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The Effect of Molecular Weight on the (Re)-Processability and Material Properties of Bio-Based, Thermoreversibly Cross-Linked Polyesters

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Abstract: A (partially) bio-based short-chain polyester is prepared through interfacial polycondensation of furan-functionalized diphenolic acid with terephthalic 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 °C, whereas the temperatures at which the retro-Diels–Alder (rDA) reaction takes place lie above 130 °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

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Citation: Beljaars, M.; Kamphuis, A.J.; Heeres, H.J.; Broekhuis, A.A.; Picchioni, F. The Effect of Molecular Weight on the (Re)-Processability and Material Properties of Bio-Based, Thermoreversibly Cross-Linked Polyesters. *Appl. Sci.* **2022**, *12*, 7287. https://doi.org/10.3390/app12147287

Academic Editor: Alejandro Rodriguez Pascual

Received: 20 January 2022
Accepted: 14 July 2022
Published: 20 July 2022

1. Introduction

In the past 20 years, the focus in the field of research on polymeric products has shifted toward the synthesis and application of polymers that 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 analogs [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 the 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 cross-links severely limit the reusability of these polymers [8], which undergo degradation (as opposed to the desired softening or melting) upon heating.

There is no viable, straightforward replacement for thermoset materials as the (densely) cross-linked networks of these materials impart superior barrier and mechanical properties compared to their (non-cross-linked) thermoplastic analogs. 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) cross-linked 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 materials, effectively preventing waste at the source. For polymer thermosets, one of the options for achieving this is to introduce thermoreversibility into the polymeric material, namely as a characteristic feature of the cross-linking reaction. This thermoreversibility gives rise to the possibility of remolding and reshaping the thermoset material by applying heat while optimally retaining the mechanical properties of the material.

One way to introduce thermoreversible cross-linking 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 cross-linking 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 at around 50 °C and below) through the Diels–Alder (DA) reaction, whereas the reaction being an equilibrium, at higher temperatures (at approximately 120 °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 cross-linked 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 its exceptional dienic character, 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 a solvent and does not need a third chemical such as a catalyst to function [18–20].

If this mechanism would be used as a cross-linking 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 cross-linking is that often not all the cross-links have to be broken for the system to be recyclable, as long as the extent of bond breakage results in a flowable polymer melt [19].

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 analog 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 a 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 a 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].

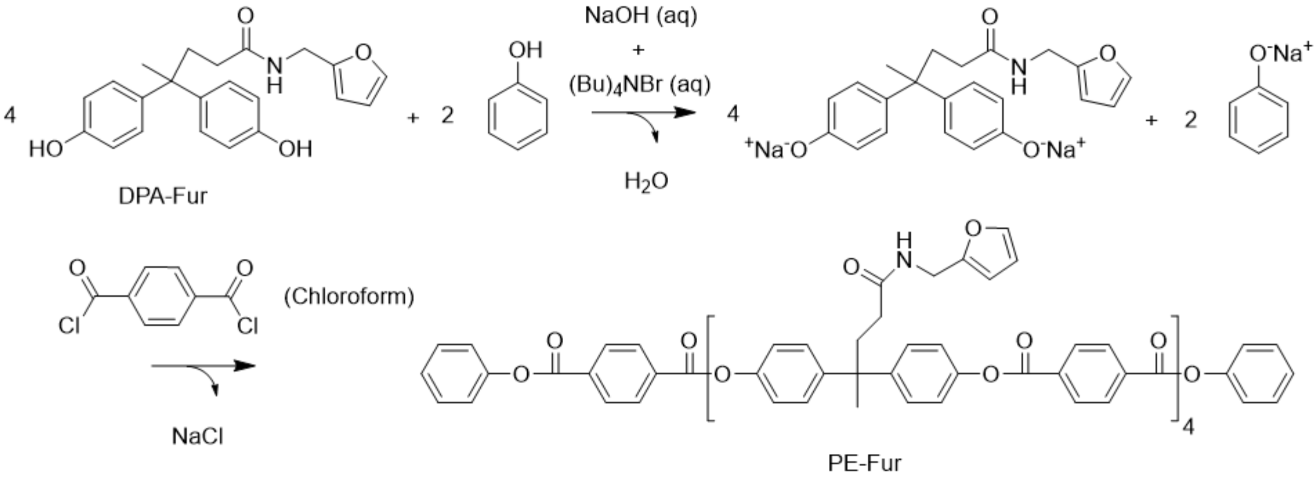


Figure 1. Synthesis of PE-fur from furan-functionalized diphenolic acid.

2. Materials and Methods

2.1. Chemicals

Phenol (≥99%, Sigma-Aldrich, St. Louis, MA, USA), tetra-n-butylammonium bromide (≥98%, TBAB, Fluka), terephthaloyl chloride (99+%, Acros, New Jersey, NJ, USA), NaOH (97%, Sigma-Aldrich), methanol (practical grade, Interchema, Vollenhove, The Netherlands), 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].

2.2. Characterization

The ^{1}H-NMR spectra were taken on a Varian Mercury Plus NMR-300 and a Varian Mercury Plus NMR-400 using DMSO-d6 as a solvent. GPC measurements were performed on an HP1100 equipped with three 300 × 7.5 mm PLgel 3μm MIXED-E columns in a 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 an eluent at a flow rate of 1 mL min-1; 140 bar; a column temperature of 42 °C; a 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 the calibration standard. DSC data were recorded on a Perkin Elmer DSC Pyris 1 from 20 °C to 180 °C at rates of 2 °C/min or 10 °C/min. TGA data were 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 °C/min. The data were measured during four cycles in a temperature range of 20 °C to 160 °C.

2.3. 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.

