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## Biobased, thermoreversibly crosslinked polyesters

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## Chapter 5

The influence of amount and type of crosslinker on thermal and mechanical properties of a thermoreversibly crosslinked biobased polyester

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## 5.1 Abstract

In an attempt to gain greater control over the product mechanical properties, a partially biobased, aromatic polyester capable of thermoreversible crosslinking via Diels-Alder chemistry is crosslinked using different types and amounts of crosslinker. The thermal and mechanical properties are analyzed by DSC and DMTA measurements, respectively. Three different bismaleimides were tested, all containing a different spacer, each in three different furan:maleimide ratios. Rather than the expected trend where lowering the crosslinker amount would lead to a reduction in the softening point a different behavior is observed where the softening point first increases and then decreases with decreasing amounts of crosslinker, displaying thus an optimum. This would imply that the ideal ratio of furans to maleimides in order to obtain the highest crosslinking degree (implied by the softening temperature) is not unity; rather a system starved in maleimides seems preferred.

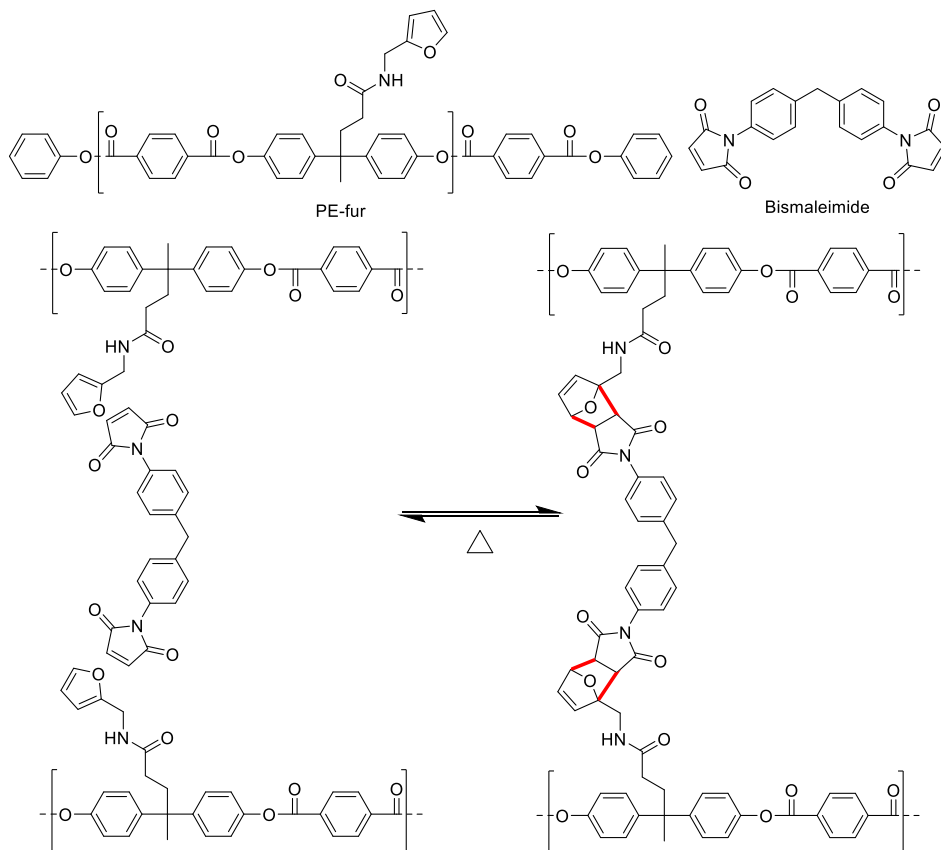
## 5.2 Introduction

The virtues of thermoreversible crosslinking of polymeric materials are well established by now<sup>1-5</sup>, in particular the possibility for *cradle-to-cradle* recycling<sup>6,7</sup>. In particular systems based on employing Diels-Alder chemistry have received much well-deserved attention<sup>8-11</sup>: many publications describe its successful incorporation into various systems of vastly differing origin and properties and act as a testimony to its versatility and ease-of application. The Diels Alder reaction is a 2-component addition reaction between a diene and a dienophile, the furan (FUR) and maleimide (MAL) pair being often used for its convenient temperature range between the Diels-Alder coupling (DA) and retro Diels-Alder (rDA) decoupling reactions. In most cases a polymer is modified to contain only one of these two functionalities; in FUR/MAL systems usually the furan group is incorporated in the polymer. This approach ensures that the base polymer matrix does not undergo unwanted self-crosslinking reactions, making it easier to process. Crosslinking is initiated by the addition of a separate di- or multifunctional maleimide moiety. The reversible nature of this crosslink allows for superior properties of the material during application<sup>12</sup> (i.e. in the crosslinked state) while simultaneously enabling re-processability at elevated temperatures<sup>9,13</sup> (i.e. in the decoupled state). However, this possibility does not

