European Polymer Journal 215 (2024) 113195

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Dissociative covalent adaptable networks from unsaturated polyesters

Jonathan B.D. Gregg [a], James A. Wilson [a,b], Steven L. Brown [c], Andrew T. Slark [a,*]

[a] Department of Chemistry, The University of Sheffield, Dainton Building, Brook Hill, Sheffield, South Yorkshire S3 7HF, UK
[b] Chemical Engineering and Applied Chemistry, Aston University, Birmingham B4 7ET, UK
[c] Scott Bader Company Ltd, Wollaston, Wellingborough NN29 7RL, Northants, UK

ARTICLE INFO

Keywords:
Covalent adaptable network
Dissociative
Unsaturated polyesters
Multifunctional furans

ABSTRACT

Unsaturated polyesters (UPEs) are a class of thermosetting resins which are prevalent in the polymer industry, offering excellent durability in many applications. However, their permanent crosslinks prevent re-use or recycling at their end-of-life. This problem is addressed using UPEs to generate dissociative covalent adaptable networks (CANs). Poly(propylene maleate) and poly(propylene fumarate) were copolymerised with furan-functionalised crosslinkers to form networks comprising reversible Diels-Alder cycloadducts. The thermal properties of each material were analysed by differential scanning calorimetry (DSC), showing that the furan-maleate networks dissociated at 130 °C compared to the furan-fumarate networks which dissociated at a significantly lower temperature (100 °C). The network formed from poly(propylene maleate) using a flexible trifunctional furan crosslinker provided the largest increase in T_g and T_{rDA}, producing the highest gel fraction (99 %) and a stable plateau modulus of 10 MPa by DMA. The networks reform at ambient temperature, although the rate of formation can be increased significantly by mild heating at 65 °C. Overall, the results indicate that furan-maleate CANs behave like reference furan-maleimide networks. Thermal analysis indicated that the furan-maleate cycloadduct was retained by heating to 150 °C, whereas isomerisation of maleate to fumarate was observed after repeated heating cycles to 180 °C. Mechanical testing showed that a bond strength of almost 10 MPa was achieved using these CANs as adhesives, which could be readily modified through changes in copolymer composition.

1. Introduction

Over 60 million metric tons of polyester were produced in 2021, [1] with both thermoplastic and thermoset materials serving a wide range of applications. Poly(ethylene terephthalate) (PET) is a common thermoplastic material found in a range of packaging applications, including bottles and films. Chemical recycling of PET is well established since the ester bond is susceptible to hydrolysis, and it can be depolymerised back into its monomers including ethylene glycol and terephthalic acid or dimethyl terephthalate. [2] However, PET is a thermoplastic and for applications requiring higher strength and durability, thermoset materials are better suited. Unsaturated polyesters (UPEs) are crosslinked by permanent covalent bonds to form a strong network, making them useful and popular for applications requiring high mechanical strength, heat resistance and durability, [3] especially in construction, transport and marine markets. However, these thermosets are very difficult to recycle, as the polyester resin is permanently bonded into an insoluble network. Chemical recycling involving pyrolysis or solvolysis is possible, but these methods are complex and expensive. [4] The creation of a crosslinked network with reversible covalent bonds would be highly advantageous to create a material that benefits from the performance advantages of thermosets in use, whilst maintaining the recyclability of thermoplastics at their end of life.

The unsaturation in the UPE backbone usually comes in the form of a fumarate group, as this confers desirable physical properties on the resin such as high heat distortion temperatures, good tensile strength and chemical resistance. Furthermore, the fumarate *trans* isomer is in a more favourable conformation for crosslinking, compared to the maleate *cis* isomer. [5] Despite this, maleic anhydride is used almost exclusively as the unsaturated monomer in most commercial resins, due to its lower cost, higher yield, ease of handling and more facile incorporation into the polyester backbone. Under typical polycondensation conditions performed at high temperatures, maleates can isomerise to the more energetically favourable conformer, fumarate, and under the correct conditions, conversions of up to 89 % are possible. [6] UPEs are commonly sold as a liquid resin using styrene as a reactive diluent,

---

* Corresponding author.
E-mail address: a.slark@sheffield.ac.uk (A.T. Slark).

https://doi.org/10.1016/j.eurpolymj.2024.113195
Received 3 March 2024; Received in revised form 31 May 2024; Accepted 3 June 2024

which solidifies through free radical copolymerisation of the chain unsaturation with the styrene to form a three-dimensional crosslinked network. The resulting materials possess excellent mechanical properties, but because of the irreversibility of the network, they cannot be reshaped and are very difficult to recycle. In addition, styrene monomer is toxic and very hazardous to manage during application.

Covalent adaptable networks (CANs) can offer a more sustainable alternative to irreversible networks. [7] These materials can display typical thermoset network properties at service temperatures (the range over which the material is required to operate in use) but can be reprocessed outside of this range *via* network rearrangement. Typically, bond exchange proceeds via an associative or dissociative process. In associative CANs, the reaction proceeds via an addition–elimination pathway where flow occurs at high temperature, but network integrity is maintained. This is a characteristic of vitrimers which were pioneered by Leibler *via* transesterification. [8] Other notable examples of associative CANs including transamination are summarised in excellent reviews. [9,10] Dissociative CANs proceed via an elimination–addition pathway with a temperature dependent equilibrium between covalent bond formation and dissociation. At a sufficiently high temperature there is a sol–gel transition and loss of network integrity. Once the temperature is reduced, the network covalently reforms.

Dissociative CANs can be produced through several methods, most commonly utilising Diels-Alder (DA) networks from the reversible cycloaddition of dienes and dienophiles. The most documented DA networks take advantage of furan- and maleimide-functionalised precursors that can be easily attached to the chain-ends of commercially available prepolymers. [11] Typically, these networks can be dissociated at temperatures between 100 and 150 ℃ without risking degradation or side reactions to the remainder of the polymer chain. [12] However, it would be more sustainable to use a dienophile that is renewable and able to be easily incorporated into a polymer chain. Fumaric acid is commonly found in nature, particularly in moss, lichen and funghi and forms part of the Krebs and citric acid cycles. The *cis*-isomer of fumaric acid, maleic acid, has been widely studied for ‘green’ synthetic routes. [13,14] Both isomers have been used in the production of UPEs through polycondensation with diol comonomers. There is already infrastructure in place to mass produce polyesters, which would make the synthesis of these new, ‘green’ materials facile and efficient. Similarly, di-esters of both isomers have been demonstrated for use in small molecule DA cycloadditions with cyclopentadiene, [15–17] furan [18] and anthracenes. [19].

