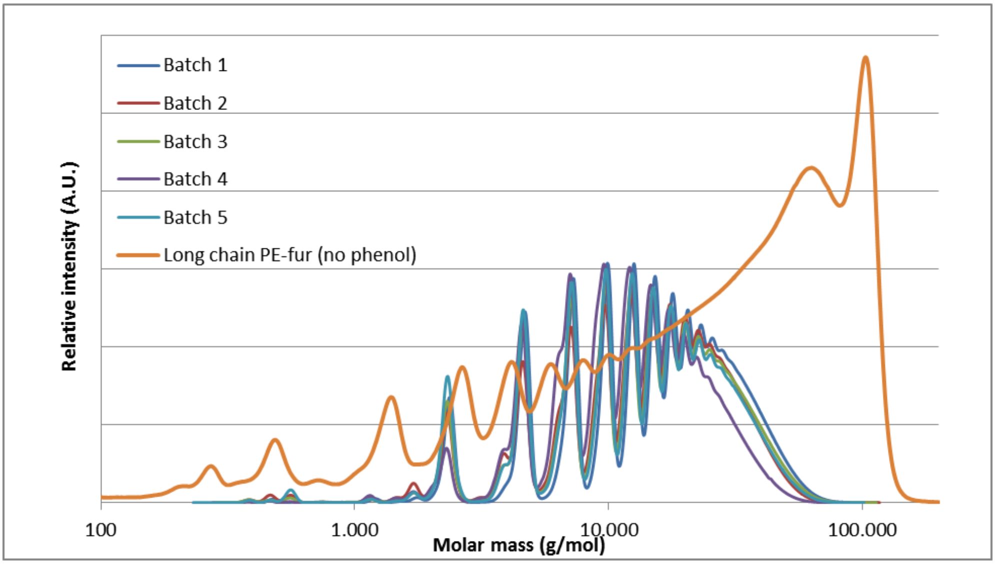


Figure 2: GPC spectrum of multiple PE-fur batches.

First, the presence of multiple peaks instead of a single smooth curve indicates that the sample consists of relative small polymers containing relatively large monomeric repeating units. This is also reported for the synthesis of cyclic polycarbonates from various bisphenol analogues[38-40]. The difference in molar mass between the various peaks is more or less the same, ranging from 2300 g/mol to 2700 g/mol. Both the height and narrow appearance of the peaks, as well as the more or less constant difference in molar mass between them are strong indications for the presence of short-chain polyesters with each peak varying one monomeric repeating unit from its neighbor. The successful application of phenol as chain stopper is evident from the elugrams of both polymers, comparing the long-chain polyester to the short-chain one (Figure 2) the latter obviously has a lower average Mw. The large peak at 200,000 g/mol in the long chain PE-fur results from the limitations of the column used, and it contains all fractions with higher Mw as well.

Differential Scanning Calorimetry was used to determine the processability of the polyester as well as the thermal reversibility of the polyester/bismaleimide networks. The glass transition temperature of PE-fur lies around 115 ^{0}C (Figure 3a). The long-chain polymer made without the use of phenol possesses a T_g of approx. 125 ^{0}C[1]. The effect of shortening the polymer chains by employing phenol as a chain stopper has led to a decrease of approximately 10 ^{0}C in T_g. The decrease in T_g with decreasing chain lengths is also seen for other linear bisphenolic polymers[41,42] and can primarily be ascribed to the loss of entanglements due to the shortening of chains (Figure 3).

3

When the temperature increases above 130 ^{0}C a transition takes place, which corresponds to the rDA reaction[7,9,22]; as evident from the peak in the DSC spectrum. This is observed in all of the three different resins and in all of the heating steps. Subsequently, during cooling down an exothermic peak is shown in the same region, indicating the occurrence of the DA reaction[22]. The position of the endothermic peak of the first cycle appears to differ from the subsequent cycles (most clearly observed in Figure 3b and d). This phenomenon has previously been reported for a furan/maleimide polyketone network[26] and a thermoreversible epoxy resin[23,43]. The shift of the endothermic peak to higher temperatures might be explained by the transition of DA adducts from the *endo* to the *exo* conformation[1,44]. The enhanced thermodynamic stability of the *exo* adduct explains the shift of the peak towards higher temperatures after the first cycles[26]. Although the next cycles appear to be very similar, a slight decrease in the peak area of the DA peak is observed. This may be due to the fact that the system does not have enough time to fully recover all the DA bonds[6,26] or that the *endo/exo* equilibrium is still shifting towards the more stable *exo* adduct[1]. The equality of the subsequent thermal cycles is a strong indication of thermoreversibility.