entail *per se* a solution to the underlying problem of depleting raw materials sources (i.e. oil) as, also in the case of *cradle-to-cradle* recyclable materials, dependence on petroleum resources might still be present, even if only to a lesser extent. To counteract this drawback, the use of biobased polymers might represent a convenient approach, provided that the possibility of recycling is retained. Previously, we described the synthesis of a highly aromatic and biobased furan-functionalized polyester<sup>14</sup> which, after modification by a chain stopper, could be thermoreversibly crosslinked by addition of bismaleimide<sup>15</sup> (see Scheme 1). This yields a thermoset-like material with excellent thermal reversibility, recyclability and re-processability. The application of a chain stopper allowed control over the properties of the uncrosslinked polymer by reducing its molecular weight and subsequently the  $T_g$  of the material before crosslinking. In the same work, the effect of the furan to maleimide ratio (in turn responsible for different crosslinking densities) was also explored. Indeed, a change in  $T_g$  of about 10°C was observed when halving the amount of crosslinker with respect to its stoichiometric amount. This preliminary result showed that the properties of the crosslinked material could be influenced as well by simple tuning of the intake of crosslinking agent. In order to achieve even greater control over the properties of the resulting material, this trend should be explored in greater detail. Besides the crosslinker intake, also the type of crosslinker (i.e. its chemical structure) employed can be used to influence the resulting material properties. Even though the chemistry of the systems remains mostly unaffected (i.e. the functional groups are still maleimides and furans), the use of different spacers between the two maleimide groups could also result in a relevant influence on the final material properties. This hypothesis is supported by a recent study investigating the effect of the spacer present in the bismaleimide crosslinker<sup>16</sup> on mechanical properties of a thermally reversible rubber network. A significant effect in mechanical properties was observed when altering the furan to maleimide ratio. Furthermore a noted difference in crosslink density and resulting mechanical properties was observed when changing the crosslinker chemical structure, namely by altering the spacer between the maleimide groups. However, due to the fact that the base material used in this study is an elastomer, and the degree of functionalization (and therefore also the degree of crosslinking) is low even at the highest furan to maleimide ratio (typically in the order of  $10^{-5}$  mol/gram), direct comparisons with

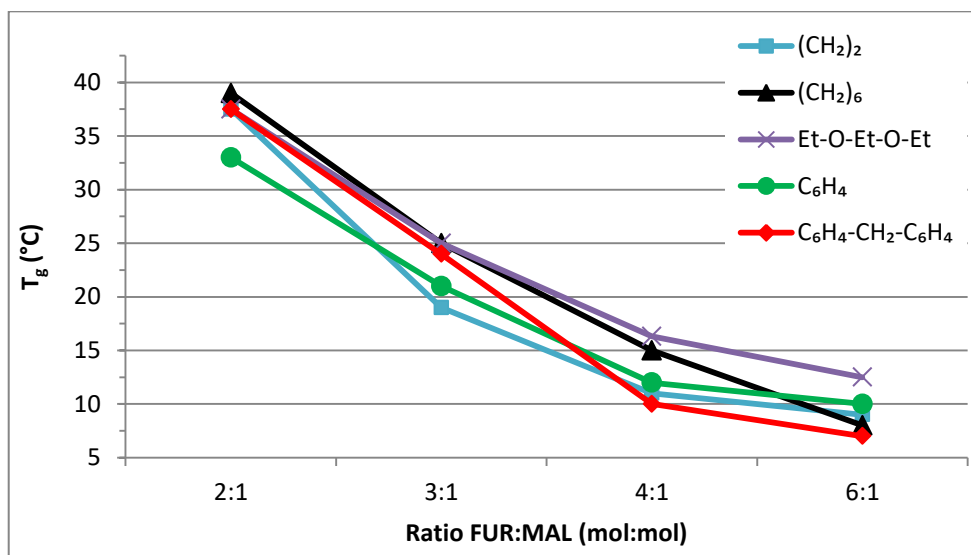
the highly functionalized polyester would be rather speculative. On the other hand, Zeng *et al*<sup>17</sup> also report significant changes in material properties by altering

**Scheme 1: Diels-Alder coupling between PE-fur and bismaleimide**



the type and amount of crosslinker employed. Indeed, for the polymer employed (a polyester of bis(hydroxymethyl)furan and succinic acid) a change in softening temperature of about 5 degrees is observed when changing the type of crosslinker spacer from  $-(\text{CH}_2)_6-$  to  $-(\text{C}_6\text{H}_4)-$ . Interestingly, the effect of the type of spacer on  $T_g$  differs for each ratio (see Figure 1): at FUR:MAL ratio 2:1 the  $-(\text{CH}_2)_6-$  spacer displays the highest  $T_g$ , and the  $-(\text{C}_6\text{H}_4)-$  spacer the lowest, while at FUR:MAL ratio 6:1 the  $T_g$  of the  $-(\text{CH}_2)_6-$  is actually lower than that of the  $-(\text{C}_6\text{H}_4)-$ , furthermore the spacers giving both the highest and lowest  $T_g$  at this ratio display identical  $T_g$  at FUR:MAL ratio 2:1. This clearly demonstrates that various factors, often in a synergic manner, display a relevant influence on the final properties of

the material. The main properties of the spacer are its rigidity and length: a longer and/or more flexible spacer should yield a less rigid material. This should be visible in the moduli of the crosslinked material. However, another influencing factor is the miscibility of the compounds: when the crosslinker is poorly miscible with the polymer matrix, its mobility throughout the material will be limited leading to less effective crosslinks. This can lead to lower softening temperatures, differing moduli or, in extreme cases, an inability to form a homogeneously crosslinked material altogether.