Zhao *et al* recently investigated the self-healing of crosslinked non-isocyanate polyurethanes based on Diels-Alder reactions of furan terminated prepolymers with unsaturated polyesters. [20] The UPE was synthesised via classical polycondensation routes, comprising both isomers (i.e., containing both maleate and fumarate groups). Resulting networks were only partially crosslinked with 40–45 % being soluble (i.e., a low gel fraction) with relatively low dissociation temperatures. In our research we investigate UPEs as dienophiles, critically comparing the properties of CANs from poly(propylene maleate) with poly(propylene fumarate), using a range of multifunctional furan crosslinkers. We show that furan-maleate networks are much more robust than furan-fumarate networks, producing a high gel fraction, higher dissociation temperature and a stable plateau modulus. The new furan-maleate CANs behave like reference furan-maleimide networks but overcome the practical limitations of applying maleimide chemistry on an industrial scale for many applications, which includes multistep synthesis, purification of products and relatively high cost.

2. Results and discussion

2.1. Synthesis of polyester CANs

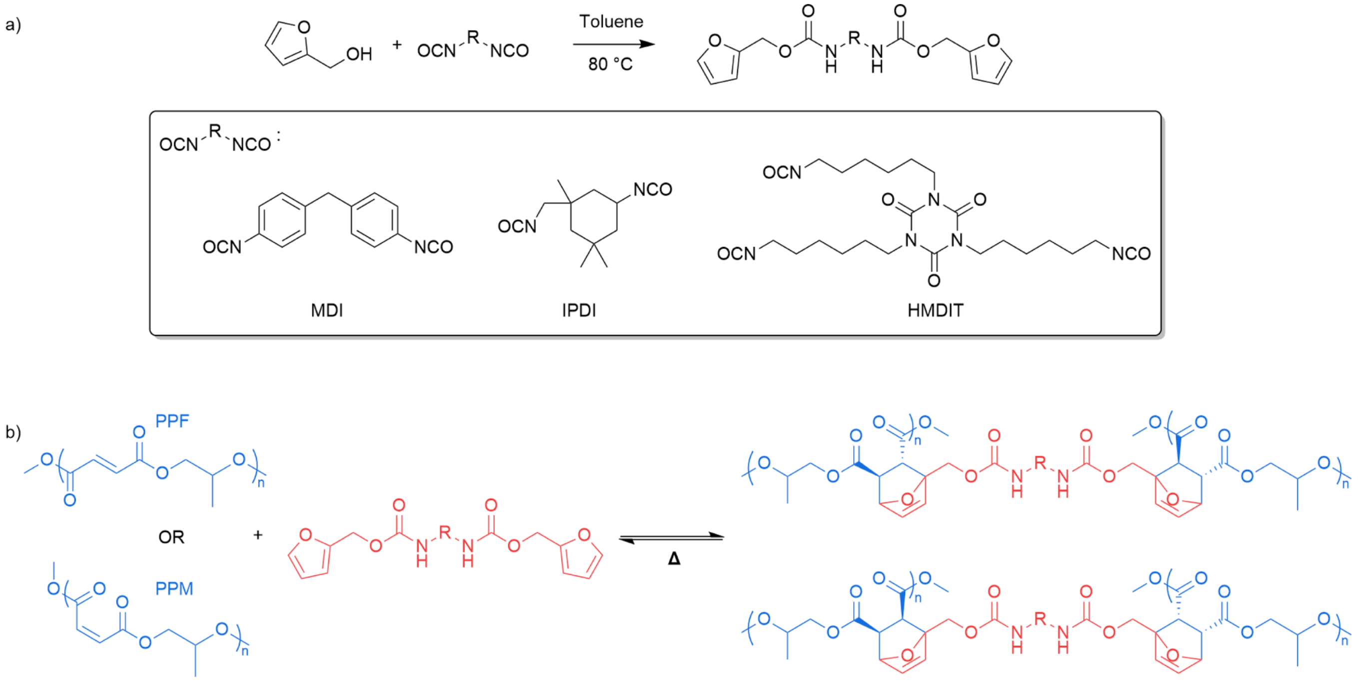
Poly(propylene fumarate) (PPF) was synthesised by classical step-growth polymerisation. A mixture of maleic anhydride and propylene glycol with a monobutyltin oxide catalyst was stirred and heated at 220 °C until completion, as determined by the volume of water distilled off and acid value calculations. The high temperatures necessary for this process cause the isomerisation of maleate to fumarate, so poly(propylene maleate) (PPM) cannot be synthesised through this standard method. [21] Instead, PPM was synthesised by ring-opening copolymerisation (ROCOP) where the milder conditions (80 °C) allow the stereochemistry of the maleate to be retained. [22,23] In a moisture-free N_2 environment, maleic anhydride, propylene oxide, a $(BHT)_2(THF)_2$ catalyst and a propargyl alcohol initiator, was made up with toluene to a 4M concentration. The polymerisation was conducted at 80 °C for 24 h before being quenched in chloroform and precipitated in diethyl ether. The stereochemistry of the polyesters was confirmed *via* ^{1}H NMR spectroscopy; fumarate protons resonate at $\delta = 6.85$ ppm and maleate protons resonate at $\delta = 6.25$ ppm (Figure S1, S7). Furan crosslinkers were produced from the addition reaction of the commercially available isocyanates 4,4′-methylene diphenyl diisocyanate (MDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate trimer (HMDIT) with furfuryl alcohol to form a urethane linkage. This produced the furan-functionalised polyurethane crosslinkers difuran methylene diphenyl carbamate (MDF – Figure S11, S12, S13, S14), difuran isophorone carbamate (IPDF- Figure S15, S16, S17, S18) and trifuran hexamethylene trimer carbamate (HMTF – Figure S19, S20, S21, S22), respectively. All products were made with high atom efficiency due to the facile addition chemistry (yield = 99 %).

Networks were synthesised through the bulk addition of the UPEs to the furan-functionalised crosslinkers at 100 °C until homogenous, followed by copolymerisation for at least 7 days at ambient temperature to allow for the furan linkers to covalently bond with the unsaturation and crosslink the polyester chains (Scheme 1). The masses of polyester and linker used were calculated to give an equimolar ratio of alkene to furan.

2.2. Thermal properties of networks

Networks were examined by differential scanning calorimetry (DSC) to quantify the *retro*-Diels-Alder (rDA) reaction at elevated temperatures. Relatively slow network reformation kinetics allows the rDA reaction to be observed in only the first heating cycle (Fig. 1, Table 1). We observed similar behaviour with networks formed from the copolymerisation of the same multifunctional furan crosslinker (HMTF) with bismaleimide prepolymers. [12,24] The dissociation is an endothermic process, with a visible peak providing a clear indicator that the network is reverting to the original furan and UPE components. Furthermore, the melting points observed in pure MDF and HMTF are not present since the linkers are dispersed well throughout the network. The rDA of all networks was observed between 100 and 130 °C, where the dynamic equilibrium of the Diels-Alder reaction favours dissociation rather than cycloaddition. The temperature of the rDA reaction (T_{rDA}) differed depending on the stereochemistry of the unsaturation, with furan-maleate cycloadducts dissociating at approximately 130 °C and furan-fumarate cycloadducts dissociating at a much lower temperature (approximately 100 °C), independent of the crosslinker used. As observed, a small change in conformation of the backbone has a substantial impact on the T_{rDA} and the resulting thermodynamic stability of the material. This difference can be attributed to the different steric environments of the unsaturated groups.