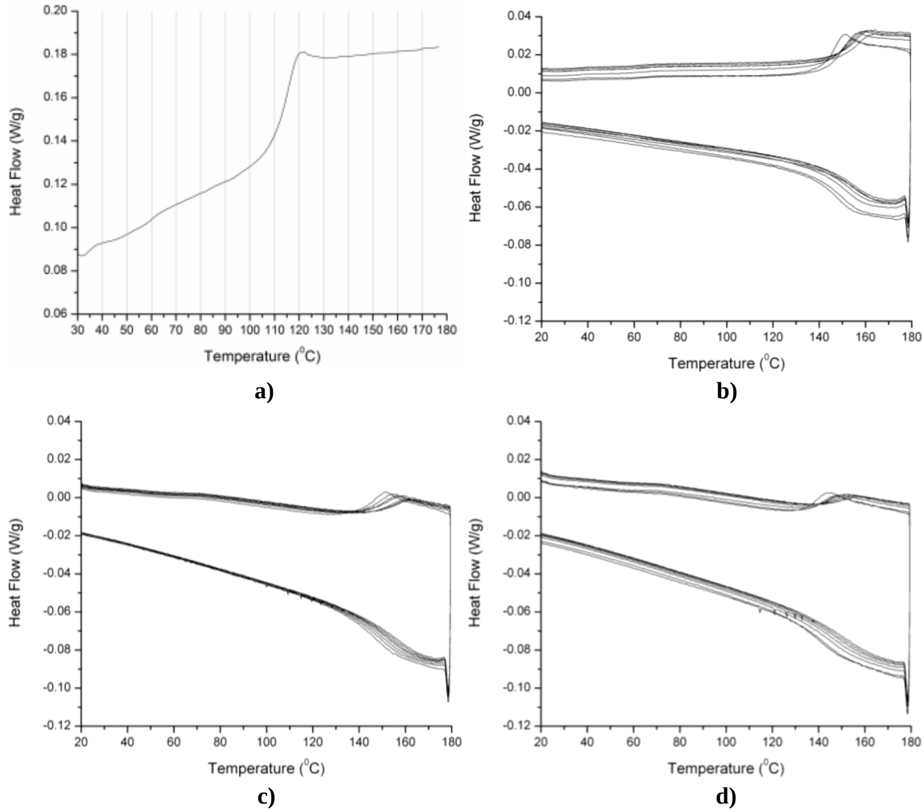


Figure 3: DSC measurements of:

(a) Tg of PE-fur. (b) PE-fur/Bism-2:1. (c) PE-fur/Bism-4:1. (d) PE-fur/Bism-8:1.

When comparing the different composition ratios of the polyester resin, the integral of the peak around 140 to 160 ^{0}C corresponding to the rDA reaction decreases in the line of PE-fur/Bism-2:1 > 4:1 > 8:1. This result confirms that lowering the amount of crosslinker reduces the amount of coupled groups and subsequently the energy needed to decouple them. This has also been reported for other systems with fixed furan content and lower crosslinking concentrations[26]. Furthermore, the temperature at which the rDA reaction occurs only changes marginally for other composition ratios of the polyester and bismaleimide, which is in agreement with reports on other furan/bismaleimide networks[26].

[1]H-NMR was employed to give more insight into the stereoselectivity of the DA reaction. It is well known that the DA reaction of furan and maleimide forms a stereoisomeric mixture. Initially the kinetically-favored *endo* adduct is formed, though at higher temperatures the thermodynamically favored *exo* conformation is obtained[45-47]. 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. 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. As evident from the shifting of the DSC RDA peak to higher temperatures. The shift from *endo* to *exo* configuration at higher temperatures is confirmed by multiple sources[45-49], often accompanied by NMR studies on model compounds. Figure 4 shows NMR spectra of PE-fur and bismaleimide after several stages.