**Figure 1: softening temperatures of poly-bis(hydroxymethyl)furan/succinic acid networks containing different crosslinker spacers in different ratios**

The aim of this work is determine the effect of systematically changing both the furane to maleimide ratio and the spacer present in the bismaleimide on thermal and mechanical properties of the resulting polymer network. In order to assess this, mixtures consisting of the aforementioned polymer (PE-fur, see Scheme 1) and various amounts of different bismaleimides have been prepared and analyzed. Aromatic and aliphatic bismaleimides are used to elucidate the effect of miscibility with the highly aromatic base-polymer on mechanical properties.

## 5.3 Experimental section

### 5.3.1 Materials and equipment:

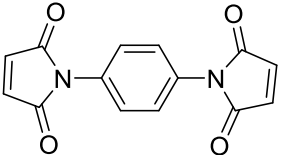
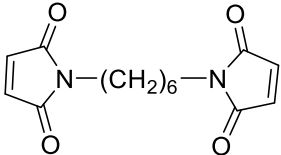
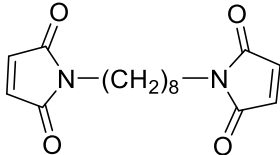
THF and *N,N'*-(1,4-Phenylene)dimaldimide were obtained from Sigma-Aldrich and used as received. *N,N'*- hexamethylene dimaleimide and *N,N'*- octamethylene dimaleimide were prepared according to the procedure described in literature<sup>14</sup>. PE-fur was synthesized according to the procedure described previously<sup>15</sup>.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer differential scanning calorimeter Pyris 1 under N<sub>2</sub> atmosphere. Before DSC's the sample was weighed (ca. 12 mg) and subsequently heated from 25 °C to 180 °C. Multiple cycles were performed at a heating rate of 10°C/min throughout the measurements. DMTA measurements were performed using a Rheometrics scientific solid analyzer (RSA II) under air using dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 5 °C/min.

### 5.3.2 Preparation:

All samples were prepared according to the following procedure:

A round bottom flask was charged with 5 gram polymer (PE-fur) and 50 ml THF. The mixture was stirred at ambient temperature until all the polymer had dissolved, after which the required amount of crosslinker was added (e.g. 1.04 grams for the C6 1:1 sample) while still stirring. When a clear solution was obtained, most of the THF was removed by airflow at ambient temperatures, the resulting gel was dried in a vacuum oven for 4 hours at 50°C yielding a yellow solid. As previously established THF removal is incomplete while following this procedure<sup>18</sup> so subsequently this solid was frozen with liquid nitrogen, ground to fine particles using an Ika industrial grinder and placed in the vacuum oven once more at 140°C overnight. This gives the final material in quantitative yields. A summary of all formulations prepared is given in Table 1

								
<b>Benz 1:1</b>	<b>Benz 2:1</b>	<b>Benz 4:1</b>	<b>C6 1:1</b>	<b>C6 2:1</b>	<b>C6 4:1</b>	<b>C8 1:1</b>	<b>C8 2:1</b>	<b>C8 4:1</b>

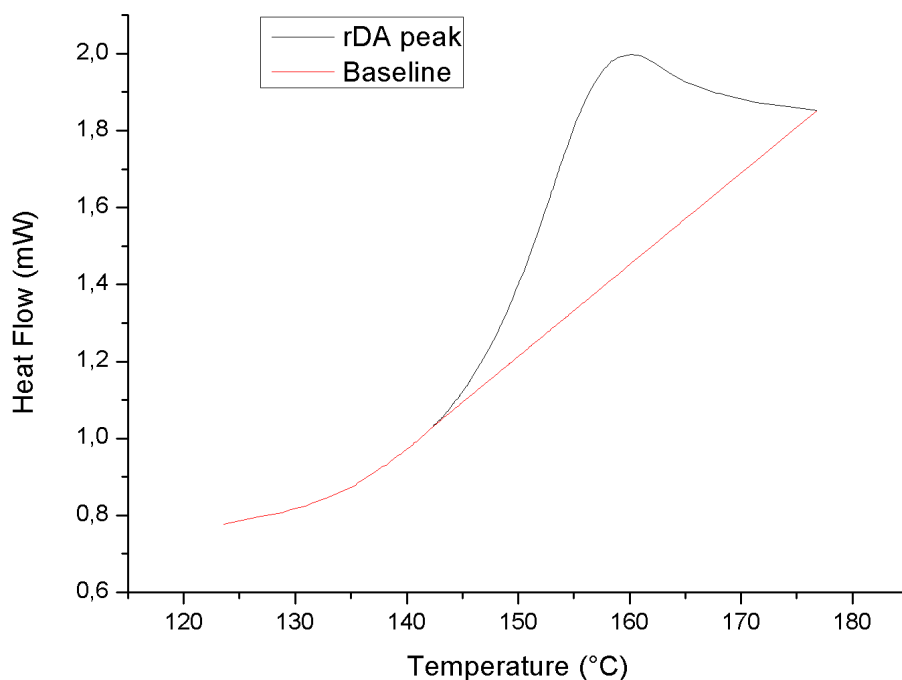
**Table 1: Overview of all formulations tested in this work, samples are identified by spacer group and FUR:MAL ratio (mol:mol)**

