

Reworkability of Covalently Adaptable Networks - Linking Dynamics to Diels-Alder Chemistry Through Infrared Spectroscopy

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ABSTRACT

The thermoreversibility of covalently adaptable networks consisting of furan-functionalised polyketones crosslinked with 1,1'-(methylene-di-1,4-phenylene)bis-maleimide have been explored. Analysis of the thermoreversibility of each polymer was investigated through Fourier-transform infrared spectroscopy and the relevant bands were explored at two different temperatures. The results of the in-situ heating and cooling of the polymer using the attached heating equipment of the spectrometer showed expected trends for the signal of the Diels-Alder adduct, with a lower amount of adduct at the decoupling temperature. These same trends were observed for both furan and maleimide; thus contradicting what was expected since more free furan and maleimide moieties should be present at the adduct de-coupling temperature. A control experiment with non-crosslinked furan grafted polyketones was carried out which showed the same trend, suggesting results from the initial experiment could be artefacts of the temperature. Characterisation after ex-situ heating and cooling of the polymer in two separate ovens didn't show any significant changes which suggests that the thermoreversibility is based on shifting the crosslinking points at higher temperatures.

1. Introduction

Thermosets are known for having stability at high temperatures and in the presence of solvents [1] as well as exceptional mechanical properties, load-bearing capacity and abrasion resistance [2]. These attributes are well-suited to applications such as for automotive and construction industries, as well as for coatings, adhesives, rubbers and abrasives [3][4]. Their covalently cross-linked nature (Figure 1a) grants them their aforementioned attributes and causes them to lack the ability to be recycled or reprocessed [2]; this is therefore a serious environmental problem in the XXI century. Cleavage of either the cross-links or other chemical bonds from the monomers have proven to be difficult and the resulting products are different from the initial thermoset [5]. Other disadvantages include lack of market for recycling and high costs [6]. For a system to become reworkable, cleavable groups must be integrated into the polymer network [7].

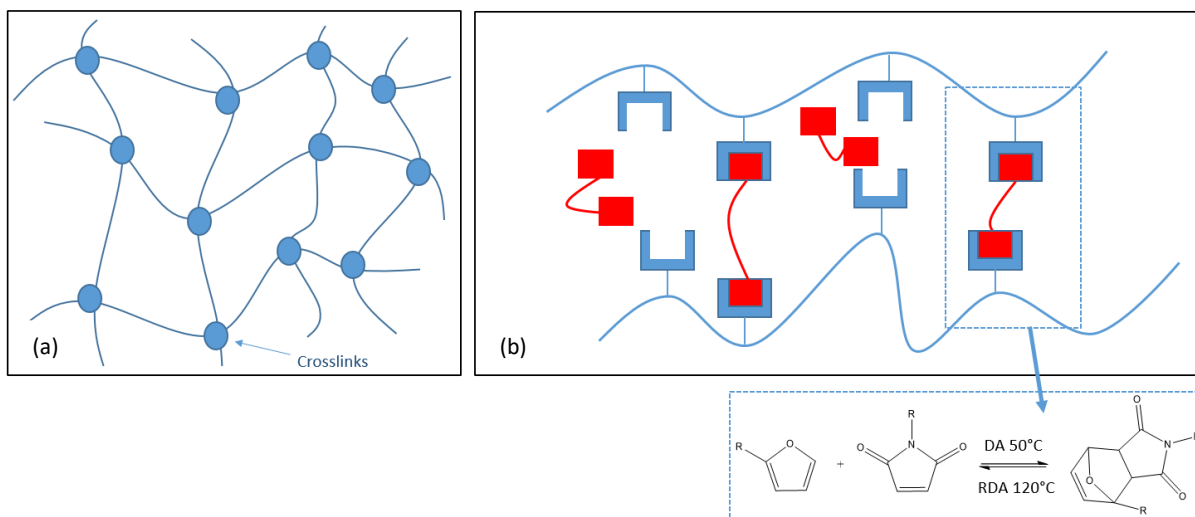


Figure 1. Scheme of a conventional thermoset (a) and a thermoreversible crosslinked polymer (b)

The use of exchangeable chemical bonds to lead to a covalently cross-linked network is a compelling strategy to instigate reformability into cross-linked polymeric systems (Figure 1b) [8]. These networks are also known as covalent adaptable networks (CANs) and contain an abundance of covalent reversible bonds which aid the response to an applied external stimulus [9]. CANs can be manufactured through combination of the dynamics of covalently reversible networks with the desirable characteristics of traditional thermosets. Furthermore, they are able to widely enable self-healing meaning that not much intervention is required for the material to repair itself [10] [11].

Covalently reversible chemical crosslinks can be broken upon an applied external stimuli such as heat or light; thus producing thermoreversible and photoreversible systems, respectively [4]. This is due to their increased bond energy and thermal stability [12]. The thermoreversible [4+2] Diels-Alder (DA) cycloaddition is one of the earliest, yet most-promising, routes towards the addition of self-healing attributes to polymeric networks [13]. This is due to the fact that no catalyst is required, no by-products are produced, and only relatively mild conditions are needed for both the forward and retro DA reactions to progress [14]. It successfully converts networks of multiple dienophile and diene components into highly cross-linked polymeric systems [4] [13]. It has been discovered that these systems have the ability to heal cuts and cracks [15]. After heating of the polymer to temperatures above 100°C, the Retro Diels-Alder (RDA) reaction activates the dissociation of the network. One of the most popular DA reaction routes is the reaction between furan and maleimide (Figure 1b); acting as diene and dienophile, respectively [16]. The RDA reaction of the furan/maleimide DA adduct has a relatively low decoupling temperature (100-120°C; with crosslinking occurring at 50-60°C) which is why it is an attractive process for self-healing and recycling applications [17].