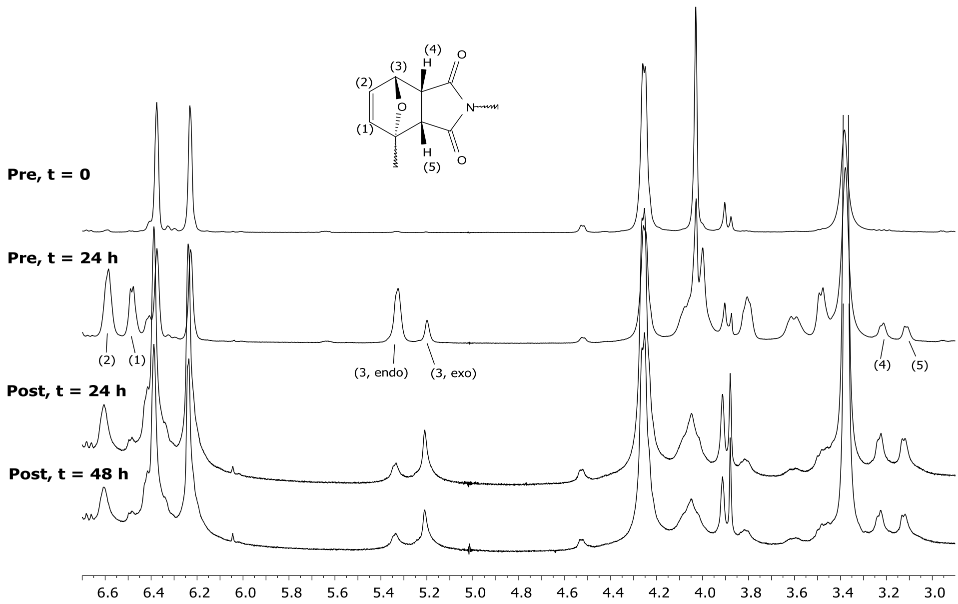


Figure 4: ^{1}H-NMR spectra of PE-fur/Bism recorded at various moments before and after heating.

First, a 10 %wt amount of PE-fur and bismaleimide was dissolved in DMSO-d_6 in a teflon capped NMR-tube. The first spectrum was recorded directly after mixing, (Figure 4top (Pre, t = 0)). Subsequently, the NMR tube was kept at room temperature for 24 hours; during this time a gel was formed, indicating crosslink formation via the DA reaction. Then the next spectrum was recorded (Figure 4 (Pre, t = 24 h)). The NMR tube containing the gelated sample was heated at 120 ^{0}C for 30 min 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. (Figure 4 (Post, t = 24h)). Finally, the last spectrum was recorded after keeping the sample at room temperature for another 24 hours, (Figure 4 (Post, t = 48 h)).

Multiple peaks corresponding to protons in the Diels-Alder adduct can be observed in the ^{1}H-NMR spectra. 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 δ5.2 and δ 5.3 ppm belong to this adjacent bridge proton and correspond to the *exo* and *endo* conformations, respectively[6,17,50].

It was found that initially (at t = 0 h) no adduct protons are present, showing that the DA reaction has not yet taken place. After 24 h at room temperature, the adduct formation is indicated by the appearance of multiple peaks (Figure 4, Pre, t=24h, peaks 1-5) corresponding to the DA adduct[6,14,17]. The intensity of the peak at δ 5.33 ppm (3), corresponding to the *endo* conformation, is much larger than that of the peak at δ 5.20 ppm (3), corresponding to the *exo* conformation. The ratio of *endo/exo* conformations after 24 hours at room temperature is 77%/23% respectively. After heating to 120 ^{0}C and cooling down for respectively 24 and 48 h ^{1}H-NMR peaks are again observed that correspond to the DA adduct. However, when comparing the *endo/exo* ratio to the gel obtained at room temperature, after heating the integral of the *exo* peak is larger; the ratio of *endo/exo* after 24 and 48 h post-heating is 32%/68% respectively. The fact that the spectra recorded after 24 and 48 h post-heating are identical indicates that equilibrium conditions in DA adduct formation are reached within the first 24 hours or that the adduct is stable at room temperature. It is worth noting that multiple reactions can occur in a small temperature window close to the rDA temperature: adduct formation via the DA reaction, adduct breakage via the rDA reaction and isomerization of the *endo* to the *exo* adduct[50]. The results obtained via the NMR experiments would indicate that the shift in the ratio of *endo/exo* conformations after a heating cycle confirms that the *exo* conformation is indeed favored at higher temperatures. This further justifies the conclusions drawn from the DSC spectra. 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 thermoremendable polymers and networks[51]. The influence of stereoselectivity on the mechanical properties of the prepared polyester resin were examined and will be discussed later on *(vide infra).* The first (strong) indication of thermoreversible crosslinking is the ability to produce homogeneous test-specimens using hot compression-molding from material that already was crosslinked in solution. This would not have been possible using material containing non-reversible crosslinks, as the final material would be a sintered compressed powder[26].