### 5.3.3 Analysis

In order to obtain the rDA enthalpy, DSC results were interpreted as follows: first a straight baseline was defined. This was done by choosing the outer limits of the peak in such a way that a straight line between these points gave the largest peak area without crossing the graph (see Figure 2 for an example). This baseline was then subtracted from the graph, after which the local maximum was determined which was defined as the softening temperature. Finally the integral of the obtained peak was obtained (Table 2 and Figure 5).

DMTA samples were prepared by placing approx. 0.5 grams of material in a mold, which is placed in a press and heated to 180°C before applying 100 bars of pressure to it for 30 minutes. Afterwards the sample was allowed to slowly cool to ambient temperature inside the press. The softening point obtained via this measurement is defined at the initial point of decrease of the modulus.

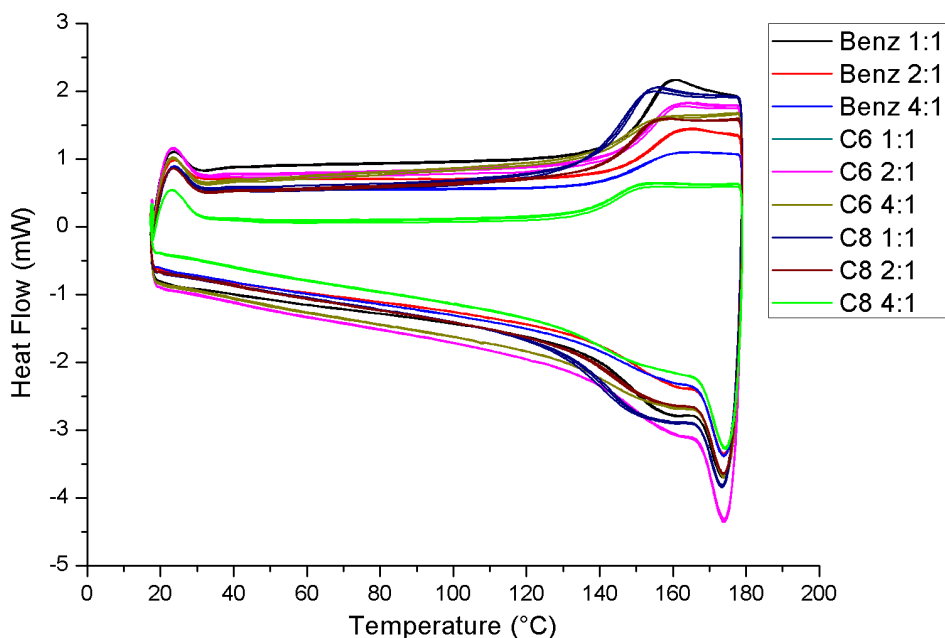




**Figure 2: Example of baseline definition**

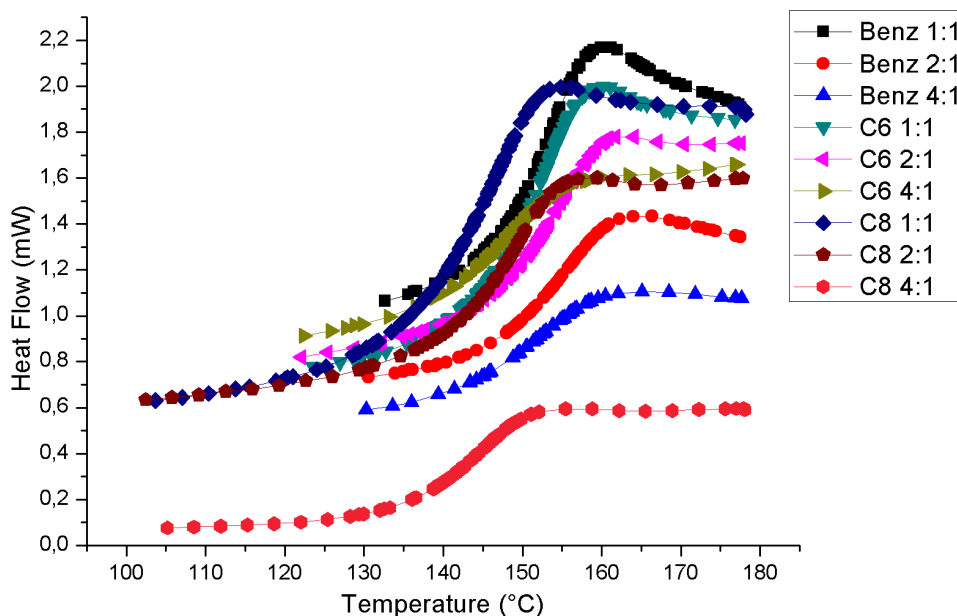
## 5.4 Results and discussion

Using the procedure described 9 compounds were successfully synthesized, each containing one of three different crosslinkers and one of three different ratios of maleimide to furan groups present (see Table 1). The difference between the crosslinkers lies in the chemical composition of the spacer. As the procedure consisted of blending followed by solvent removal all yields are stoichiometric. IR analysis of the formulations in order to assess the degree of crosslinking proved impossible due to peak overlap with background signal. Therefore analysis was based on the thermal and mechanical properties. First the thermal behavior of all prepared samples was analyzed by DSC (see experimental part) on consecutive heating/cooling cycles from ambient temperature to 180°C (Figure 3).