A potential downfall is the radical homopolymerisation of maleimide as a side reaction at temperatures above 200°C. However, research has also shown that the RDA adduct already becomes unstable after 140°C. Maleimide reacts with itself in an irreversible reaction that can incapacitate the reworkability of the polymer; meaning that less free maleimide is available to reform the DA adduct with each thermoreversible cycle [18]. The formation of a donor-acceptor complex between maleimide groups is understood to be the reason for the self-initiation of the homopolymerisation [19].

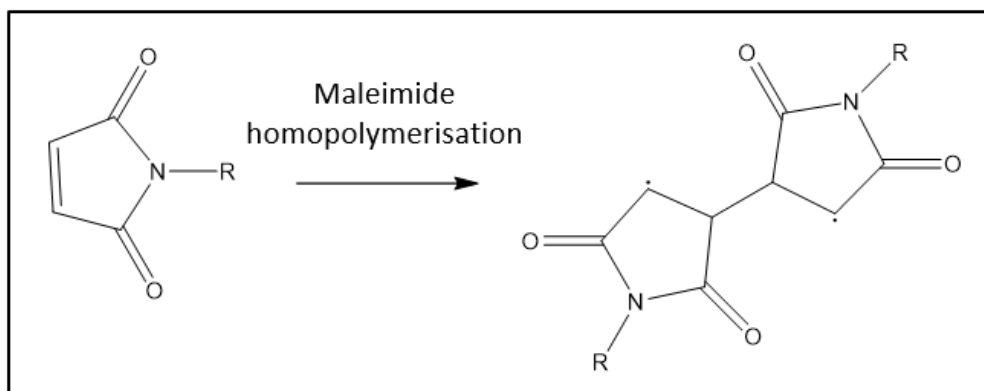


Figure 2. Reaction scheme of the homopolymerisation of maleimide at higher temperatures of 200°C

Nonetheless, furan-modified alternating polyketones cross-linked with bis-maleimide display excellent thermoreversibility for up to seven cycles with no significant loss in mechanical properties [4]. These alternating polyketones are easily obtained by the terpolymerisation of carbon monoxide, ethene and propene, and are then modified with furfurylamine through the Paal-Knorr reaction to obtain PK-furan (furan-modified polyketone) [4] [13] [20]. The highly cross-linked polymer network can then be formed through addition of 1,1'-(methylene-di-1,4-phenylene)bis-maleimide.

This work aims to investigate, through Fourier-transform infrared spectroscopy (FTIR), the thermoreversibility of PK-based polymers based on the Diels-Alder chemistry of furan and maleimide by heating to 120°C and subsequent cooling to 50°C in three successive cycles. The effects of the reaction dynamics after initiation of maleimide homopolymerisation, once additional heating to 150°C during the second cycle has proceeded, will also be analysed. The analysis will be carried out on two different PK-based polymers consisting of four different crosslinking densities.

2. Experimental

2.1 Materials

Polyketones synthesised through the terpolymerisation of carbon monoxide, ethylene and propylene were modified with furfurylamine so that 50% of carbonyl groups were converted. Two different mol% of ethylene of 0% and 30% constituted the olefinic part of the polyketone; named PK-0 and PK-30, respectively. Crosslinking of the furfurylamine-modified polyketones with 1,1'-(methylene-di-1,4-phenylene)bis-maleimide lead to cross-linked polymers of four different maleimide crosslinking densities for each mol% of ethylene; 0.35, 0.43, 0.60 and 0.70 (mmol/g).

2.2 Modification of alternating polyketones with furan

PK-30 was heated in an oil bath, equipped with a reflux condenser, to 110°C. The polyketone was stirred at 600rpm and furfurylamine was then added dropwise. Once all furan was added, the product was dissolved in chloroform and extracted. A separating technique was then carried out to extract the product with water, with the product being soluble in the water phase. The resulting compound was a dark brown solid once dried in a vacuum oven.

2.3 Crosslinking of furan-modified polyketones with bis-maleimide

The product was then again dissolved in chloroform in a flask equipped with a reflux condenser and an oil bath at 50°C. 1,1'-(methylene-di-1,4-phenylene)bis-maleimide was added and the reaction was left to run for twenty four hours and the product was then left to dry in a vacuum oven [13].

2.4.a In-situ characterisation by FT-IR

FT-IR spectroscopy using a Shimadzu IRTracer-100 Fourier Transform Infrared Spectrophotometer was used to analyse the changes made to the PK-0 and PK-30 polymers of the four different crosslinking densities during three successive heating and cooling cycles. The spectra were taken at a resolution of sixteen with thirty two scans. Heating of the polymers took place using the heating element of the FT-IR spectrometer. The first cycle began at 120°C for the Retro Diels-Alder reaction to take place and the polymer was left at said temperature for two minutes before taking a spectrum. Subsequent cooling to 50°C then occurred to observe the Diels-Alder reaction and the polymer was left at this temperature for forty five minutes before a spectrum was taken. This was repeated three times per polymer.

Baseline correction was carried out on each spectrum to obtain a more accurate normalisation of the changing peaks with the reference peak [See Appendix A.1]. This was done by using the heights of each relevant peak. Below the most relevant FT-IR peaks are reported for the crosslinked polymers.