The stereochemistry of the dienophile is maintained in the cyclohexene product, meaning fumarates will produce enantiomeric *pseudo-trans* cycloadducts, whereas maleates will form *pseudo-cis* diastereoisomers with an *exo* ester conformation and an *endo* conformation that is the preferred product by the Alder *endo* rule (Scheme 2). [25] The T_{rDA} of the fumarate networks appears at a lower temperature since the di-ester dihedral angle increases from 120° to 180° during dissociation, relieving steric strain. Likewise, undergoing rDA relieves further steric strain induced from diaxial interactions between the bridged oxygen and *exo* ester groups in the cycloadduct. On either side of the equilibrium,



Scheme 1. Synthesis of a) furan-functionalised linkers from the reaction of furfuryl alcohol with a di- or tri-isocyanate, followed by b) network formation through bulk copolymerisation with an unsaturated polyester.

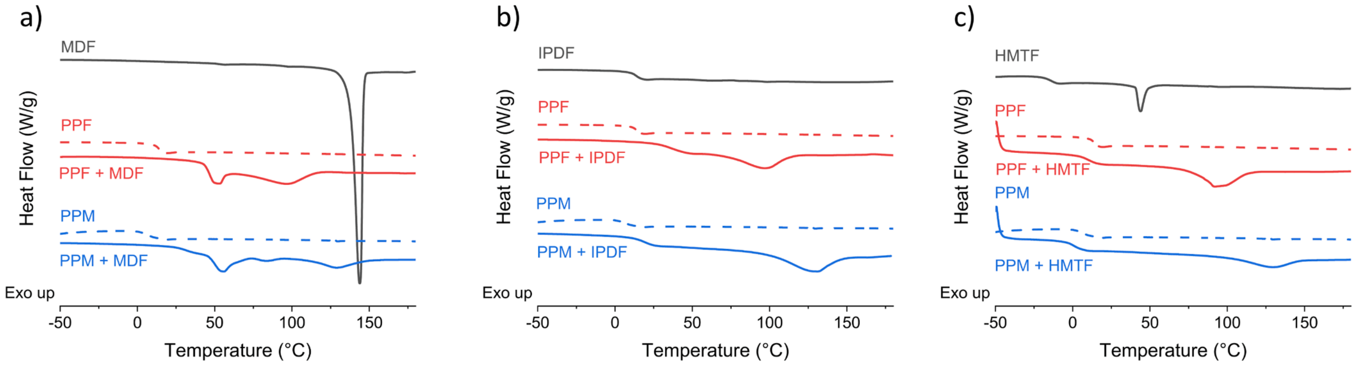


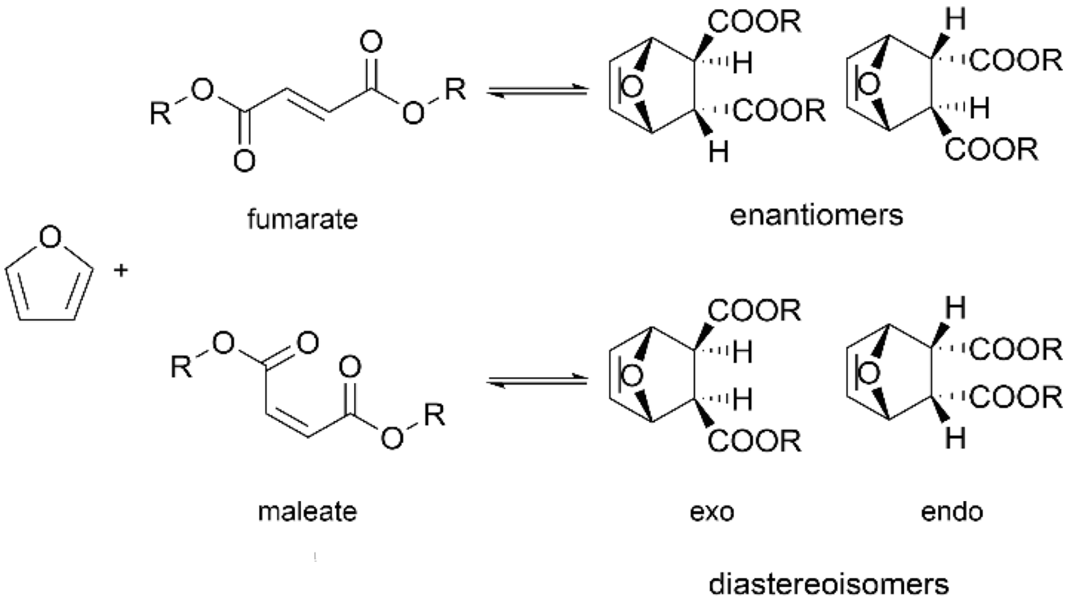
Fig. 1. DSC thermograms of the initial heating cycle from −50 to 180 °C at 10 °C.min^{-1} on a) MDF, b) IPDF and c) HMTF and the corresponding networks with PPF or PPM. Taken 1 week after synthesis.

Table 1
Properties and thermal properties of synthesised materials.

Material	f_g [a] (mol kg^{-1})	T_{rDA}^{b} (°C)	ΔH_{rDA} (J/g)[b]		η[c] (P)		T_g^{b} (°C)		Gel fraction[d] (%)
			1 week	26 weeks	115 °C	125 °C	1 week	60 weeks	
PPM	6.4	–	–	–	3.7	3.6	4	–	0
PPM + MDF	2.63	128.8	12	24	20.1	7.6	50	61	55
PPM + IPDF	2.74	128.6	20	40	6.4	4.9	20	63	76
PPM + HMTF	2.37	129	14	46	4.8	2.7	2	45	99
PPF	6.4	–	–	–	18.8	10.8	14	–	0
PPF + MDF	2.63	96.9	16	19	19.9	7.3	46	55	0
PPF + IPDF	2.74	97	22	24	8.7	3	37	45	0
PPF + HMTF	2.37	91.9	24	26	8.4	3.3	11	20	0

[a] Concentration of alkene groups in the material. [b] Determined by differential scanning calorimetry. [c] Viscosity determined at 750 RPM. [d] Determined by Soxhlet extraction after 26 weeks.

the di-ester groups in maleates remain eclipsed meaning no enthalpic gain is achieved from dihedral steric strain relief, which coupled with no diaxial steric strain in the preferred *endo* cycloadduct conformation, means little enthalpic gain to undergoing rDA and therefore, requires a higher temperature for dissociation. This trend is seen throughout literature, for example, in a fulvene and dichloromaleate system, which



Scheme 2. Different possible stereoisomers that can form from the Diels-Alder cycloaddition of a furan to a fumarate or maleate group.

creates a more sterically hindered adduct comparable to a furan and maleate adduct, where the T_{rDA} occurs at a low temperature of 37 °C. [24] The presence of the electron-withdrawing chlorine on the dienophile would normally promote the forward DA reaction.