Firstly, it is observed that during the first cycle, E’ and E” drop at elevated temperatures (most clearly seen for ratio 2:1, Figure 5). This is due to buckling of the bars as a result of the sideway forces exerted by the DMTA-machine sample holder. At elevated temperatures (starting from 132 ^{0}C for ratio 2:1 and 114 ^{0}C for ratio 4:1) a large decrease in moduli is observed, it is also in this region that tan δ increases rapidly (Figure 5a, b and c). This change is due to the DA-rDA equilibrium that shifts to favor the rDA reaction. This results in decrosslinking in the polymer resin. This yields a softening point at elevated temperatures after which the polymer exhibits viscous behavior, rather than elastic[52]. During the multiple DMTA-cycles the mechanical properties remain the same in the glassy region, while the temperature of the softening point shifts to higher values after each cycle. The shift of the softening point has previously been attributed to an increase in crosslink density[21]. However, recent publications attribute this to the change in conformation of the DA adduct from *endo* to *exo*[53]. 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 (due to the fact that the adduct becomes more stable) after multiple heating cycles[53].

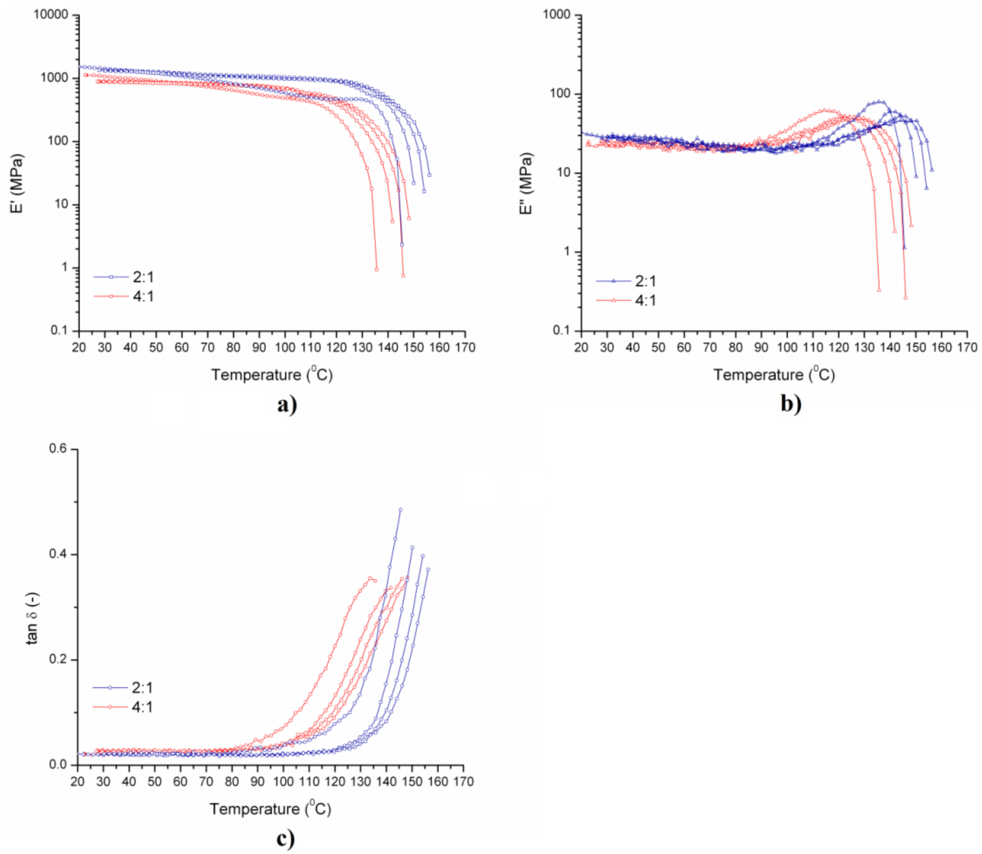
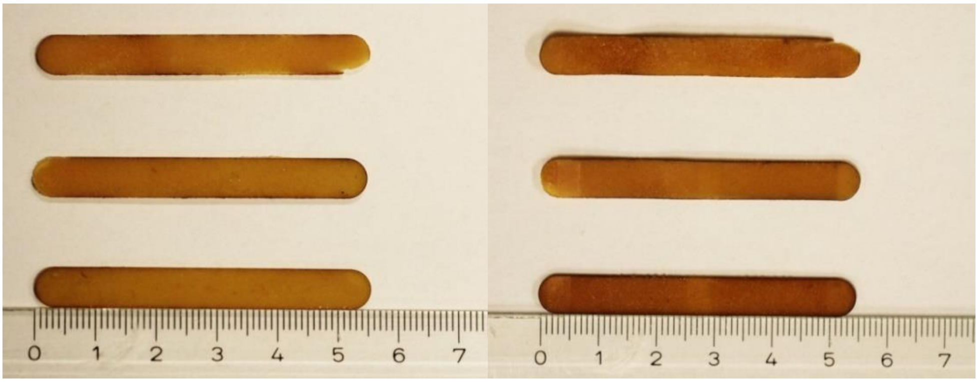