IR: 2970 (ref), 1700 (s, CO), 1378 (m, CN maleimide), 1182 (m, C-O ether peak), 1072 (w, CC stretching), 1012 (m, CH in plane bending), 734 (m, C-H out-of-plane aromatic rings) [See Appendix A.2]

2.4.b Ex-situ characterisation by FT-IR

Analysis was carried out in a similar fashion to the one above but differed in the location of where the polymers were heated. Heating of the polymers took place in two separate ovens at 120°C for ten minutes and 50°C for forty five minutes to show if this technique would produce clearer results than the previous one. Three spectra were taken at each temperature and an average was calculated. Relevant reported peaks remain the same.

3. Results and discussion

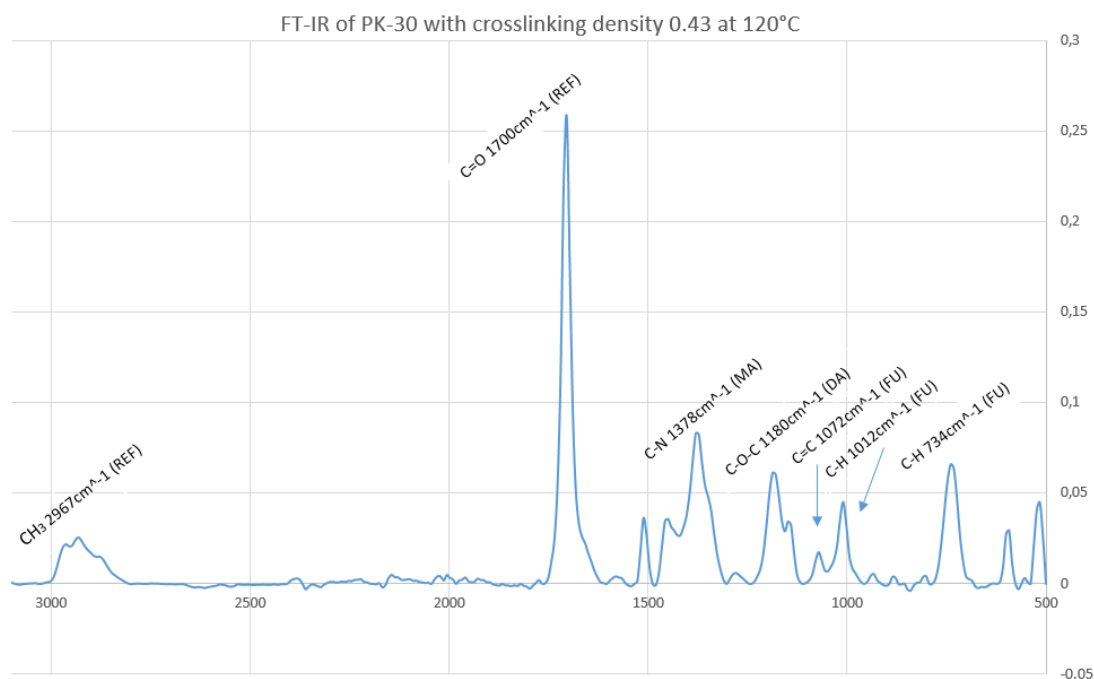


Figure 3. FT-IR spectra of polymer PK-30 with a crosslinking density of 0.43 at 120°C for the first cycle. All relevant peaks have been assigned with the corresponding band assignments and the molecule from which it came from. The two reference peaks are also indicated.

After obtaining the FT-IR spectra at each temperature for each polymer, the relevant bands were assigned to each peak in correspondence with literature (Figure 3) [See Appendix A.2]. Baseline correction was performed to obtain a clearer spectra so the ratio of each changing peak to the reference peaks could be obtained.

All relevant peaks shown above were firstly normalised with respect to the peak at 2967cm^{-1} : at both 50°C and 120°C . This peak is a reference peak (contributing to νCH_3), which shows no significant changes throughout the de-crosslinking/crosslinking of the polymer network [4]. It can be seen that the signal attributed to the maleimide, given as an example (Figure 4a), for the PK-30 polymer with a crosslinking density of 0.43, shows an irregular trend with significantly large standard error bars. This occurs with the other relevant peaks, with the exception of the DA adduct, for both PK-30 and PK-0 polymers at the different crosslinking densities.

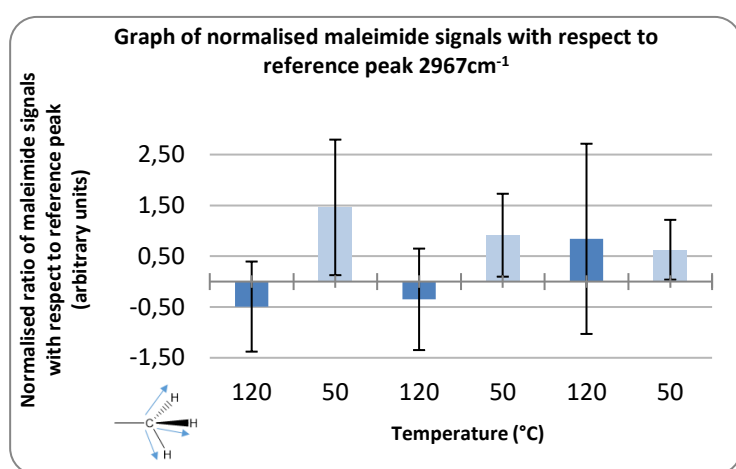


Figure 4a. Graph of maleimide signals at 1378cm^{-1} for a PK-30 polymer at a crosslinking density of 0.43. The spectra were normalised with respect to the peak at 2967cm^{-1} (νCH_3). The structural formula of νCH_3 is shown.