Dissociation of the networks is confirmed by the low melt viscosity obtained at 115–125 °C for all materials (<20P). In the molten state, the stereochemistry of the backbone becomes less significant compared to the composition of the material. However, it was noted that the maleate networks took a few minutes to melt when placed on the heated stage whereas the fumarate networks took a few seconds.

The magnitude of the enthalpy change of the rDA endotherm (ΔH_{rDA}) is a good indication of the relative number of covalent bonds formed in the network, as a larger concentration of Diels-Alder cycloadducts will lead to a higher enthalpy change of dissociation. All networks contain similar degrees of functionality (f_g), or concentration of alkene groups, and should therefore contain comparable crosslink density in the networks *if* all the functional groups participated in bonding. As there are differences in the ΔH_{rDA} of the materials observed by DSC, it is probable that some networks are more efficient at bond formation than others. The broad endotherms make accurate integration difficult and thus, only general observations can be made. After 1 week, the network of PPM + IPDF produced the largest ΔH_{rDA}, almost 2 times higher than PPM + MDF, suggesting that the IPDF linker is much better at reacting with maleate moieties compared to MDF. This is also observed in the fumarate-functionalised backbone, but less pronounced when analysed by DSC. The materials were analysed again after 6 months and the PPF networks showed little increase in ΔH_{rDA}, suggesting these materials had reached an equilibrium in crosslinking density after 7 days. This is comparable to previously reported CANs formed through maleimide-furan cycloadditions. [12,24] In contrast, the PPM networks produced much larger changes in ΔH_{rDA} after 6 months, increasing substantially by 2–3 fold.

The $T_{g,}$ values for the networks formed from the bifunctional crosslinkers MDF and IPDF after 1 week at ambient temperature are considerably higher than the original UPE polyesters, due to the chemical crosslinks formed restricting the rotation of polymer segments. The higher T_g of the MDF networks can be rationalised by the higher rigidity of this aromatic crosslinker. This may also explain the enthalpic relaxation at the glass transition which only occurs for the MDF networks. However, the T_g obtained after 7 days was observed to decrease slightly for the polyester networks formed from the trifunctional aliphatic HMTF crosslinker. The hexamethylene arms increase the overall flexibility of the network, allowing more chain movement and hence, a lower T_g is observed. The T_g of all networks increases after further storage at ambient temperature, with the furan-maleate network from PPM and HMTF producing the largest increase (by +43 °C). This is also likely to result from the higher flexibility of this crosslinker.

Dynamic mechanical analysis (DMA) was used to highlight the differences in crosslinking between maleate and fumarate networks produced from PPM and PPF, respectively, caused by the different stereochemistry of the backbone. Only networks containing PPM + HMTF and PPF + HMTF were analysed (Fig. 2) because of the brittleness of the other networks being too high to make suitable tensile bar samples for analysis using DMA. The networks from PPM and PPF show the same modulus (3 GPa) in the glassy state. The T_g for the furan-maleate network (from PPM + HMTF) is significantly higher than the analogous furan-fumarate network (from PPF + HMTF), corresponding to the observations from DSC (previously, Table 1). Above T_g, the furan-fumarate network (PPF + HMTF) exhibits an inflection in modulus at approximately 1 MPa, with significant network dissociation at 80 °C followed by flow at approximately 90 °C. In complete contrast, the

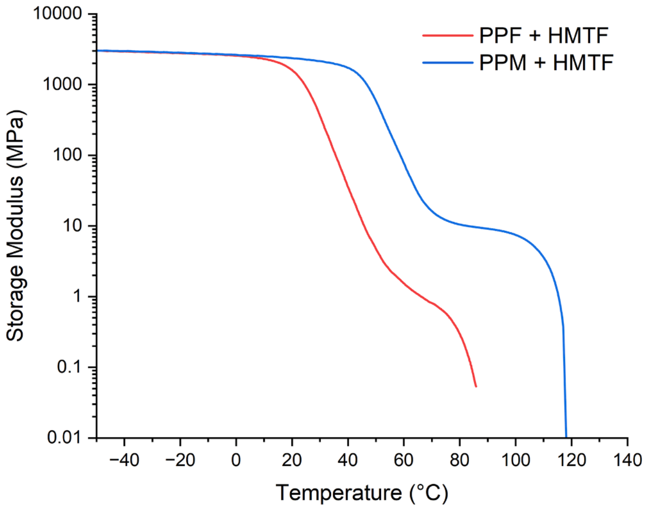


Fig. 2. DMA thermogram showing the different rubbery plateau of PPF + HMTF and PPM + HMTF.

furan-maleate network (PPM + HMTF) is mechanically stable above T_g to a much higher temperature, producing a pronounced flat rubbery plateau with a higher modulus of 10 MPa. This network begins to dissociate at a much higher temperature (110 °C) and begins to flow at approximately 120 °C. The magnitude of the storage modulus (E') in the rubbery region can be used to determine the molecular weight between crosslinks (M_c) Equation (1).

$$M_c = \frac{3RTd}{E'_{rubbery}} \tag{1}$$

where R is the universal gas constant, T is the absolute temperature and d is the density of the polymer. Since E' in the rubbery region is inversely proportional to M_c, a larger E' indicates a shorter chain length between crosslinks. With E' from the furan-maleate network above T_g (approx. 10 MPa) being an order of magnitude higher than the furan-fumarate network (approx. 1 MPa), the crosslinking density for the maleate network is therefore much higher than the fumarate network. The density of both networks was found to be 1.27 g cm^{-3} using helium pycnometry. From equation (1), M_c was determined as $M_c =$ 1130 g.mol^{-1} for the furan-maleate network and M_c = 10,680 g.mol^{-1} for the furan-fumarate network, showing the ineffective network formation in the latter.

The dissociation temperature of the furan-maleate network is remarkably similar to the dissociation temperature of related networks comprising furan-maleimide cycloadducts from bismaleimide prepolymers and trifunctional furan crosslinkers. [12,24] This has not been previously investigated in reversible CANs. The UPEs used as dienophiles are made from commercially available raw materials with high atom efficiency and are cost-effective for many industrial applications. In contrast, incorporating maleimide functional groups is relatively expensive since the ring closure to form the maleimides from the intermediates is less atom efficient and requires purification, making materials relatively expensive and unsuitable for large scale applications [26].