**Figure 3: Cyclical DSC measurements for all prepared samples**

The first observation that can be made is the overlap of all cycles (i.e. comparing thermograms of the same sample upon different heating/cooling cycles): this means that the thermal properties do not change over the course of heating and cooling. The next observation is that all samples display a peak around 150°C. This peak is attributed to the rDA reaction<sup>14</sup>. The fact that these peaks are present in each heating step indicates that all samples undergo the rDA reaction during heating. The corresponding peaks in the cooling steps also confirm the (re)occurring of Diels Alder upon cooling. It is worthwhile to stress that the rDA peak shifts depending on the kind and amount of crosslinker. In order to elucidate this more clearly (Figure 4), further analysis was carried out.



**Figure 4: DSC 2<sup>nd</sup> heating cycles of all materials.**

The exact rDA temperature and enthalpies of all samples were determined (see experimental part for the procedure) and are summarized in Table 2 and Figure 5. As the value obtained directly from DSC corresponds to the enthalpy per gram, a normalization was applied to obtain the enthalpy per mole bismaleimide present.

Crosslinker	Benz			C <sub>6</sub>			C <sub>8</sub>			
	FUR:MAL Ratio (mol:mol)	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
Temperature (°C)		159	162	159	158	160	156	152	155	152
$\Delta H_{rDA}$ per gram		9.9	5.0	3.8	9.1	5.8	5.0	12.6	7.0	5.0
$\Delta H_{rDA}$ per mole bismaleimide		15.9	14.7	21.3	14.6	17.1	28.0	20.6	20.8	28.2

**Table 2: Softening temperatures and enthalpies from DSC**

On initial inspection it appears that the rDA enthalpies follow the expected trend where halving the amount of crosslinker present leads to halving (roughly and within the experimental error of the measurement) of the area of the rDA peak. This behavior is expected as the area of the rDA peak is correlated to the extent of

the rDA reaction. Sample C6 4:1 breaks this trend, but this is likely due to the analysis method: the proximity of the endotherm to the baseline result in higher relative error for the area.