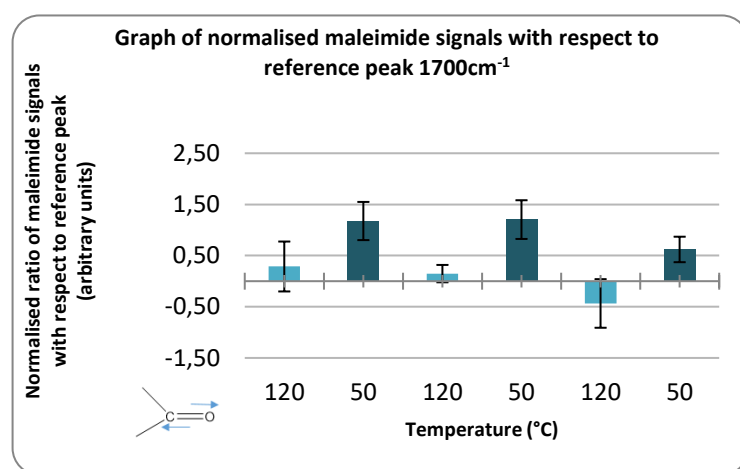


Figure 4b. Graph of maleimide signals at 1378cm^{-1} for a PK-30 polymer at a crosslinking density of 0.43. The spectra were normalised with respect to the peak at 1700cm^{-1} ($\text{C}=\text{O}$). The structural formula of $\text{C}=\text{O}$ is shown.

In an attempt to remove these irregularities and see sharper results, another reference peak at 1700cm^{-1} was used (contributing to $\nu_{\text{as}}\text{C}=\text{O}$) and the spectra were then normalised with respect to this peak. This reference corresponds to the carbonyl in the maleimide which remains unchanged during the de-crosslinking/crosslinking cycles and shows no significant difference between $\text{C}=\text{O}$ stretching from maleimide and the succinic ring [21]. The maleimide signal for the same polymer has been given again as an example (Figure 4b). It can be seen that maleimide is now following a clearer trend through the cycles and the standard error bars are smaller. This was also the case for the other polymers that were analysed, so for this reason 1700cm^{-1} was taken to be a more accurate reference and was used throughout the rest of this work.

Three of the peaks corresponding to maleimide (1378cm^{-1}), the Diels-Alder adduct (1182cm^{-1}), and furan (1072cm^{-1}) were then chosen for further analysis of the trends occurring during the heating and cooling cycles of the polymers. Polymer PK-30 with a crosslinking density of 0.43 was once again chosen as this polymer showed the sharpest results of the general trends that were shown in each polymer analysed.

It was observed that the Diels-Alder adduct shows the trend that was expected (Figure 5). The first cycle, beginning at 120°C, displays a significantly lower amount of DA adduct than that of the amount at 50°C since at 120°C the DA adduct has de-crosslinked into the RDA adduct. This continues through the next two cycles which shows that de-crosslinking and re-crosslinking is taking place during each heating and cooling cycle; thus suggesting the thermoreversibility of the polymer network and potentially confirming that both the DA and RDA reactions are occurring. The standard error bars appear small which highlights that there were no significantly large differences in the results obtained for each repeated experiment.

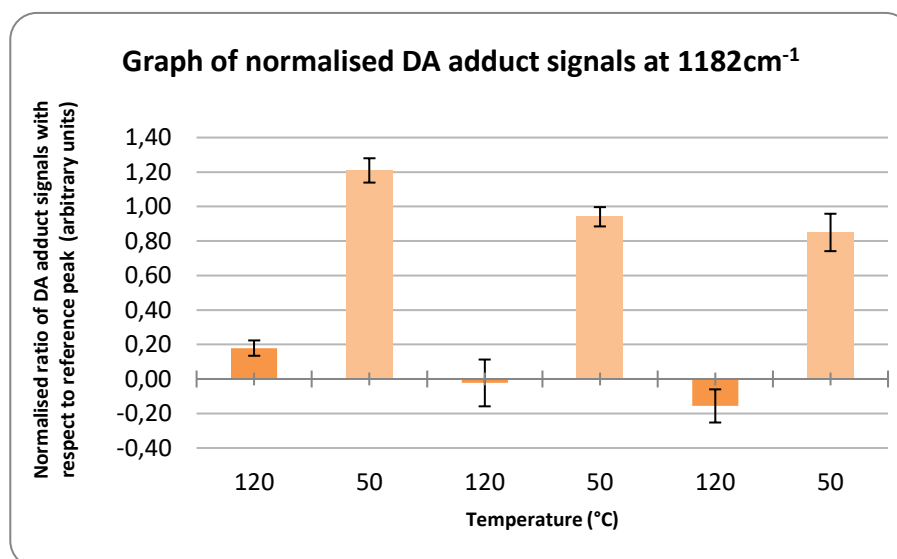


Figure 5. Graph of the normalised Diels-Alder adduct signals at 1182cm⁻¹ for the polymer PK-30 with a crosslinking density of 0.43.

The graph for the furan signal indicates that the same trend is occurring as that for the DA adduct signals, this time with substantially large error bars for the second and third cycle at 50°C (Figure 6a); indicating that the trend was not followed so precisely and there were significant differences in the results at 50°C each time the thermoreversible cycles were repeated. This was also shown for the other polymers analysed and was not what was expected since furan should follow the opposite trend than that of the DA adduct. This is due to the fact that at 120°C, the DA adduct would have de-crosslinked, leaving more free furan and maleimide in the sample.