2.3. Solvent resistance

The increased stability of the furan-maleate cycloadduct over the furan-fumarate is also evident in the solvent resistance of the networks. An aliquot of each network (formed after 1 week at ambient temperature) was added to ethyl acetate or THF and left for a further week at ambient temperature, after which each sample had dissolved to varying degrees (Table S3). The solvent resistance was determined qualitatively by examining how much material remained undissolved and discolouration of the solvent (Figure S25, S26). Solvent resistance was observed to be best with the use of the trifunctional crosslinker (HMTF) compared to both bifunctional furan crosslinkers (MDF and IPDF). This is likely a consequence of increased crosslinking density and urethane/ester H-bonding hindering dissociation. Networks using an UPE with a maleate backbone provided better solvent resistance compared to networks using a fumarate-based UPE. It has been previously observed that solvent can slowly dissociate some networks because of the effect of concentration on the dynamic equilibrium. [27] Once a cycloadduct dissociates, the resultant DA pairs are then soluble at a low concentration, making it unlikely they will reform and can shift the dynamic equilibrium in favour of dissociation, which may lead to full dissolution.

Since both network T_g and T_{rDA} were found to increase with time, solvent resistance was also evaluated after 26 weeks, using Soxhlet extraction under identical conditions (Table 1). The starting linear UPE polyesters (PPF and PPM) and all of the furan-fumarate networks produced from PPF were completely soluble with no gel fraction (0%). This agrees with the previous report from Zhao *et al* who showed that networks made from UPE comprising fumarate groups were only partially formed with high dissolution ratios. [20] The Soxhlet extraction was performed at a temperature which is likely to be close to the dissociation temperature, accounting for the effect of heating rate. In contrast, the furan-maleate networks made from PPM produced different gel fractions depending on the type of multifunctional crosslinker (gel fractions 55%, 76% and 99% for networks from the multifunctional furan crosslinkers MDF, IPDF and HMTF, respectively). This further supports previous observations that furan-maleate networks formed from PPM are much more robust, with the more flexible and trifunctional HMTF providing the best network properties with a very high gel fraction. This correlates with the largest increase in T_g, the highest ΔH_{rDA} and the highest plateau modulus for this system, discussed previously. The density of functional groups on the UPE is relatively high (one unsaturation for each repeating unit) and may be constrained from reactivity to form cycloadducts, therefore the higher functionality and flexibility of the HMTF increases the likelihood of reaction of the furan with the alkene.

In order to investigate the hydrolytic stability of PPM + HMTF networks, samples were immersed in aqueous media of deionised water, 1 M HCl or 1 M NaOH for 48 h. Samples were weighed and dried for 48 h before being weighed again and also analysed by DSC. The soluble fraction and swelling ratio of the networks were found to be low, showing reasonable hydrolytic stability in the media tested (Table S4). Similarly, DSC analysis showed no change in thermal properties after immersion in any of the aqueous solutions (Figure S27 and Table S5).

2.4. Network reformation

A DSC experiment was conducted where the furan-maleate network from PPM + IPDF was dissociated by heating to a temperature of 150 °C for 10 min and then post-curing in ambient conditions. Different samples were taken from this material daily to undergo one heating cycle by DSC and the enthalpy of the T_{rDA} reaction was recorded (Fig. 3). The network showed an enthalpy change (ΔH_{rDA}) of 2.5 J.g^{-1} at the T_{rDA}, which remained similar for the first few days and increased to above 5 J.g^{-1} after 7 days. This is a relatively slow rate of formation, but it is comparable to maleimide and furan networks, which can also take a week or more to equilibrate.[24] Maleimide and furan addition is often considered “click chemistry”, so materials reacting at a similar rate whilst being maleimide free is noteworthy. [28] It is important to highlight that the T_{rDA} does not change after heating to 150 °C and remains consistent indicating that the maleate functionality does not isomerise under these conditions.

In a separate experiment, the same furan-maleate network made was subjected to multiple heating and cooling cycles via DSC (in the same sample pan), with 24-hour time periods between heating cycles to allow time for network reformation (Fig. 4a). In this case, the network was dissociated by heating to 180 °C at 10 °C.min^{-1} and equilibrating for 10 min. The networks were observed to reform every time, evidenced by the reappearance of the rDA endotherm after each cycle at 130 °C due to furan-maleate cycloadducts. However, the evolution of an additional endotherm just below 100 °C was observed after repeated heating cycles, indicating the increasing presence of furan-fumarate Diels-Alder cycloadducts. The enthalpy of the furan-fumarate rDA at lower temperature increased after each heat cycle, whilst simultaneously the original furan-maleate rDA enthalpy decreased. This suggests that after heating to 180 °C, some maleate isomerises to fumarate, during each cycloreversion, gradually changing the proportion of the unsaturation in the backbone to be more fumarate (Fig. 4b). This was confirmed *via* ^{1}H NMR spectroscopy with the appearance of the fumarate alkene proton resonances at δ = 6.85 ppm (maleate proton resonances occur at δ = 6.25 ppm). After a single heating to 180 °C, the data suggests that 5 % of the unsaturation isomerised to fumarate (as determined by the integration of the maleate resonance at δ = 6.25 ppm and the fumarate resonance at δ = 6.85). Heating PPM without crosslinker under the same circumstances did not show any isomerisation of the maleate to the fumarate, indicating that the cycloreversion facilitates the isomerisation at this higher temperature.