An amount of 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. Afterward, 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 °C for a couple of hours to yield a yellowish-white solid (PE-fur, best yield achieved 74%).

The ^{1}H-NMR (300 MHz, DMSO-d6) measurements were 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-), and 1.66 (s, 3H, -CH3).

2.4. 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 of monomeric repeating units with a molecular weight of 496.53 g/mol (1 DPA-fur group and 1 therephthaloyl 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 and 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). Although the mixture was stirred at 60 °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 °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.

2.5. Preparation of DMTA Specimens

DMTA specimens were obtained by hot compression-molding of a mixture of PE-fur/Bism into bars with dimensions of 54 × 6 × 1 mm (length, width, height). The pressing sequence consisted of first cold-pressing the polymer in the mold for 2 min at room temperature and 10 Mpa. Subsequently, the polymer was pressed in a pre-heated press for 2 h 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 h. Specimens from different molar ratios of furan/bismaleimide were prepared: 2:1, 4:1, and 8:1.

3. Results and Discussion

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 the comparable yields under identical reaction conditions. There is, however, a small negative impact on the 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 the chain length as shown in the GPC elugraphs of five different batches prepared under the same experimental conditions. A significantly shorter polymer is obtained when comparing the obtained PE-fur with the long-chain PE-fur described before [1] (Figure 2).

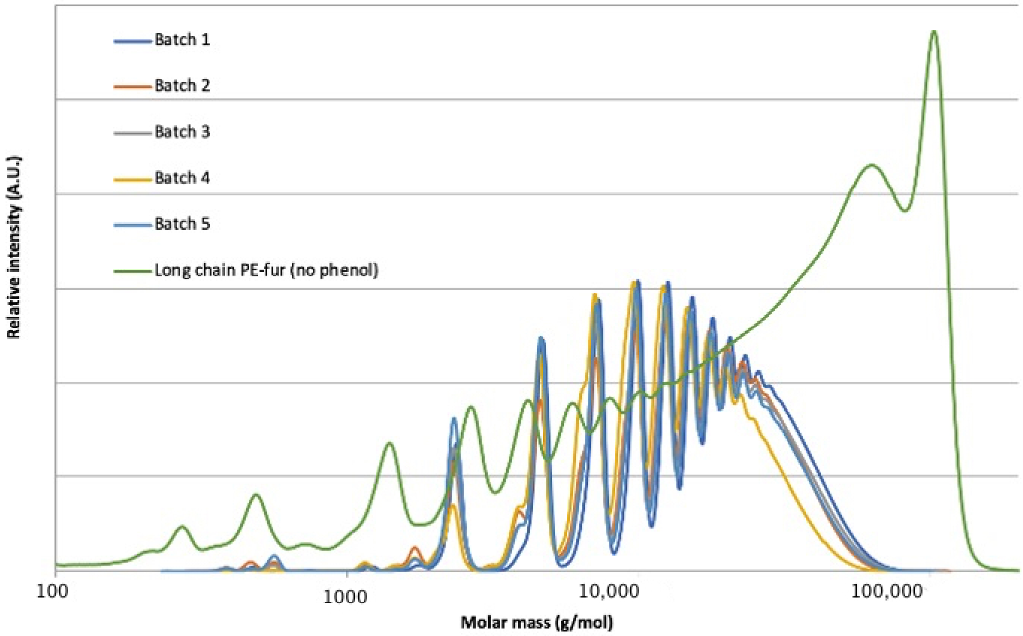
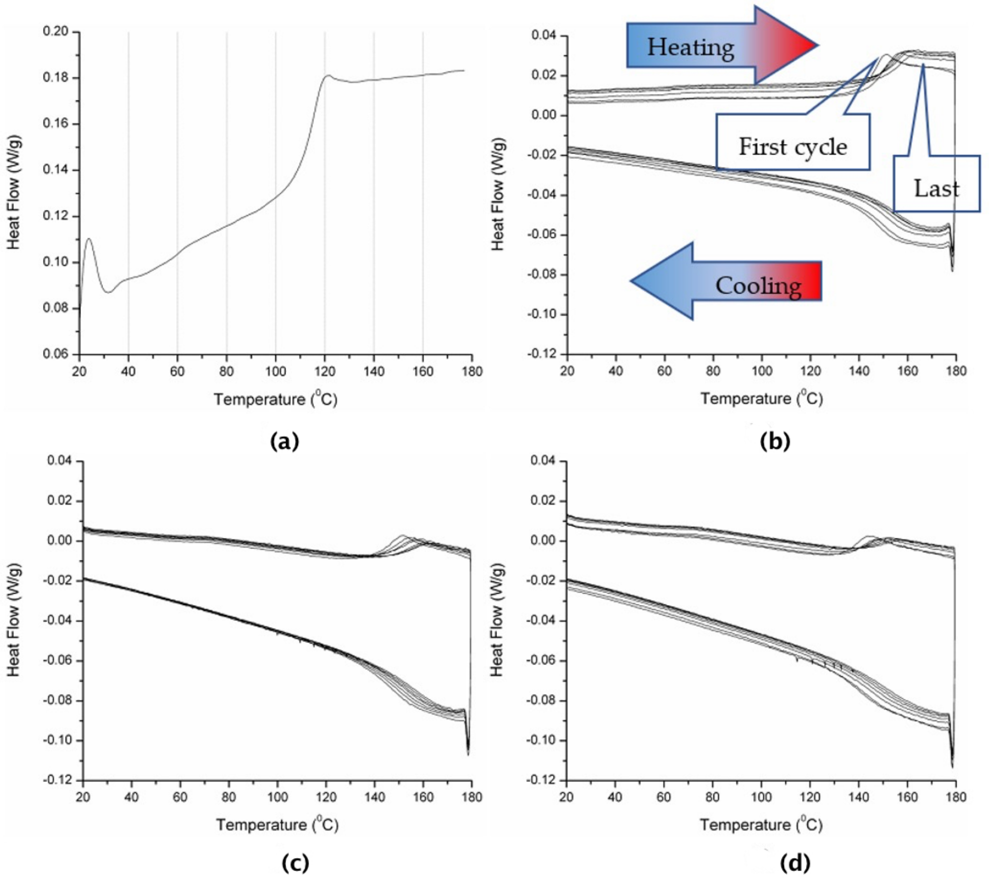


Figure 2. GPC spectrum of multiple PE-fur batches (for reaction conditions see Experimental Section).