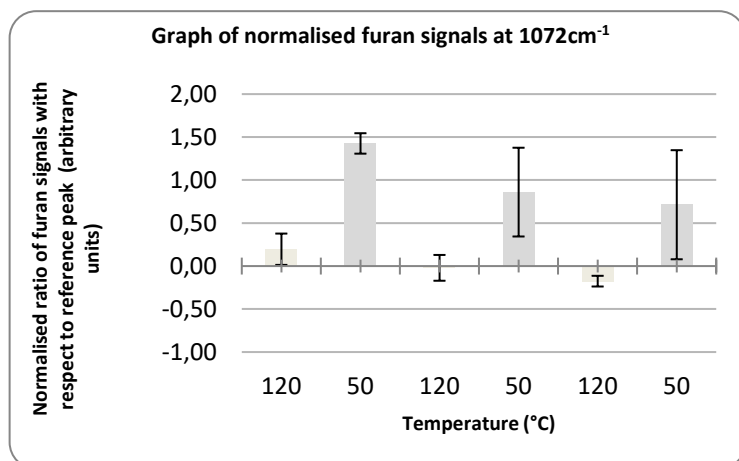


Figure 6a. Graph of the normalised furan signals at 1072cm⁻¹ for the polymer PK-30 with a crosslinking density of 0.43.

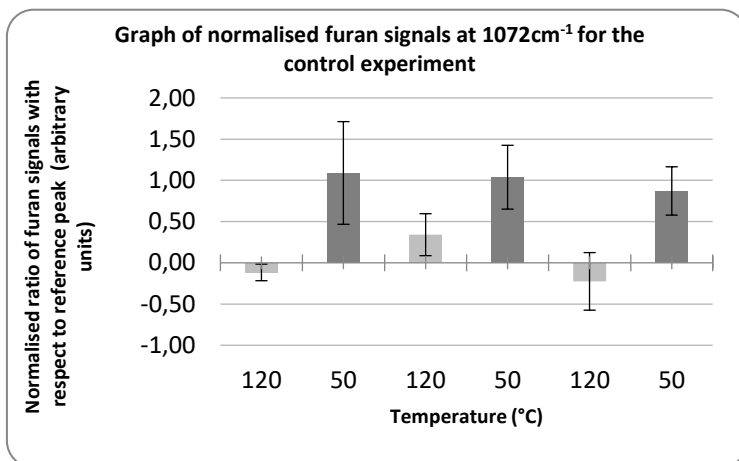


Figure 6b. Graph of the normalised furan signals at 1072cm⁻¹ for the polymer PK-30 with a crosslinking density of 0.

This trend was shown for nearly all the polymers analysed so further investigation was carried out. A control experiment of the polymer without the crosslinking of maleimide was performed (Figure 6b) and it was observed that the furan signal once again follows this same trend, even without the de-crosslinking and re-crosslinking of maleimide from the furan during the heating and cooling of the polymer. This shows that the trend for the furan signals could be an artefact of the temperature and therefore, despite the clear results and expected trend, the results of the DA adduct signals could also be an artefact of the temperature. This could be due to the experimental design and possible temperature dependence of the measurements. Furthermore, standard error bars are significantly high at almost all temperatures which confirms relatively big differences between data when the experiments were repeated. The signals for the maleimide peaks followed the same trend as that of the crosslinked furan signals. This makes sense if it is to be considered that the results obtained are artefacts of the temperature. The furan and maleimide signals should follow the same trend as each other since the de-crosslinking and re-crosslinking affects the amounts of free furan and maleimide in the same way.

A different approach for the analysis of the thermoreversibility of the DA adduct using FT-IR was performed in which the characterisation was carried out directly after ex-situ heating of the polymer to 120°C for ten minutes and cooling to 50°C for forty five minutes in two ovens. This was to try to enhance the technique in the hope that better results could be obtained that would be able to show the results originally expected. This is due to the fact that the heating and cooling is not taking place in the sample compartment of the FT-IR but in an oven where the chemical bonds between the furan and maleimide have potentially more free space to break and move around.

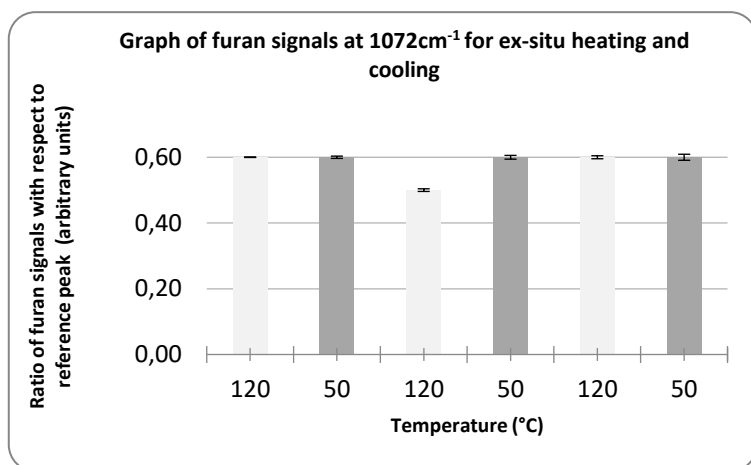
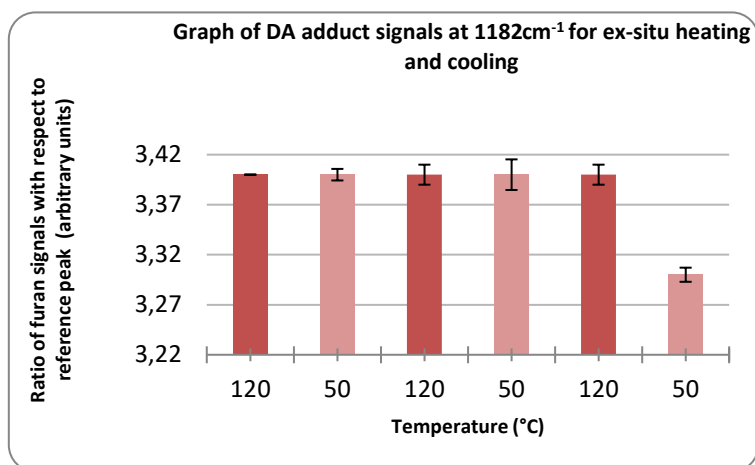


Figure 7a. Graph of the DA adduct signals at 1182cm⁻¹ for the polymer PK-30 with a crosslinking density of 0.59 during ex-situ characterisation.