The rate of network reformation can be increased significantly by

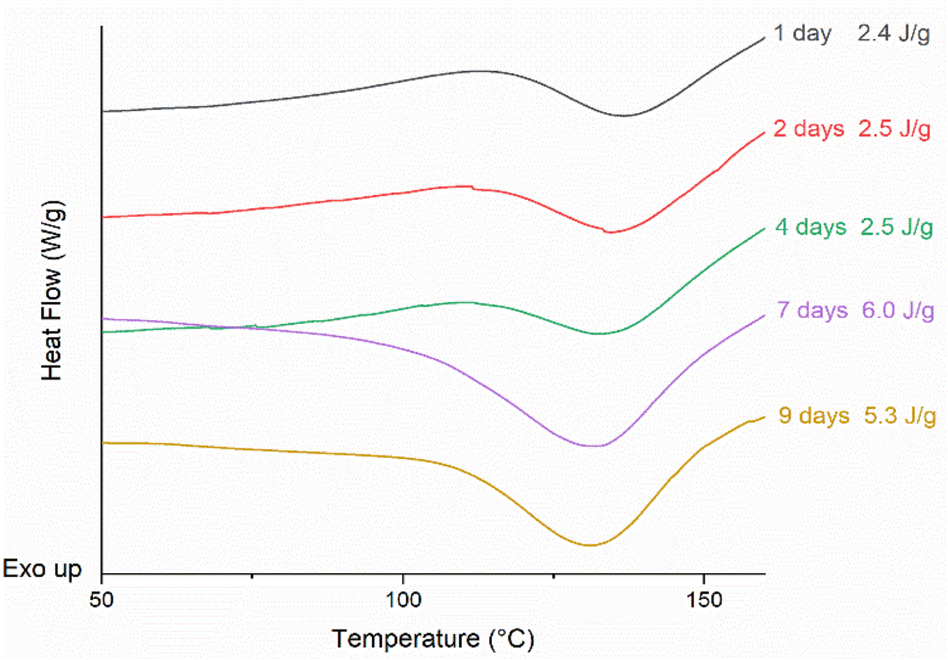


Fig. 3. The increase in the enthalpy change of rDA endotherms of PPM + IPDF with changing cure time at ambient temperature.

gentle heating. Such an effect has been observed for the cycloaddition of maleimides and furans, where the rate of reaction can be accelerated significantly by heating to 60 °C. Fresh samples of all materials were prepared, half of each network was cured overnight at room temperature and the other half was cured overnight at 65 °C. Analysis by DSC of the networks showed that the elevated temperature had minimal effect on the ΔH_{rDA} of the PPF-based furan-fumarate networks, whereas the PPM-based furan-maleate networks showed significant increases, independent of the type of multifunctional furan crosslinker (Fig. 5). The T_g of the furan-maleate networks made from PPM also increases significantly. It is likely that the higher curing temperature of 65 °C also affects the rate of the reverse DA reaction in the furan-fumarate networks which occurs at a lower temperature, counterbalancing the increase in rate of the forward DA cycloaddition. The heating rate of the DSC (10 °C.min^{-1}) used means there will be some thermal lag in the transitions observed, and the true T_{rDA} will be lower than shown by DSC at this heating rate. We previously observed this for networks involving cycloadditions of maleimides and furans. [24] The furan-maleate networks benefited remarkably from the increased curing temperature, reaching a ΔH_{rDA} of > 20 J.g^{-1}, a 4–10 fold increase. The previous data in Table 1 shows that at ambient temperatures, the materials take 1 week to reach a similar value for ΔH_{rDA}.

2.5. Mechanical properties

The networks produced were used to bond two aluminium substrates together in lap-shear joints. The samples were evaluated via tensile testing to determine the peak stress and extension of the joint at peak (Table 2). The network produced from PPF + HMTF showed a remarkably higher bond strength. This is likely to result from the additional flexibility provided by the HMTF trifunctional crosslinker (compared to the more rigid MDF and IPDF crosslinkers), reducing T_g and enabling deformation before failure. The average peak stress of 9.95 MPa (Figure S28) is similar to the bond strength achieved (approx. 10 MPa) when reporting the mechanical strength of aluminium substrates joined with poly(ester urethane) adhesives comprising Diels-Alder cycloadducts from maleimides and furans. [24].

The other networks displayed relatively low bond strength. As mentioned previously, the alkene content of the UPE backbones in PPM and PPF is high, comprising one unsaturation within each repeating unit. This means that access to all these functional groups for cycloaddition reactions could be challenging due to steric constraints. In order to dilute the alkene functionality on the UPE backbone, the distance between unsaturated groups in the polyester chain was investigated by synthesising different copolyesters of propylene glycol, replacing some of the unsaturated groups with succinate groups (Figure S4, S5, S6). Due to practical reasons, this was easier to perform *via* the classic step growth polymerisation – the succinate group is a saturated analogue of the fumarate group, allowing the dienophile to be separated with minimal effect on the overall chain composition. Increasing the distance between unsaturated groups on the backbone reduces the concentration of resulting Diels-Alder bonds, which is likely to lower crosslink density and the T_g. Additionally, succinate groups are more flexible than fumarate groups – whereas the π bond of the fumarate is locked in conformation, the σ bond of the succinate group can rotate, providing an increase in the flexibility of the material.[29].

Poly(propylene fumarate-*co*-propylene succinate) (PPF-PS) with a 50:50 M ratio of fumarate to succinate was synthesised through step-growth polymerisation in bulk from maleic anhydride, propylene glycol and succinic acid. This PPF-PS copolymer was combined in the melt with all three furan crosslinkers in an equimolar ratio of unsaturation to furan functionality to produce new UPE CANs with lower crosslinking density and greater flexibility (*via* lower f_g, Table 3). As expected, the resulting DSC thermograms of the networks taken a week after synthesis showed a clear decrease in T_g with a reduction in the concentration of fumarate. This increase in flexibility improves the bond strength by an order of magnitude for the original networks crosslinked with MDF and IPDF (0.72 MPa to 8.70 MPa and 0.72 MPa to 7.78 MPa, respectively – Figure S29, S30). In contrast, the incorporation of the succinate in the network crosslinked with HMTF suppresses the T_g to an extent that the original high bond strength reduces substantially, since the material is too ductile (Figure S31). This highlights how the performance of the UPE CANs can be significantly changed *via* manipulating T_g through a simple change in the composition of the polyester. From Table 3, the networks which provide high bond strength have a similar T_g (11–15 °C) – therefore it seems that the bond strength is highly dependent on T_g and independent of the crosslinker used.