First, the presence of multiple peaks instead of a single smooth curve indicates that the sample consists of relatively small polymers containing relatively large monomeric repeating units. This is also reported for the synthesis of cyclic polycarbonates from various bisphenol analogs [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 of the presence of short-chain polyesters, with each peak varying one monomeric repeating unit from its neighbor. The successful application of phenol as a 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 also contains all fractions with a higher Mw. 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 at around 115 °C (Figure 3a). The long-chain polymer made without the use of phenol possesses a T_g of approx5. 125 °C. The effect of shortening the polymer chains by employing phenol as a chain stopper has led to a decrease of approximately 10 °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).



(a) (b) (c) (d)

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 the temperature increases above 130 °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 three different resins and 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,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 could be explained by the transition of DA adducts from the *endo* to the *exo* conformation [1,44] (the chemical structures of these adducts are provided in the Supplementary Materials). The step-in heat capacity observed for this transition instead of a proper melting/cooling peak is merely an artifact as the broad transition is cut in the DSC thermogram. This is necessary as running the DSC to a higher temperature entails the appearance of side reactions. The general shape is in agreement with the previous literature on this subject [23,26,43]. The enhanced thermodynamic stability of the *exo* adduct explains the shift of the peak toward 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 toward the more stable *exo* adduct [1]. The equality of the subsequent thermal cycles is a strong indication of thermoreversibility.

When comparing the different composition ratios of the polyester resin, the integral of the peak around 140 to 160 °C corresponding to the rDA reaction decreases in the line of PE-fur/Bism-2:1 > 4:1 > 8:1. These results confirm that lowering the amount of cross-linker reduces the amount of coupled groups and subsequently the energy needed to decouple them. This has also been reported for other systems with a fixed furan content and lower cross-linking concentrations [26]. Furthermore, the temperature at which the rDA reaction occurs only changes marginally for the 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 the 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* configurations at higher temperatures is confirmed by multiple sources [45–49], often accompanied by NMR studies on model compounds. Figure 4 shows the NMR spectra of PE-fur and bismaleimide after several stages.

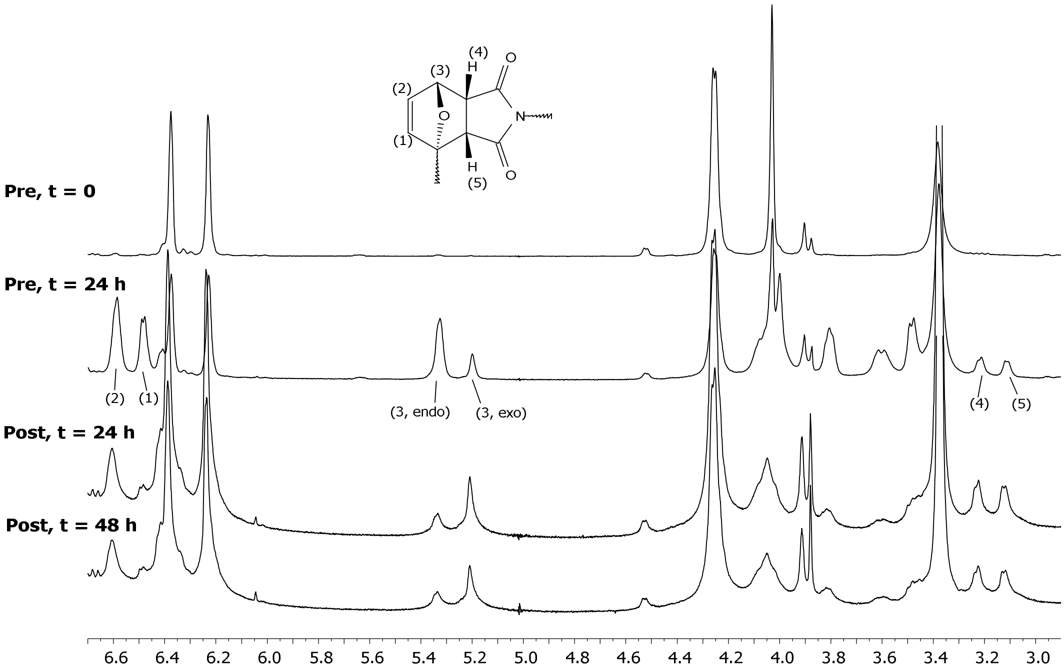


Figure 4. ^{1}H-NMR spectra of PE-fur/Bism recorded at various moments before and after heating.