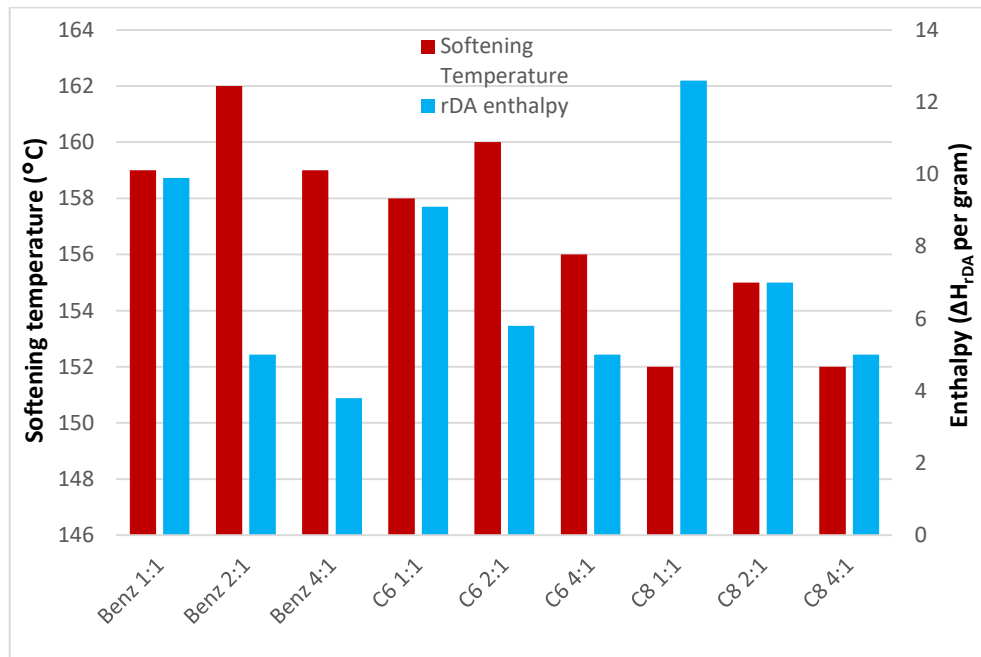


Figure 5: Softening temperature and rDA enthalpy for all samples

Interestingly, it appears that both the type of spacer as well as the ratio of maleimides to furans have an effect on the rDA temperature. As far as the ratios are concerned, a trend is observed where the samples with ratio 1:1 and 1:4 have a comparable rDA temperature while for the sample with a ratio of 1:2 this shifts to several degrees higher. It would seem that the network formed plays a role in the rDA temperature: at the 1:1 FUR:MAL ratio the sample seems to be oversaturated, meaning that many bismaleimides are only bound with a single maleimide group. Once this single maleimide undergoes rDA decoupling it is no longer part of the network, and can move around freely. The 1:2 FUR:MAL samples likely consist of a (tight) network where most, if not all, bismaleimides are bound with both maleimide groups, when the first maleimide group undergoes rDA decoupling, it is kept in place by the remaining polymer matrix, which still consists of highly crosslinked material. This lack of mobility increases

the local concentration of maleimide and furans leading to a more stable DA adduct. In the case of the 1:4 FUR:MAL ratio it seems that the residual polymer matrix obtained after breaking the first DA couple is not rigid enough to hamper the mobility and the resulting softening temperature is similar to the 1:1 ratio. This explanation is supported by the normalized enthalpy values: the enthalpy per mole of bismaleimide increases significantly over the range of ratios examined with the 1:4 samples yielding the highest values. This value represents the energy consumed per mole of bismaleimide present, which means it can serve as an indication of crosslinking effectiveness: a lower value would indicate that on average more maleimide groups are not participating in Diels-Alder coupling (*e.g.* do not require energy to decouple). The samples with the lowest amount of bismaleimide present (1:4) display the highest rDA enthalpy per mole, which is therefore indicative of the highest degree of DA coupling. The fact that the 1:2 sample displays a lower normalized enthalpy (*i.e.* enthalpy per mole) indicates that not each maleimide present is participating in DA adduct formation, leading to singular adducts of bismaleimide. These singularly bound bismaleimides will undergo rDA decoupling first leaving a rigid polymer network (*vide supra*). Finally, the 1:1 sample displays an even lower normalized enthalpy, which in turn implies that most bismaleimide molecules are only bound via DA adducts with a single maleimide group. There is no rigid network keeping these bismaleimides in place hence the softening temperature is lower.

It seems that the type of spacer also has an effect on the rDA temperature. This is somewhat surprising as the spacer is unable to participate in the reaction, *i.e.* the coupling occurs between the furan and maleimide, which are the same for all spacers. When comparing the spacers for each ratio, a trend is observed where the rDA temperature decreases steadily from benz to C6 with C8 giving the lowest values (Figure 6). A possible explanation for this behavior can be found in the compatibility of polymer matrix and crosslinker (bismaleimide). One would assume that due to the polymer being highly aromatic and the crosslinker quite aliphatic the miscibility of C6 and C8 in particular is quite poor. However, when looking at the solubility parameters of all chemicals (Table 3) it becomes clear that the C8 crosslinker is most miscible with the polymer due to the similarity of their solubility parameter ( $\delta$ ). Furthermore the high miscibility of the C8 spacer combined with the lowered rDA temperature suggests that decoupled maleimide

is free to move about the polymer driving the reaction to the decoupled products at lower temperature.