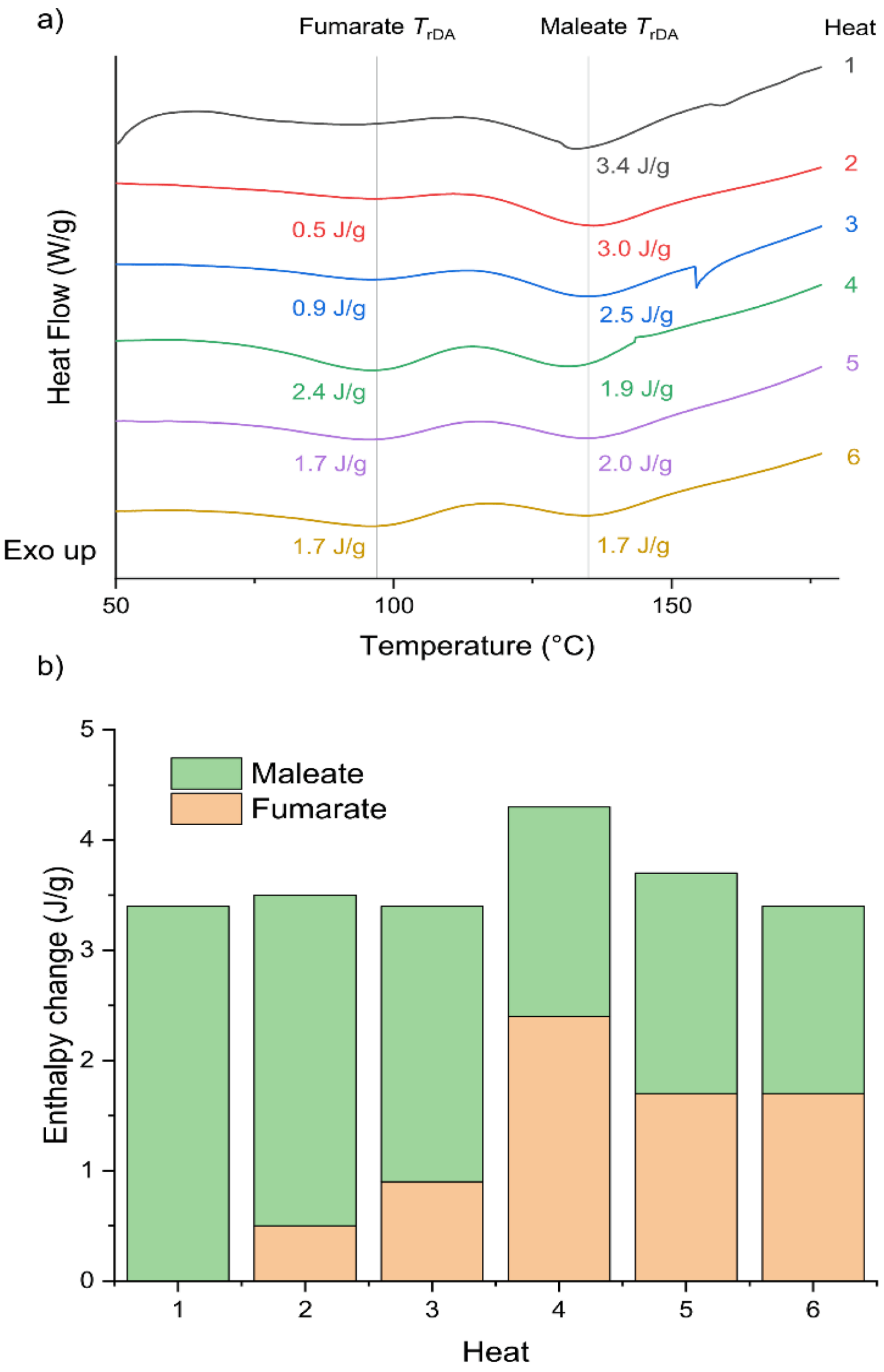


Fig. 4. (a) Repeated heating ramps on a single sample of PPM + IPDF to 180 °C, 24 h apart. (b) The maleate and fumarate content of the unsaturation in the polyester backbone after an increasing number of heating cycles.

2.6. *Comparing networks comprising furan-maleate cycloadducts to reference furan-maleimide cycloadducts*

Overall, our investigations indicate that Diels-Alder polymer networks comprising furan-maleate cycloadducts behave in a similar way to furan-maleimide cycloadducts reported in the literature: [12,24].

- Crosslinked networks are formed at ambient temperature with the rate of formation being increased by mild heating.
- The networks formed are robust with a gel fraction of > 95 %.
- DSC experiments indicate a dissociative temperature of 130 °C whereas DMA experiments (slower heating rate) indicate dissociation and material flow at 100 °C.
- The materials dissociate to a low viscosity fluid (20P) and reform on cooling.
- The materials are stable to 150 °C. At 180 °C, maleimide homopolymerisation occurs and maleate isomerises to fumarate.

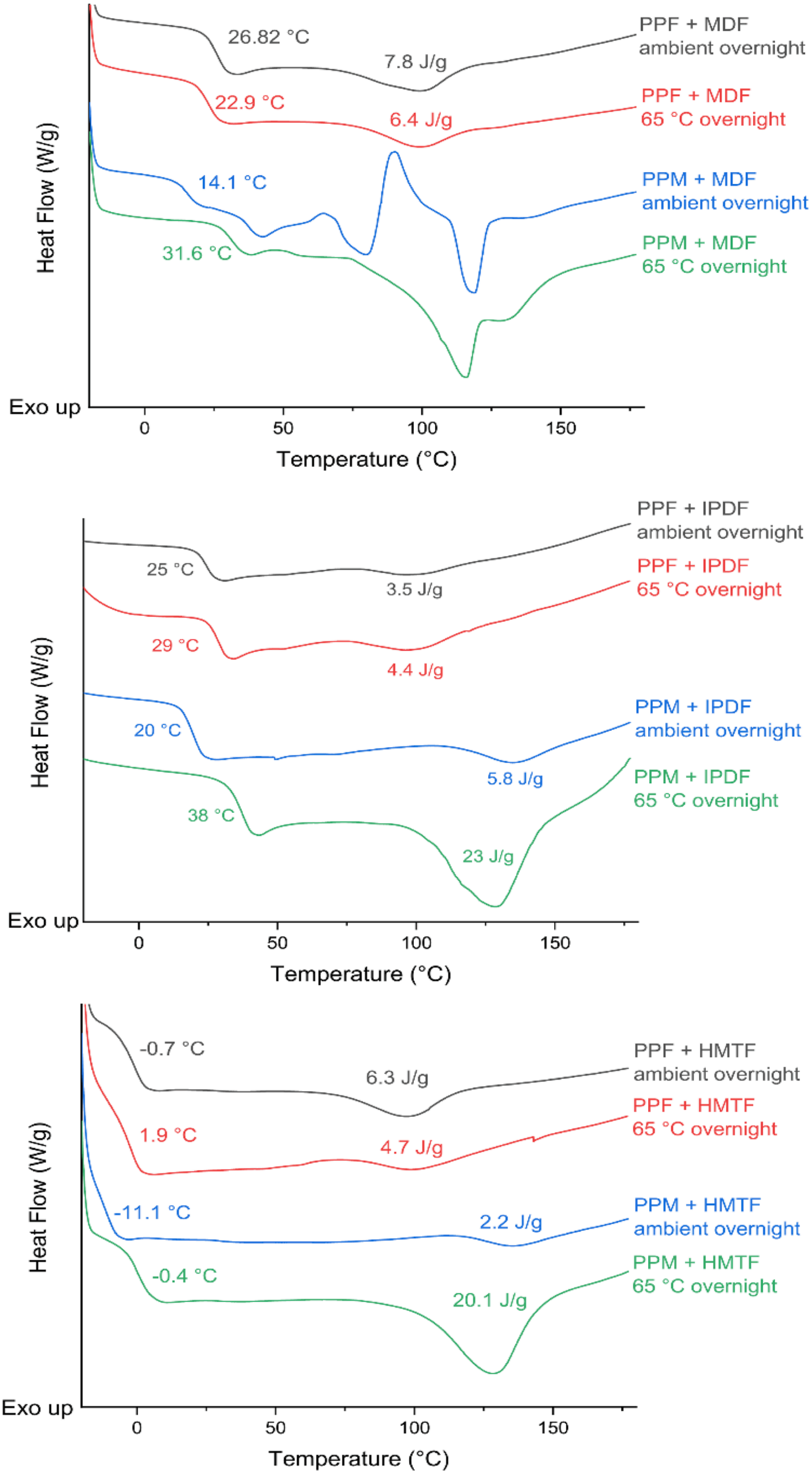


Fig. 5. The effect of curing at elevated temperatures on the ΔH_{rDA} and T_g of (a) MDF networks, (b) IPDF networks and (c) HMTF networks.