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 4 top (Pre, t = 0)). Subsequently, the NMR tube was kept at room temperature for 24 h; during this time, a gel was formed, indicating cross-link 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 °C for 30 min in an NMR tube oven, after which the oven was switched off. The sample was kept in the oven for 24 h, in order to slowly cool down the sample to room temperature. (Figure 4 (Post, t = 24 h)). 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 the 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 = 24 h, 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 ratios of the *endo/exo* conformations after 24 h at room temperature are 77/23%, respectively. After heating to 120 °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 ratios of *endo/exo* after 24 and 48 h post-heating are 32/68%, respectively. The fact that the spectra recorded after 24 and 48 h post-heating are identical, indicates that the equilibrium conditions in the DA adduct formation are reached within the first 24 h 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 thermoremendable polymers and networks in particular [51]. The influence of stereoselectivity on the mechanical properties of the prepared polyester resin was examined and will be discussed later on *(vide infra).* The first (strong) indication of thermoreversible cross-linking is the ability to produce homogeneous test specimens using hot compression molding from material that had already been cross-linked in solution. This would not have been possible using a material containing non-reversible cross-links, as the final material would be a sintered compressed powder [26].

First, 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 the buckling of the bars as a result of the sideways forces exerted by the DMTA machine sample holder. At elevated temperatures (starting from 132 °C for ratio 2:1 and 114 °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–c). This change is due to the DA–rDA equilibrium that shifts to favor the rDA reaction. This results in de-cross-linking in the polymer resin, which 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, whereas 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 cross-link 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].

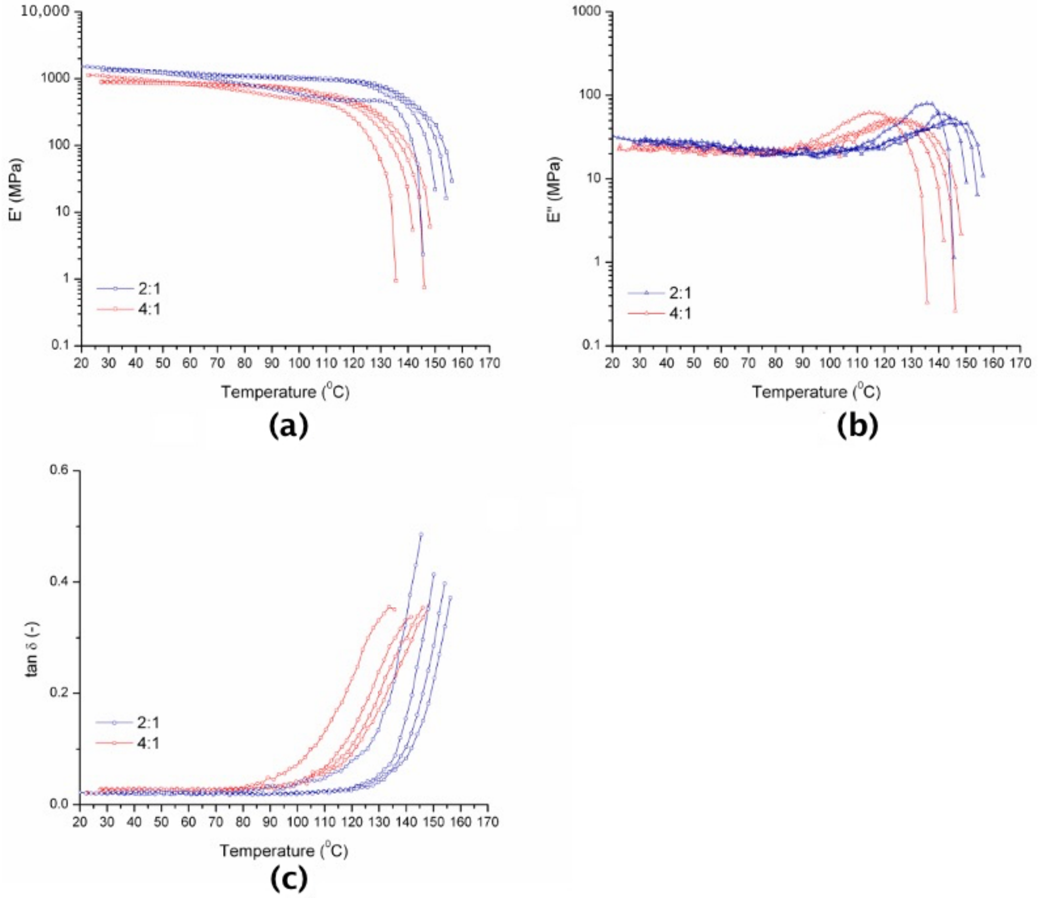


Figure 5. DMTA of various specimens of PE-fur/Bism (**a**) Storage modulus E′. (**b**) Loss modulus E″. (**c**) Damping factor tan δ. Only the heating steps are shown for clarity.

When comparing the mechanical properties for the different ratios of polyester/cross-linker, 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. A 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 cross-link density [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 °C and 136 °C for PE-fur/Bism-2:1 and -4:1, respectively. The softening points are determined from the points of the 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 °C and 136 °C for furan/bismaleimide mixtures with 2:1 and 4:1 molar ratios, respectively. Thus, it can be concluded that the addition of a chain stopper has had a negligible effect on the stability of the polymer network. It must be noted here that these softening temperatures are in overall agreement with the rDA ones determined by DSC (see the Supplementary Materials for a comparison). The slight differences might be due to the broadness of the DSC peaks but are also the result of more profound reasons. Although the DSC rDA temperatures refer to a molecular conversion of DA adducts into the corresponding precursors under static conditions, the DMTA-derived ones refer to a dynamic system in which the chains are mechanically stressed. In particular, during DMTA, the rupture of the first DA adducts allows translation and rotation to polymer segments. This might in turn favor the rupture of other DA adducts in a cooperative manner.

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 °C −160 °C −20 °C), an optical change in the appearance/shape of the bars was visible (Figure 6b); the test specimens 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 afterward. Since no antioxidants had been added, this color change may have been caused by the oxidation of the material. Analysis of the material by NMR and IR however, showed no (significant) formation of side products or any indication of degradation (see the Supplementary Materials for FT-IR and NMR spectra).