Figure 7b. Graph of the furan signals at 1072cm⁻¹ for the polymer PK-30 with a crosslinking density of 0.59 during ex-situ characterisation.

It can be seen in the graph for the DA adduct (Figure 7a) that no trend has been followed and the results are inconclusive. Despite spectra being taken almost directly after removal from the oven, the DA and RDA reactions cannot be seen to occur. It can also be seen from the graph for the furan signals that no trend is occurring either (Figure 7b) and almost no changes are occurring at all during each cycle. The results for the maleimide signals also appear inconclusive. This was once again not expected and it was concluded that the ex-situ approach, with this experimental design, was not a better way to see the changes in the amounts of maleimide and furan throughout each heating and cooling cycle. Therefore, this highlights further that the results of the in-situ heating and cooling may be just artefacts of the temperature after de-crosslinking at 120°C. The graphs shown for the ex-situ characterisation were not normalised since the graphs after normalisation were difficult to interpret. Due to the results of both in-situ and ex-situ characterisation, and of the control experiment, it was concluded that the investigation into how the initiation of maleimide homopolymerisation affects the thermoreversibility was not to be carried out with this technique.

It can thus be assumed that issues with the experimental design could have occurred. For example, human error could've played a role since some time passed between removal of the polymer from the oven and spectra taken; cooling could have taken place quickly, especially when heated to 120°C. Furthermore, more inaccuracy during the baseline correction of each peak could have occurred since each correction for each spectra taken could not have been completely identical each time due to the fact that some spectra were slightly different to others because of the different crosslinking densities and different temperatures. Calculations for the normalisation of each peak with the reference peak were carried out by hand which could have also led to human error. These factors may have further contributed to the unexpected results that were already clear to see from the data. Only three repetitions were carried out for each polymer due to time constraints which meant there was only a small sample size for the analysis. An additional two repetitions were carried out for the polymer PK-30 of crosslinking density 0.43 to see if significant differences in the standard error bars could be seen [See Appendix A.3]. It can be seen from the graphs that there are not such profound differences between the graphs taken from the averages of three samples and those taken from five samples. This

could be due to the other issues with the experimental design playing a greater role. Furthermore, changes in the polymer may just be too small to be detected using this method.

According to Yuliati et al., the same technique of FT-IR characterisation of the DA and RDA reactions with the expected opposite trends of maleimide and furan compared to the DA adduct, was proven successful. However, in this case, much lower crosslinking densities were used and the polymer was thus able to be dissolved in a solvent at high temperatures, permitting complete cleavage of the chemical bonds; unlike the polymers used in the experiment performed in this work [22]. Successful results were still visible even when the polymer was not dissolved in solution. This was because of improved mobility of the polymer which meant that when the bonds between furan and maleimide were cleaved during de-crosslinking, they were able to move more freely and did not come back into contact with each other. This could be another issue with the experiment carried out in this work since the polymers used were of a high crosslinking density and thus had limited mobility. This means that bonds could have reshuffled and then reattached easily after cleaving of the CANs at 120°C since they did not have the required freedom to move.

Despite much research through FT-IR with different polymers of different crosslinking densities, the thermoreversibility, and thus the reworkability, of the system cannot clearly be shown through this characterisation technique. Notwithstanding the clear results from the DA adduct, it cannot be verified that the results are not an artefact of the temperature due to the behaviour of furan during the heating and cooling of the polymer without crosslinking.

For this technique to be more successful in the future, different approaches could be taken to try and improve experimental design. For example, during baseline correction of the spectra, the area under the peak could be used instead of the height of the peak to give a more accurate correction. This would thus lead to more accurate calculations of the ratio of the relevant signals to the reference peak and clearer trends closer to what was originally expected may be seen. Furthermore, using another reference peak than the C=O stretching peak at 1700cm⁻¹ could also provide better accuracy during calculations as this peak corresponds to two different peaks; one from the carbonyl stretch in maleimide, and one from the carbonyl stretch in the succinic ring. As can be seen from the spectra [See Appendix A.1], this signal looks like one peak because the two stretches are just a few cm⁻¹ away from each other. Therefore, this was taken as one peak in this work. However, it cannot be clear how much of this peak corresponds to the stretching in maleimide or the succinic ring and since the area under each peak was not determined, this cannot be a viable peak to use as a reference. Analysis could thus be continued using the reference peak at 2967cm⁻¹ instead.

Moreover, Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) was used throughout this work which may have not been the most feasible way to clearly see the changes in the polymers through the thermoreversible cycles. Transmittance Infrared Spectroscopy (T-IR) may be a more preferable approach since ATR-IR does not penetrate very deep into the sample. In addition to this, a larger sample size could increase the accuracy of the experiment and the standard error bars could therefore show a more realistic deviation in the results.

4. Conclusion

The results presented conclude that the use of Fourier-transform infrared spectroscopy cannot be a viable method for analysing the thermoreversibility of a furan-maleimide system with crosslinking density as high as was used with the experimental design utilised in this work. It can be seen initially

from the graphs interpreted that the Diels-Alder reaction does seem to take place as the distinction of the fluctuating ratio of DA adduct at the different temperatures is clear. However, due to the behaviour of the furan signals, which can be seen from both the crosslinked polymer and the control experiment with the un-crosslinked polymer, it cannot be confirmed that the DA adduct signals are not just following the trend of the furan signals and are therefore not just an artefact of the temperature. This could also be due to discrepancies in the experimental design, notably with the baseline correction of each spectra and with the small sample sizes used for analysis. Lack of accurate normalisation, using the height of the peak instead of the area under the peak, of the relevant signals with the reference could have also potentially affected the trends shown for the furan signal.