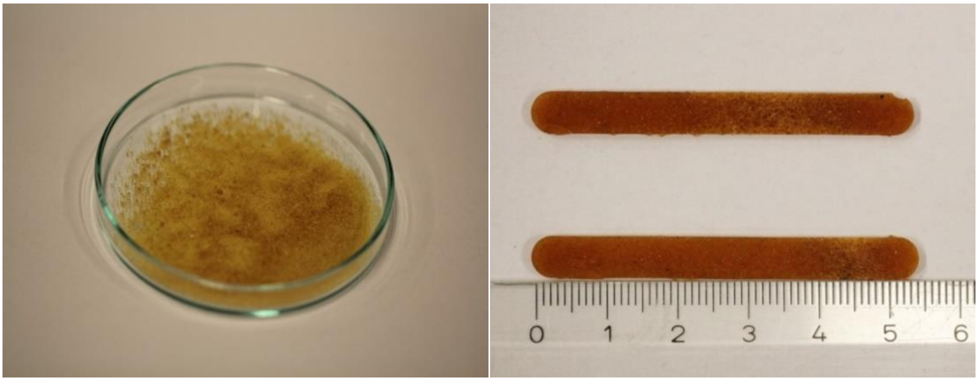
Figure 5: DMTA of various specimens of PE-fur/Bism (a) Storage modulus E'. (b) Loss modulus E". (c) Damping factor tan δ. Only the heating steps are shown for clarity

When comparing the mechanical properties for different ratios polyester/crosslinker, a slight decrease in the storage modulus (E') is observed for the ratio of 4:1 (polyester/bismaleimide) with respect to 2:1. The maximum of tan δ also slightly shifts to a lower temperature. Similar material response upon varying the furan/maleimide ratios was also observed for other furan/maleimide systems[6,26]. The stiffness of the polymers generally decreases with the crosslink densitiy[6,54-56]. The loss moduli (E") for the various ratios are more or less similar at lower temperatures, though here also a ratio dependent softening temperature is observed. The softening points of the different samples are 146 ^{0}C and 136 ^{0}C for PE-fur/Bism-2:1 and -4:1 respectively. The softening points are determined from the points of maximum decrease of the storage moduli during the first cycles. In a previous publication describing[1] measurements on long-chain PE-fur/Bism networks comparable softening points have been reported: 138 ^{0}C and 136 ^{0}C for furan/bismaleimide mixtures with 2:1 and 4:1 molar ratios respectively. Thus, it can be concluded that the addition of chain stopper has had a negligible effect on the stability of the polymer network.