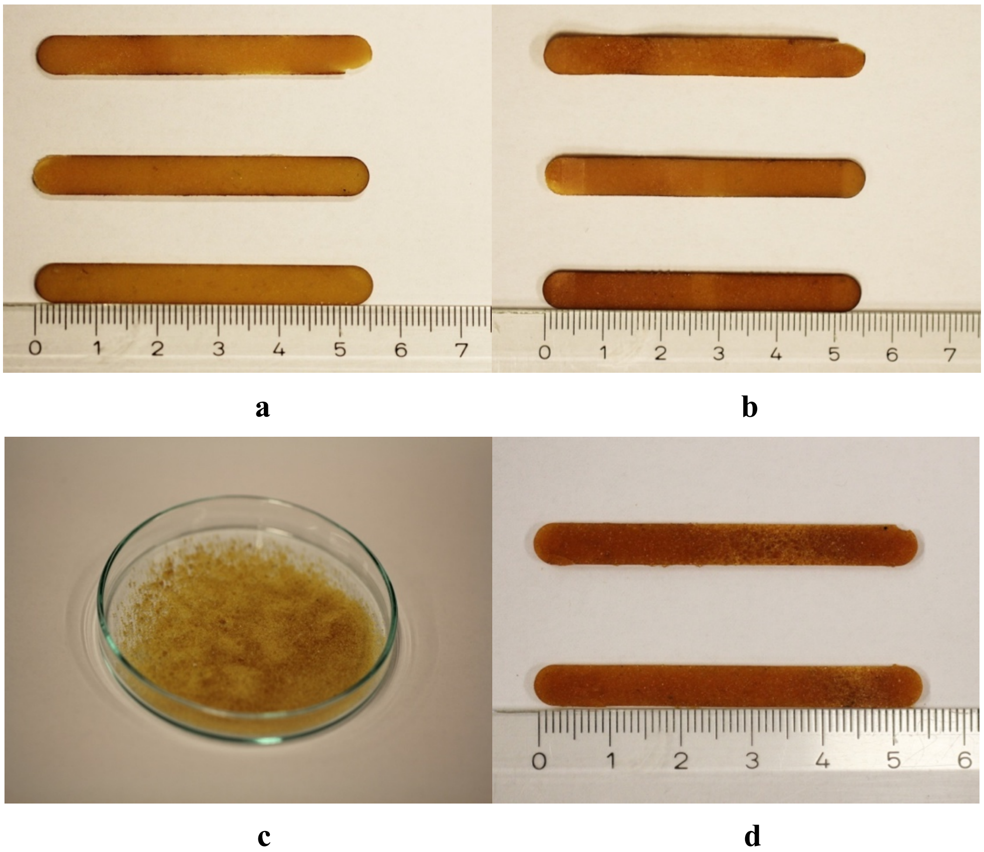


Figure 6. Bars prepared from PE-Fur/Bism (**a**) Hot-pressed PE-Fur/Bism bars. (**b**) PE-Fur/Bism bars after 4 DMTA cycles. (**c**) Reground PE-Fur/Bism bars after DMTA. (**d**) Recycled PE-Fur/Bism bars.

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 displayed an even darker brown color in comparison to the dark-yellow and light-brown colors seen in Figure 6a,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 in the storage and loss moduli is also visible during the first DMTA cycle of the recycled test bars due to the buckling of the test specimens (Figure 7), as a result of the sideways forces exerted by the DMTA machine sample holder.