Furthermore, these unexpected trends could also likely be due to the polymer's lack of ability to move freely once heated to 120°C. The covalent bonds between furan and maleimide would have broken but the polymer is only confined to a small space and not free to move around, unlike at lower crosslinking densities; thus causing the bonds to reattach. This also confirms why no significant trends can be shown when the polymer is heated ex-situ.

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Appendix

A.1 Graphs of FT-IR with and without baseline correction

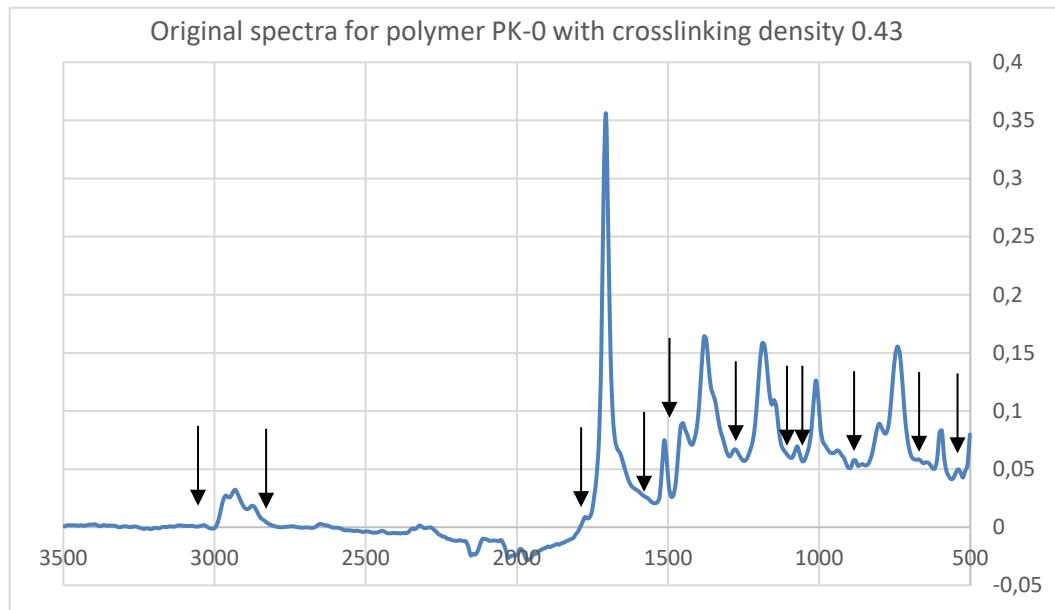


Figure A.1.1. Graph of FT-IR spectra for polymer PK-30 with crosslinking density 0.43 before baseline correction. The arrows indicate the points where the correction was carried out.

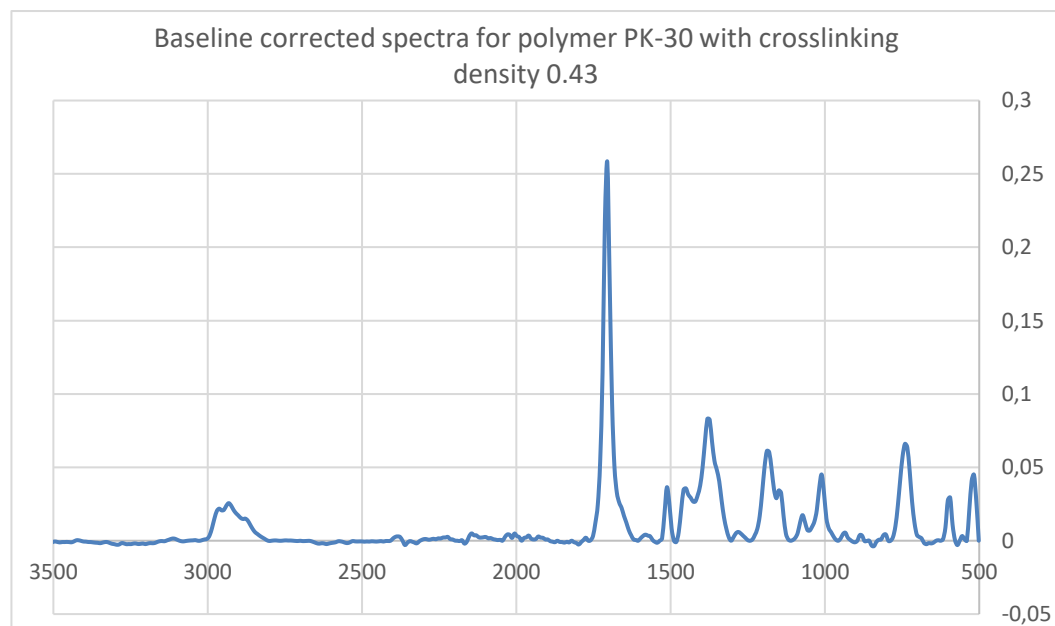


Figure A.1.2. Graph of FT-IR spectra for polymer PK-30 with crosslinking density 0.43 after baseline correction.