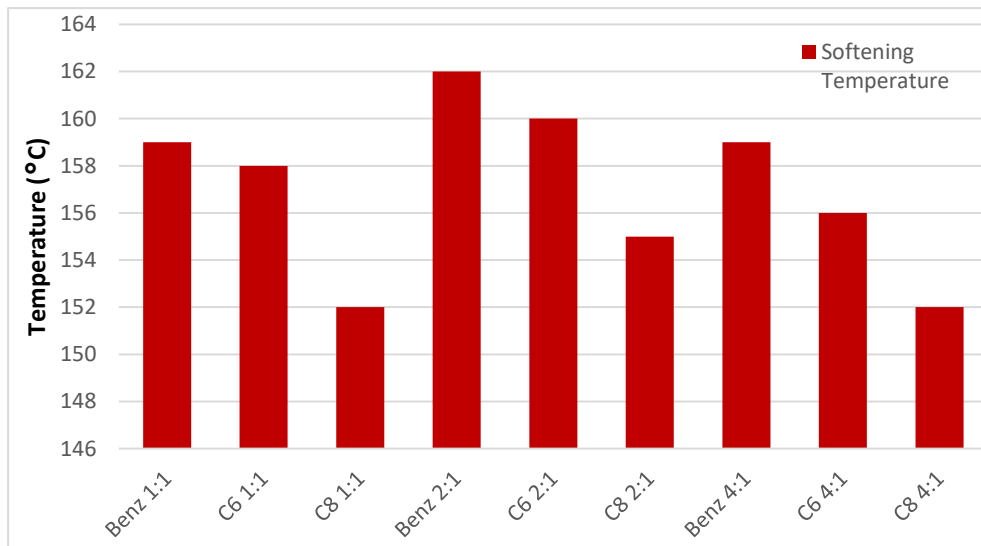


Figure 6: softening temperatures grouped per FUR:MAL ratio

This in turn suggests that the poor miscibility of the C8 and aromatic spacers are responsible for the higher rDA temperatures, and the more stable adduct.

	Solubility parameter (J/cm <sup>3</sup> ) <sup>2</sup>		Solubility parameter (J/cm <sup>3</sup> ) <sup>2</sup>
Polyester	11.4		12.6
	15.1		11.9

Table 3: solubility parameters of all chemicals involved<sup>19</sup>

## 5.5 Mechanical analysis (DMTA)

In order to gain further insight into the behavior of all samples, mechanical properties were determined by DMTA as well (Figure 7). Unfortunately it turned out to be impossible to isolate the pressed bars of sample benz 4:1 as these

turned out too brittle to remove from the mold intact, possibly due to the poor miscibility of the polymer and crosslinker. The first heating steps of all DMTA measurements are depicted in Figure 7. Upon closer inspection an interesting observation can be made: all samples (sample Benz 1:1 being a slight outlier) display basically the same modulus. Considering that identical moduli indicate identical crosslinking degrees<sup>20</sup>, this observation supports the hypothesis that the 1:1 samples are oversaturated. However, the 2:1 and 4:1 samples displaying the same modulus, challenges this statement as this would indicate that also the 2:1 samples are oversaturated or are otherwise forming inefficient crosslinks. However, as these measurements are performed on the bulk of the material, their nature makes it impossible to draw conclusions on a molecular level. While the first bond breakage can be detected with DSC as the start of a peak, DMTA only gives an outcome when enough bonds have broken to have a significant influence on the material properties.

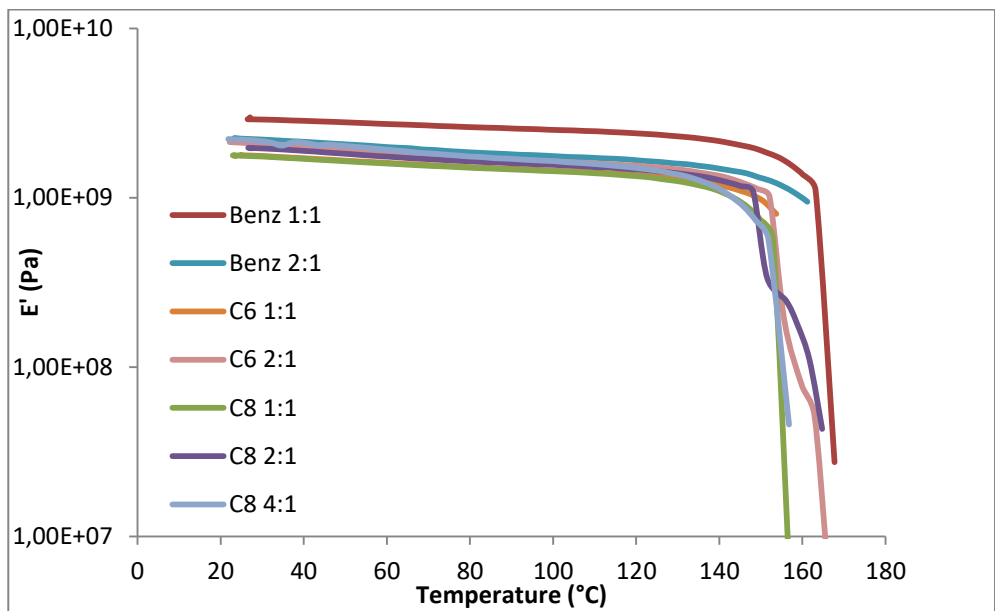


Figure 7: DMTA results of all samples measured, only E' values for the first cycles are shown

The softening temperature has been determined from these DMTA results. It is defined as the steep decrease in modulus which occurs around 150°C. The values obtained thusly are given in Table 4.

	Softening point (°C)		Softening point (°C)		Softening point (°C)
Benz 1:1	160	C6 1:1	154	C8 1:1	153
Benz 2:1	161	C6 2:1	152	C8 2:1	148
				C8 4:1	152

**Table 4: softening points obtained from DMTA results**

The first thing to notice is the fact that some samples (C6 2:1 and C8 2:1 in particular) display a two-step softening. This further supports the hypothesis that the resulting polymer matrix is able to support DA formation by keeping both groups in close proximity. A possible explanation for this phenomenon could be that the first step corresponds to the opening of only part of the bonds, leaving a material which still possesses a relatively strong network, and thus a relatively high modulus. When the softening temperatures are compared to the DSC results the trend where the 2:1 samples display a softening temperature several degrees higher seems no longer present due to their two-step softening profile. However, if the softening point is defined differently, namely as the final point measurable, the trend persists.