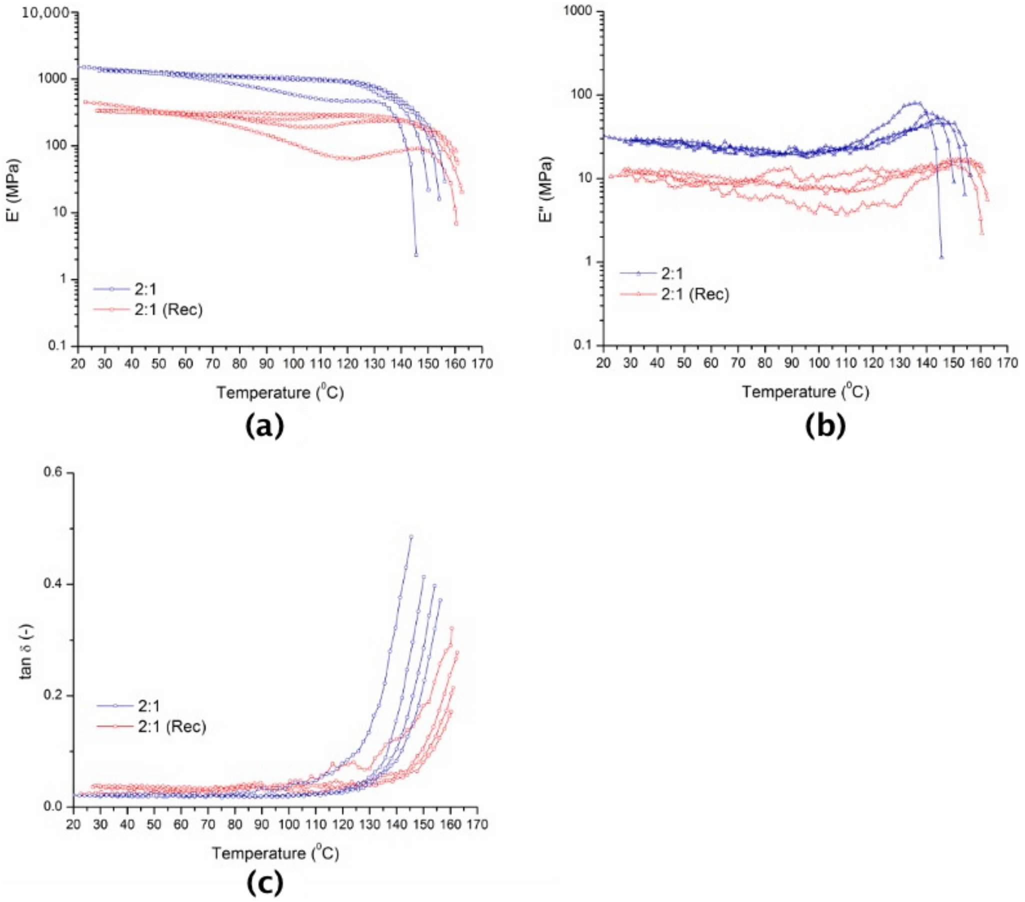


Figure 7. Dynamic Mechanical Thermal Analysis of recycled specimens of PE-fur/Bism (**a**) Storage modulus E′. (**b**) Loss modulus E″. (**c**) Damping factor tan δ.

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 proves that even after complete recycling, the mechanical properties are still equivalent.

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, it is fair to assume that the recycled polyester network possesses a relatively higher amount of thermally stable adducts. Again, this ultimately results in the 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 thermoreversible recyclable polymer.

4. 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 cross-linkers. This polyester possesses a lower glass transition temperature than the long-chain polyester described previously (i.e., 115 °C versus 125 °C), which results in improved processability.

The short-chain, furan-functionalized polyester has been reacted with bismaleimide, which acts as a cross-linking 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 cross-linker versus furans. A decrease in the softening point from 146 to 136 °C was observed upon halving the amount of bismaleimide. Thermoreversibility was shown by cyclic DSC measurements as the observed transitions during heating and cooling corresponding 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 show that initially, the *endo* adduct is favored during room temperature cross-linking in solution. Subsequently exposing the solution to elevated temperatures (120 °C) shows the 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 °C to 160 °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 the accompanying decrease in mechanical properties at temperatures above 110 °C apart from a minor shift in the softening point due to the aforementioned *endo-exo* isomerism. When changing the molar ratio of furan: maleimide from 1:1 to 2:1, a decrease in the softening point is seen (from 146 °C to 136 °C) as well as a decrease in the storage modulus, indicating a less densely cross-linked network with poorer mechanical properties for lower amounts of cross-linkers. This is supported by the fact that proper test specimens for the furan: maleimide ratio at 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 the virgin as well as recycled polymeric material during multiple thermal cycles indicates 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.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12147287/s1.

Author Contributions: Conceptualization, F.P. and A.A.B.; methodology, M.B.; validation, M.B. and A.J.K. formal analysis, F.P.; investigation, M.B.; resources, H.J.H. and F.P.; data curation, M.B. writing—original draft preparation, M.B. and A.J.K.; writing—review and editing, F.P.; visualization, M.B.; supervision, A.A.B., H.J.H. and F.P.; funding acquisition, H.J.H. and F.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Biobased Performance Material (BPM) research program, grant number BPM 052.