A life-cycle of the test-specimens prepared from PE-fur/Bism shows newly compression molded bars prepared according to the method described in the experimental section (Figure 6). After a four cycle DMTA experiment (20^{0}C-160^{0}C-20^{0}C) an optical change in the appearance/shape of the bars was visible (Figure 6b): the test-specimens have buckled under the force exerted during the DMTA measurement. Furthermore, a change in color is observed, changing from dark yellow before the DMTA to brown afterwards. Since no antioxidants had been added, this color change may be caused by oxidation of the material. Analysis of the material by NMR and IR however, showed no (significant) formation of side products, nor any indication of degradation.



a) **b)**



c) **d)**

Figure 6: Bars prepared from PE-Fur/Bism (a) Hot-pressed PE-Fur/Bism bars. (b) PE-Fur/Bism bars after 4 DMTA Cycles. (c) Reground PE-Fur/Bism bars after DMTA. (d) Recycled PE-Fur/Bism bars.

After measuring, the bars were reground into powder using a motorized hand-grinder (Figure 6c). Ultimately, the reground powder was again processed into DMTA bars via the same compression molding procedure (Figure 6d). These resulting, recycled PE-fur/Bism bars display an even darker brown color in comparison to the dark-yellow and light-brown colors seen in Figure 6a and b respectively. Analysis of the reprocessed material still indicated no impurities. As noted, the coloring is likely due to the formation of very small amounts of highly colored products that are undetectable by ^{1}H-NMR. This life-cycle sequence of PE-fur/Bism test-specimens emulates the ultimate goal in terms of thermoreversibility: recycling polyester resin material after usage.

A temporary decrease of the storage and loss moduli is also visible during the first DMTA cycle of the recycled test bars due to buckling of the test specimen (Figure 7), as a result of the sideway forces exerted by the DMTA-machine sample holder.

In contrast to the virgin PE-fur/Bism-2:1 material, it is seen that the recycled material exhibits a slightly lower storage modulus and loss modulus, indicating somewhat less mechanical strength. However, this difference is only marginal and proofs that even after complete recycling, the mechanical properties are still equivalent.

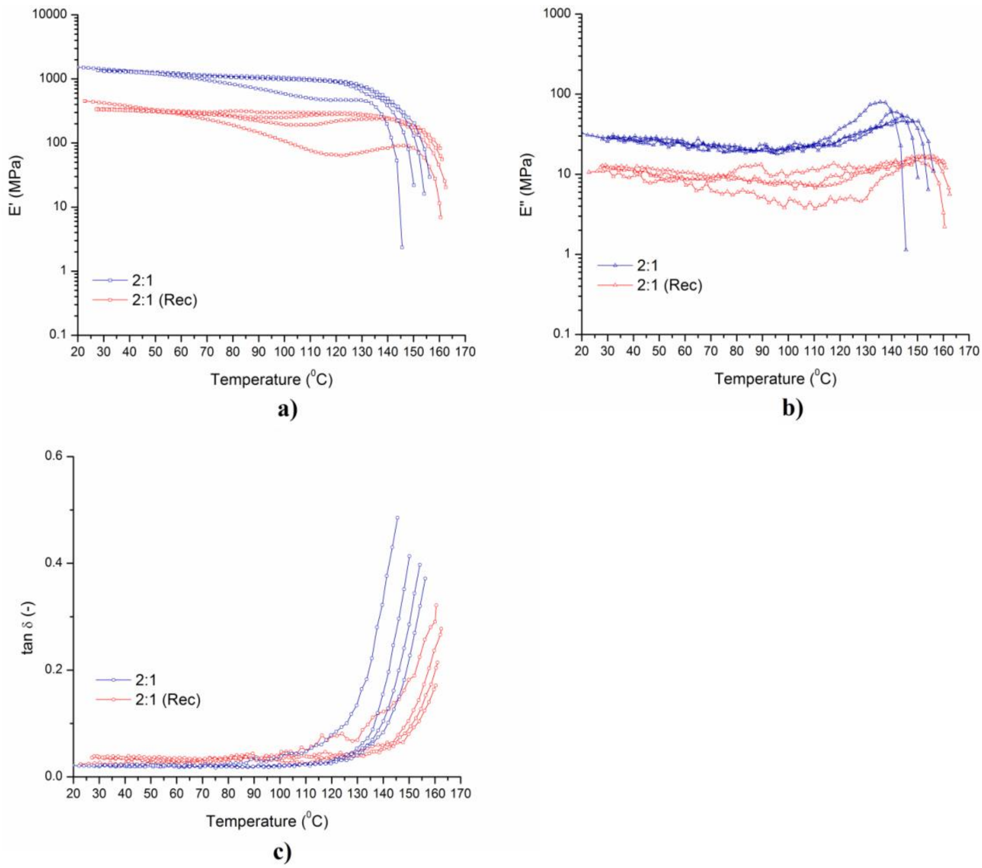


Figure 7: Dynamic Mechanical Thermal Analysis of recycled specimens of PE-fur/Bism (a) Storage modulus E'. (b) Loss modulus E". (c) Damping factor tan δ