After the first heating cycle all samples were cooled while still in the device and measured again, these cycles were repeated twice more. Looking from the 2<sup>nd</sup> heating cycles onwards some differences begin to appear: the moduli of different ratios start to diverge, however as they become more erratic comparing the samples becomes difficult. For the aromatic spacer a small decrease in modulus is observed by halving the amount of crosslinker present. As the second cycle constitutes the re-crosslinked material it makes sense that the sample with more crosslinker present is able to form a material with a higher modulus and thus a higher crosslinking density. The material displays a consistent softening point for all heating cycles, indicating thermoreversible crosslinking capabilities with no side reactions. For the C6 spacer, the data for the second cycle onwards is even more erratic and the modulus fluctuates greatly during the measurement. As stated, these measurements are on recrosslinked materials. Therefore it is likely that the poor miscibility of polymer and crosslinker hamper the formation of a crosslinked network. The 2:1 sample, for instance, displays the lowest modulus of all samples measured (below  $10^8$  pa) indicating the lowest crosslinking degree. And while the 4:1 sample initially maintains the same modulus as the 1:1 sample,



in the final measurement the modulus also drops below  $10^8$  pa. Finally, the C8 spacer displays the trend observed in DSC where once again the 2:1 sample displays a lower modulus, and both 1:1 and 4:1 samples give very similar results.

When comparing the results obtained with previous findings<sup>21</sup> some interesting conclusions can be drawn. Firstly, using the same polymer and a dibenzyllic bismaleimide softening points of 146°C and 136°C were reported for 1:1 and 1:2 ratios respectively, as determined by DMTA. These values are significantly lower than all the values obtained with the three crosslinkers described here. Furthermore, the softening points adhere to the “classical” explanation where the value obtained for the 2:1 is lower than that of the 1:1 by a significant amount (10°C). The solubility parameter ( $\delta$ ) of this spacer is  $13.5 \text{ (J/cm}^3)^{1/2}$ , which is between the aromatic and C6 spacers. There are two possible explanations: firstly the dibenzyllic crosslinker is capable of participating in  $\pi$ - $\pi$  interactions with the (highly aromatic) polymer by virtue of its two benzene rings. This interaction could be beneficial, giving the two components better compatibility ultimately leading to better miscibility despite the large difference in solubility parameters. As seen for the C8 spacer, good miscibility lowers the rDA temperature. Secondly, however, is the fact that since these are DMTA values the size of the crosslinker also plays an important role: in DSC only the thermal properties are observed. This means that a (longer) spacer between two groups only has an effect on miscibility, the strength of the resulting material is not taken into account. In a DMTA measurement however, the strength of the resulting material is measured, and a longer spacer is expected to give a wider, more flexible (i.e. less densely crosslinked) network. This should result in a lowering of the modulus as well as the softening temperature as the material is already relatively mobile even in its crosslinked state.

## 5.6 Conclusions

The PE-fur polyester has successfully been crosslinked using bismaleimides in various ratios of maleimide to furans and containing different bismaleimide spacers. The resulting products display successful thermoreversibility in both DSC and DMTA analyses. Both thermal and mechanical properties show little change over the course of consecutive heating/cooling cycles. The rDA- or softening temperatures obtained for the three crosslinkers follow a trend that corresponds to their miscibility with the polymer: the benz spacer, having the poorest miscibility due to a significantly different solubility parameter, displays the highest rDa temperature. Next is the C6 spacer, having a better miscibility and a comparable solubility parameter and finally, the C8 spacer having a nearly identical solubility parameter displays the lowest rDA temperature. As the Diels-Alder reaction is an equilibrium reaction it is within expectations that a poor compatibility of chemicals leads to a shift away from this mixture (i.e. an increase in rDA temperature which would yield the decoupled products). The DSC integrals (which represent the rDA enthalpies) on first inspection would suggest that most of the maleimide groups are participating in DA additions as halving the amount of maleimide roughly halves the integral. However upon normalizing the values for the amount of bismaleimide present, it appears that samples 1:1 and 1:2 are oversaturated in bismaleimide as the rDA enthalpy per mole is significantly lower compared to the 1:4. Furthermore from DMTA data it appears a significant amount of bismaleimide molecules do not participate in effective crosslinking as the moduli of samples containing a 1:1 FUR:MAL ratio are nearly identical to samples containing a 2:1 ratio. If all maleimides partake in effective crosslinking, a more rigid material should be formed for the 1:1 ratio as this should be more densely crosslinked. Consequently a significant effect would be observed when halving the amount of bismaleimide.

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