Data Availability Statement: Data are available via the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Beljaars, M.; Heeres, H.J.; Mevius, L.; Broekhuis, A.A.; Picchioni, F. Bio-based aromatic polyesters reversibly crosslinked via Diels-Alder reaction. *Appl. Sci.* **2022**, *12*, 2461. [CrossRef]
2. Almanza, L.O.; Chanaga, Q.T.M.; Ramirez, S.I.B. Proceso para la Produccion de Propileno y Etileno a Partir de Etanol Empleando un Catalizador Zeolitico. PCT Patent WO2012085690A1, 28 June 2012.
3. Beauprez, J.J.; de Mey, M.; Soetaert, W.K. Microbial succinic acid production: Natural versus metabolic engineered producers. *Process Biochem.* **2010**, *45*, 1103. [CrossRef]
4. Belgacem, M.N.; Gandini, A. (Eds.) *Monomers, Polymers and Composites from Renewable Resources*; Elsevier: Amsterdam, The Netherlands, 2008.
5. Mittal, M.; Sharma, C.B. Studies on Lignin-Based Adhesives for Plywood Panels. *Polym. Int.* **1992**, *29*, 7–8. [CrossRef]
6. Zhang, Y.; Broekhuis, A.A.; Picchioni, F. Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers? *Macromolecules* **2009**, *42*, 1906–1912. [CrossRef]
7. Toncelli, C.; Reus, D.D.; Broekhuis, A.; Picchioni, F. *Thermoreversibility in Polymeric Systems*; CRC Press: Boca Raton, FL, USA, 2011; pp. 199–248.
8. Kloxin, C.J.; Bowman, C.N. Covalent adaptable networks: Smart, reconfigurable and responsive network systems. *Chem. Soc. Rev.* **2013**, *42*, 7161–7173. [CrossRef]
9. Scheltjens, G.; Brancart, J.; Graeve, I.; Mele, B.; Terryn, H.; Assche, G. Self-healing property characterization of reversible thermoset coatings. *J. Therm. Anal. Calorim.* **2011**, *105*, 805–809. [CrossRef]
10. Hansen, W.; Christopher, M.; Verbuecheln, M. Available online: http://www.arctic-transform.eu/files/projects/2013/1921-1922_background_paper_waste_en.PDF (accessed on 1 July 2016).
11. Gujral, S.S.; Popli, A. Introduction to Diels Alder Reaction, Its Mechanism and Recent Advantages: A Review. *Indo Am. J. Pharm. Res.* **2013**, *3*, 1–24.
12. Brieger, G.; Bennett, J.N. The Intramolecular Diels-Alder Reaction. *Chem. Rev.* **1980**, *80*, 63–97. [CrossRef]
13. Martin, J.G.; Hill, R.K. Stereochemistry of the Diels-Alder Reaction. *Chem. Rev.* **1961**, *61*, 537–562. [CrossRef]
14. Zhang, M.; Rong, M. Design and synthesis of self-healing polymers. *Sci. China Chem.* **2012**, *55*, 648–676. [CrossRef]
15. Craven, J.M. Cross-Linked Thermally Reversible Polymers Produced from Condensation Polymers with Pendant Furan Groups Cross-Linked with Maleimides. U.S. Patent 3,435,003, 25 March 1969.
16. Domingo, L.R.; Aurell, M.J.; Pérez, P.; Contreras, R. Quantitative characterization of the global electrophilicity power of common diene/dienophile pairs in Diels–Alder reactions. *Tetrahedron* **2002**, *58*, 4417–4423. [CrossRef]
17. Gheneim, R.; Perez-Berumen, C.; Gandini, A. Diels-Alder reactions with novel polymeric dienes and dienophiles: Synthesis of reversibly cross-linked elastomers. *Macromolecules* **2002**, *35*, 7246–7253. [CrossRef]
18. Araya-Hermosilla, R.; Fortunato, G.; Pucci, A.; Raffa, P.; Polgar, L.; Broekhuis, A.A.; Pourhossein, P.; Lima, G.M.R.; Beljaars, M.; Picchioni, F. Thermally reversible rubber-toughened thermoset networks via Diels–Alder chemistry. *Eur. Polym. J.* **2016**, *74*, 229–240. [CrossRef]
19. Gaina, C.; Ursache, O.; Gaina, V.; Buruiana, E.; Ionita, D. Investigation on the thermal properties of new thermo-reversible networks based on poly (vinyl furfural) and multifunctional maleimide compounds. *Express Polym. Lett.* **2012**, *6*, 129–141. [CrossRef]
20. Chen, X.; Dam, M.A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S.R.; Sheran, K.; Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science* **2002**, *295*, 1698–1702. [CrossRef]
21. Tian, Q.; Yuan, Y.C.; Rong, M.Z.; Zhang, M.Q. A thermally remendable epoxy resin. *J. Mater. Chem.* **2009**, *19*, 1289–1296. [CrossRef]
22. Liu, Y.; Hsieh, C. Crosslinked epoxy materials exhibiting thermal remendablility and removability from multifunctional maleimide and furan compounds. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 905–913. [CrossRef]
23. Tian, Q.; Rong, M.Z.; Zhang, M.Q.; Yuan, Y.C. Synthesis and characterization of epoxy with improved thermal remendability based on Diels-Alder reaction. *Polym. Int.* **2010**, *59*, 1339–1345. [CrossRef]
24. Palmese, G.R.; Petersen, A.M.; Jensen, R.E. *Remendable Polymeric Materials Using Reversible Covalent Bonds*; Drexel University: Philadelphia, PA, USA, 2008.
25. Peterson, A.M.; Jensen, R.E.; Palmese, G.R. Room-temperature healing of a thermosetting polymer using the Diels−Alder reaction. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1141–1149. [CrossRef]
26. Toncelli, C.; de Reus, D.C.; Picchioni, F.; Broekhuis, A.A. Properties of Reversible Diels–Alder Furan/Maleimide Polymer Networks as Function of Crosslink Density. *Macromol. Chem. Phys.* **2012**, *213*, 157–165. [CrossRef]
27. Gotsmann, B.; Duerig, U.; Frommer, J.; Hawker, C.J. Exploiting chemical switching in a Diels–Alder polymer for nanoscale probe lithography and data storage. *Adv. Funct. Mater.* **2006**, *16*, 1499–1505. [CrossRef]
28. Mcelhanon, J.R.; Russick, E.M.; Wheeler, D.R.; Loy, D.A.; Aubert, J.H. Removable foams based on an epoxy resin incorporating reversible Diels–Alder adducts. *J. Appl. Polym. Sci.* **2002**, *85*, 1496–1502. [CrossRef]
29. Peterson, A.M.; Jensen, R.E.; Palmese, G.R. Thermoreversible and remendable glass–polymer interface for fiber-reinforced composites. *Compos. Sci. Technol.* **2011**, *71*, 586–592. [CrossRef]
30. Adzima, B.J.; Aguirre, H.A.; Kloxin, C.J.; Scott, T.F.; Bowman, C.N. Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels−Alder Polymer Network. *Macromolecules* **2008**, *41*, 9112–9117. [CrossRef] [PubMed]