The same phenomenon described earlier (the shift of the softening point to higher temperatures after each cycle) is also observed for the recycled polyester

resin. This, again, suggests increasing difficulty for the rDA reaction to occur after multiple heating cycles, possibly due to conformational changes of the adducts resulting in DA adducts with higher thermal stability. (e.g. from *endo* to *exo*[1])
When comparing the softening temperatures of the newly prepared test-specimens with those of the recycled ones, it is seen that the softening points of the recycled specimens lie at higher temperatures. Since the recycled test specimen has been exposed to more heating cycles than the virgin material has, it is fair to assume that the recycled polyester network possesses a relative higher amount of thermally stable adducts. Again, this ultimately results in increased temperatures needed to induce the rDA reaction. This phenomenon, however, does not seem to have any significant effect on the mechanical properties of the material.

The mechanical properties of the recycled material are unchanged throughout the subsequent DMTA-cycles. This shows that the recycled material does not yield poorer mechanical properties, even after multiple measurements at various temperatures. Ultimately, the fact that the mechanical properties of the virgin and the recycled PE-fur/Bism material are comparable indicates that this indeed constitutes a fully thermoreversibly recyclable polymer.

3.5 Conclusions

A (partially) bio-based, short-chain polyester has been synthesized to incorporate furan moieties that are capable of undergoing Diels-Alder reactions with bismaleimide crosslinkers. This polyester possesses a lower glass transition temperature than the long-chain polyester described[1] previously (i.e. 115 ^{0}C versus 125 ^{0}C), which results in improved processability.

The short-chain, furan-functionalized polyester has been reacted with bismaleimide which acts as a crosslinking agent, yielding a thermoreversible covalent network through the Diels-Alder reaction. The mechanical properties of the network have been influenced by varying the ratio of crosslinker versus furans. A decrease in softening point from 146 to 136 was observed upon halving the amount of bismaleimide. Thermoreversibility was shown by cyclic DSC measurements as the observed transitions during heating and cooling correspond to the rDA and DA reactions respectively. The small variations observed between subsequent cycles are attributed to the transition of the DA adducts from the *endo* to the *exo* conformation, these variations are confirmed by ^{1}H-NMR measurements which shows that initially the *endo* adduct is favored during room temperature crosslinking in solution. Subsequently exposing the solution to elevated temperatures (120 ^{0}C) shows preferred formation of the *exo* adduct.

DMTA measurements also show thermoreversibility of the polyester resin during multiple cycles of measurements in a temperature range of 20 ^{0}C to 160 ^{0}C. The mechanical properties of the examined polyester networks remained identical during the multiple cycles even after the thermally induced softening of the material due to the rDA reaction and accompanying decrease of mechanical properties at temperatures above 110 ^{0}C apart from a minor shift in softening point due to the aforementioned *endo-exo* isomerism. When changing the molar ratio of furan:maleimide from 1:1 to 2:1 respectively, a decrease in softening point is seen (from 146 ^{0}C to 136 ^{0}C) as well as a decrease in storage modulus, indicating a less densely crosslinked network with poorer mechanical properties for lower amounts of crosslinker. This is supported by the fact that proper test-specimens for the furan:maleimide ratio 4:1 could not be obtained due to cracking of the material during hot compression-molding.

Ultimate recyclability has been shown in a practical way by re-molding used DMTA specimens into new test-specimens after pulverization of the initial sample by mechanical grinding. Recycling in this manner does not impart a significant detrimental effect on the thermoreversibility of the recycled material, as demonstrated by performing cyclic DMTA measurements where the obtained mechanical properties of the recycled PE-fur/Bism material were retained during these consequent cycles.

The excellent conservation of the tested properties of both virgin as well as recycled polymeric material during multiple thermal cycles indicates an already excellent recyclability. The additional re-processing of used material without any real loss of mechanical properties proves it is possible to fully recycle the described polyester/bismaleimide polymer using Diels-Alder chemistry.

3.6 References

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