A.2 Table of relevant FT-IR peaks including band assignments

Wavenumber (cm ⁻¹)	Group	Band Assignment	Intensity	Reference
2967	Reference peak	C-H asymmetric stretching	Medium	[23]
1700	Carbonyl peak of maleimide (reference)	C=O stretching	Strong	[21][23]
1378	Maleimide ring	C-N stretching	Medium	[12]
1182	DA adduct	C-O-C ether peak of reacted furan	Medium	[12]
1072	Pyrrole and furan	C=C stretching	Weak	[12]
1012	Pyrrole	C-H in plane bending	Medium	[12]
734	Furan rings at side chain	C-H out-of-plane aromatic rings	Medium	[13][4]

Table A.2. Table of relevant FT-IR peaks for the DA adduct, furan and maleimide from literature including band

A.3 Graphs of two different sample sizes

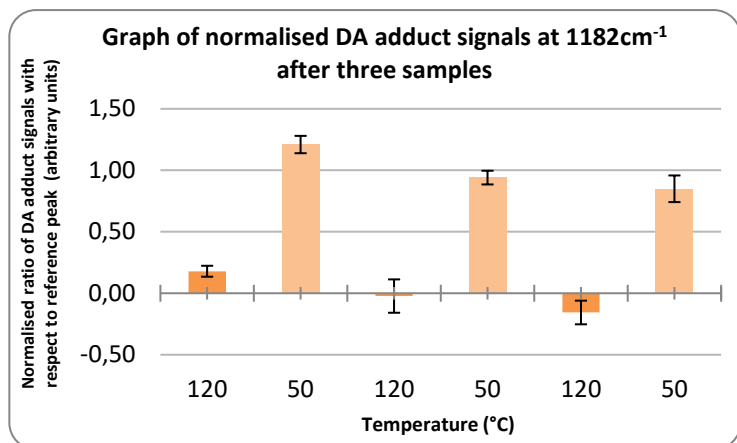


Figure A.3.1. Graph of the normalised Diels-Alder adduct signals at 1182cm^{-1} for the polymer PK-30 with a crosslinking density of 0.43 after three samples.

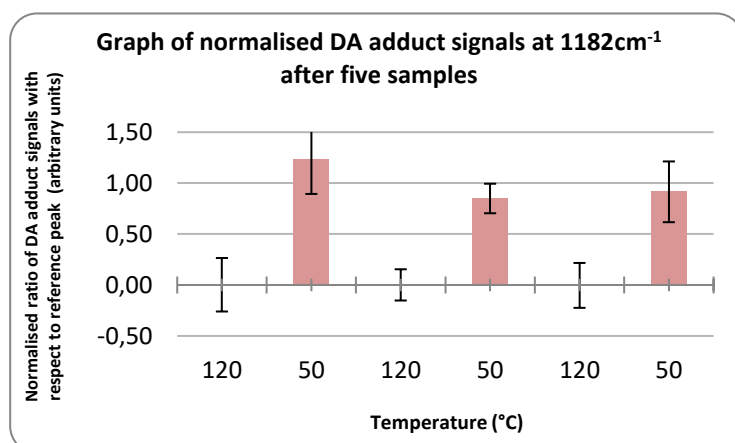


Figure A.3.2. Graph of the normalised Diels-Alder adduct signals at 1182cm^{-1} for the polymer PK-30 with a crosslinking density of 0.43 after five samples.

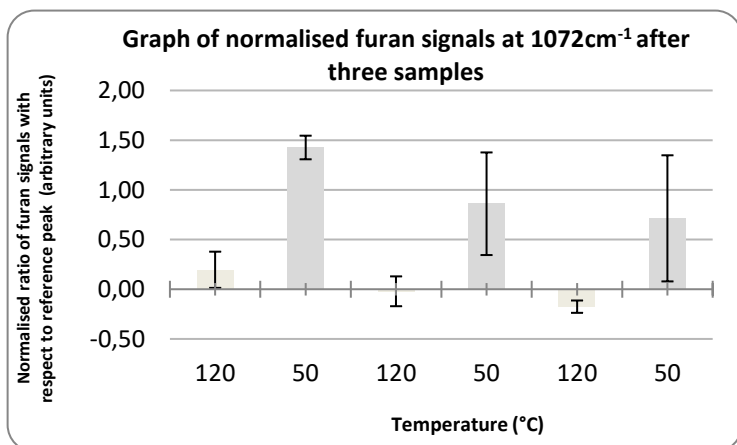


Figure A.3.3. Graph of the normalised furan signals at 1072cm^{-1} for the polymer PK-30 with a crosslinking density of 0.43 after three samples.

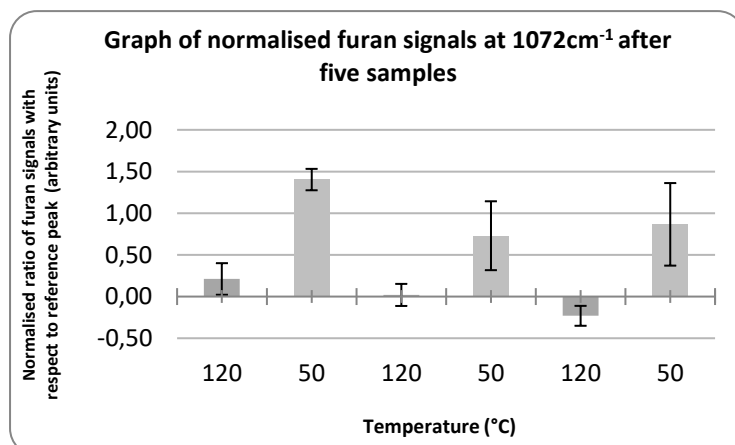


Figure A.3.4. Graph of the normalised furan signals at 1072cm^{-1} for the polymer PK-30 with a crosslinking density of 0.43 after five samples.