31. Aubert, J.H. Note: Thermally removable epoxy adhesives incorporating thermally reversible diels-alder adducts. *J. Adhes.* **2003**, *79*, 609–616. [CrossRef]
32. Hayes, D.J.; Fitzpatrick, S.; Hayes, M.H.; Ross, J.R. The Biofine Process: Production of levulinic acid. furfural and formic acid from lignocellulosic feedstocks. *Biorefineries* **2006**, *1*, 139–164.
33. Ben-Jonathan, N.; Steinmetz, R. Xenoestrogens: The emerging story of bisphenol A. *Trends Endocrinol. Metab.* **1998**, *9*, 124–128. [CrossRef]
34. Yadav, G.; Kirthivasan, N. Synthesis of bisphenol-A: Comparison of efficacy of ion exchange resin catalysts vis-à-vis heteropolyacid supported on clay and kinetic modelling. *Appl. Catal. A Gen.* **1997**, *154*, 29–53. [CrossRef]
35. Teramoto, N.; Arai, Y.; Shibata, M. Thermo-reversible Diels–Alder polymerization of difurfurylidene trehalose and bismaleimides. *Carbohydr. Polym.* **2006**, *64*, 78–84. [CrossRef]
36. Wang, M.; Xu, C.; Leitch, M. Liquefaction of cornstalk in hot-compressed phenol-water medium to phenolic feedstock for the synthesis of phenol-formaldehyde resin. *Bioresour. Technol.* **2009**, *100*, 2305–2307. [CrossRef]
37. Cheng, S.; Yuan, Z.; Anderson, M.; Leitch, M.; Xu, C. Synthesis of biobased phenolic resins/adhesives with methylolated wood-derived bio-oil. *J. Appl. Polym. Sci.* **2012**, *126*, E431–E441. [CrossRef]
38. Kricheldorf, H.R.; Böhme, S.; Schwarz, G.; Schultz, C. Cyclic polycarbonates by polycondensation of bisphenol A with triphosgene. *Macromolecules* **2004**, *37*, 1742–1748. [CrossRef]
39. Kricheldorf, H.R.; Böhme, S.; Schwarz, G.; Schultz, C. Syntheses of cyclic polycarbonates by the direct phosgenation of bisphenol M. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 1248–1254. [CrossRef]
40. Kricheldorf, H.R.; Schwarz, G.; Böhme, S.; Schultz, C.; Wehrmann, R. Macrocycles, 22. *Macromol. Chem. Phys.* **2003**, *204*, 1398–1405. [CrossRef]
41. Caroselli, C.D.; Pramanik, M.; Achord, B.C.; Rawlins, J.W. Molecular weight effects on the mechanical properties of novel epoxy thermoplastics. *High Perform. Polym.* **2012**, *24*, 161–172. [CrossRef]
42. Marref, M.; Mignard, N.; Jegat, C.; Taha, M.; Belbachir, M.; Meghabar, R. Epoxy-amine based thermoresponsive networks designed by Diels–Alder reactions. *Polym. Int.* **2013**, *62*, 87–98. [CrossRef]
43. Tian, Q.; Rong, M.Z.; Zhang, M.Q.; Yuan, Y.C. Optimization of thermal remendability of epoxy via blending. *Polymer* **2010**, *51*, 1779–1785. [CrossRef]
44. Kavitha, A.A.; Singha, N.K. "Click Chemistry" in Tailor-Made Polymethacrylates Bearing Reactive Furfuryl Functionality: A New Class of Self-Healing Polymeric Material. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1427–1436. [CrossRef]
45. Peterson, A.M.; Palmese, G.R. Reversible Diels–Alder Cycloaddition for the Design of Multifunctional Network Polymers. In *Click Chemistry for Biotechnology and Materials Science*; Wiley: Hoboken, NJ, USA, 2009; pp. 195–215.
46. Jegat, C.; Mignard, N. Effect of the polymer matrix on the thermal behaviour of a furan-maleimide type adduct in the molten state. *Polym. Bull.* **2008**, *60*, 799–808. [CrossRef]
47. Goussé, C.; Gandini, A. Diels-Alder polymerization of difurans with bismaleimides. *Polym. Int.* **1999**, *48*, 723–731. [CrossRef]
48. Rulíšek, L.; Šebek, P.; Havlas, Z.; Hrabal, R.; Čapek, P.; Svatoš, A. An experimental and theoretical study of stereoselectivity of furan-maleic anhydride and furan-maleimide Diels-Alder reactions. *J. Org. Chem.* **2005**, *70*, 6295–6302. [CrossRef] [PubMed]
49. Watanabe, M.; Yoshie, N. Synthesis and properties of readily recyclable polymers from bisfuranic terminated poly (ethylene adipate) and multi-maleimide linkers. *Polymer* **2006**, *47*, 4946–4952. [CrossRef]
50. Goussé, C.; Gandini, A.; Hodge, P. Application of the Diels-Alder reaction to polymers bearing furan moieties. 2. Diels-Alder and retro-Diels-Alder reactions involving furan rings in some styrene copolymers. *Macromolecules* **1998**, *31*, 314–321. [CrossRef]
51. Canadell, J.; Fischer, H.; van Benthem, R.A. Stereoisomeric effects in thermo-remendable polymer networks based on Diels–Alder crosslink reactions. *J. Polym. Sci. Part A Polym. Chem.* **2010**, *48*, 3456–3467. [CrossRef]
52. Gandini, A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, *38*, 1–29. [CrossRef]
53. Xu, Z.; Zhao, Y.; Wang, X.; Lin, T. A thermally healable polyhedral oligomeric silsesquioxane (POSS) nanocomposite based on Diels-Alder chemistry. *Chem. Commun.* **2013**, *49*, 6755–6757. [CrossRef]
54. Brancart, J.; Scheltjes, G.; Diaz, M.; van Mele, B.; van Assche, G. Studying the healing behavior at a microscopic scale. In Proceedings of the 4th International Conference on Self-Healing Materials, Ghent, Belgium, 16–20 June 2013.
55. Yu, F.; Cao, X.; Zeng, L.; Zhang, Q.; Chen, X. An Interpenetrating HA/G/CS BiomimicHydrogel via Diels-Alder Click Chemistry for Cartilage Tissue Engineering. *Carbohydr. Polym.* **2013**, *97*, 188–195. [CrossRef]
56. Nimmo, C.M.; Owen, S.C.; Shoichet, M.S. Diels−Alder Click Cross-Linked Hyaluronic Acid Hydrogels for Tissue Engineering. *Biomacromolecules* **2011**, *12*, 824–830. [CrossRef]