Table 2
Mechanical properties of the synthesised networks.

Material	T_g (°C)	Peak stress (MPa)[a]		Extension at peak (mm)[a]	
		Mean	± Standard deviation	Mean	± Standard deviation
PPF + MDF	27	0.72	0.08	0.03	0
PPF + IPDF	36	0.72	0.22	0.04	0.01
PPF + HMTF	11	9.95	0.47	0.93	0.08
PPM + MDF	25	0.79	0.13	0.04	0.01
PPM + IDPF	20	1.66	1.11	0.1	0.09
PPM + HMTF	2	0.38	0.09	1.29	0.26

[a] Lap shear joints were evaluated after application of the adhesive and conditioning at ambient temperature for 1 week to cure.

Table 3
Mechanical properties of the networks from PPF-PS comprising fewer alkene groups compared to previous networks from PPF.

Material	f_g[a] (mol. kg^{-1})	T_g (°C)	Peak stress (MPa)[b]		Extension at peak (mm)[b]	
			Mean	± Standard deviation	Mean	± Standard deviation
PPF + MDF	2.63	27	0.72	0.08	0.03	0
PPF-PS + MDF	1.87	15	8.70	1.24	0.71	0.24
PPF + IPDF	2.74	36	0.72	0.22	0.04	0.01
PPF-PS + IPDF	1.92	13	7.78	0.61	1.18	0.22
PPF + HMTF	2.37	11	9.95	0.47	0.93	0.08
PPF-PS + HMTF	1.73	2	1.48	0.19	0.82	0.26

[a] Concentration of alkene groups in the material. [b] Lap shear joints were evaluated after application of the adhesive and conditioning at ambient temperature for 1 week to cure.

While maleimides are often used as the dienophile in Diels-Alder reactions, there are limitations to their commercial exploitation due to the relatively high cost resulting from the challenges of atom efficiency and the need for purification to remove by-products. Unsaturated polyesters are very easy to manufacture with high atom efficiency in a safe and cost-effective manner. The range of possible polymer compositions is very broad, meaning that it is possible for material properties to be varied in a facile manner and finely tuned to meet a range of application requirements. We are now exploring a wider range of UPEs containing maleate functional groups, using step-growth polymerisation to change molecular weight and copolymer composition. Other multifunctional furan crosslinkers will be investigated to show the versatility of this approach, including non–isocyanate crosslinkers. The DSC data which shows network dissociation followed by reformation on cooling suggests that these systems are likely to self-heal using heat as a stimulus. Details of self-healing and reprocessing will be investigated further during future studies.

3. Conclusions

The synthesis of dissociative CANs produced from UPEs and multifunctional furan crosslinkers was achieved under industrially relevant conditions, with high atom efficiency. Both maleate- and fumarate-based UPEs were shown to form dissociative CANs with the T_{rDA} of networks comprising furan-maleate cycloadducts being significantly higher than furan-fumarate networks (approximately 130 ℃ and 100 ℃, respectively) by DSC. Both the T_g and T_{rDA} increased after network formation with the largest effect produced by the flexible tri-functional crosslinker. The furan-maleate network from this crosslinker was more robust, producing a high gel fraction (99 %) and a stable plateau modulus of 10 MPa by DMA. The networks can be easily dissociated with heat and reformed multiple times, as shown by the reappearance of a *retro*-Diels-Alder endotherm in each heating run. The networks repeatedly reformed after heating to 150 °C, whereas isomerisation of maleates into fumarates was observed at 180 °C. The rate of reformation of cycloadducts and resulting networks can also be accelerated substantially by applying mild heating at 65 °C. The materials can be used as adhesives, producing bond strengths (approx. 10 MPa) comparable to dissociative CANs made from furans and maleimides. Bond strength can be changed significantly by manipulating T_g through a small change in the copolymer composition to enable higher flexibility. Overall, the data suggests that maleates could be used as an alternative dienophile to maleimides in the thermally reversible formation of Diels-Alder cycloadducts, overcoming the limitations of low atom efficiency and high cost.

CRediT authorship contribution statement

Jonathan B.D. Gregg: Writing – review & editing, Validation, Methodology, Investigation. **James A. Wilson:** Writing – original draft, Supervision, Methodology. **Steven L. Brown:** Supervision, Resources, Methodology. **Andrew T. Slark:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

A.T.S. thanks the EPSRC for a Manufacturing Fellowship (EP/R012121/1) and a Doctoral Training Partnership CASE award for J.B.D. G. Scott Bader Ltd is thanked for support of this PhD studentship and for permission to publish this work. We thank Matthew L. Becker (Duke University) for providing poly(propylene maleate) samples for evaluation.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2024.113195.

References

[1] Statista, Production of polyester fibers worldwide from 1975 to 2022, https://www.statista.com/statistics/912301/polyester-fiber-production-worldwide/, (accessed 10/03/2023).

[2] C. Jehanno, I. Flores, A.P. Dove, A.J. Müller, F. Ruipérez, H. Sardon, Green Chem. 20 (2018) 1205–1212.

[3] T. Composites, https://www.tricelcomposites.co.uk/blog-polyester-resin/, (accessed 10/03/2023).

[4] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Angew. Chem. Int. Ed. Engl. 59 (2020) 15402–15423.
[5] L.G. Curtis, D.L. Edwards, R.M. Simons, P.J. Trent, P.T. Von Bramer, Ind. Eng. Chem. Res. 3 (1964) 218–221.
[6] I. Vancsó-Szmercsányi, K. Maros-Gréger, E. Makay-Bödi, J. Polym. Sci. 53 (1961) 241–248.
[7] C.J. Kloxin, T.F. Scott, B.J. Adzima, C.N. Bowman, Macromolecules 43 (2010) 2643–2653.
[8] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Science 334 (2011) 965–968.
[9] G.M. Scheutz, J.J. Lessard, M.B. Sims, B.S. Sumerlin, J. Am. Chem. Soc. 141 (2019) 16181–16196.
[10] J.M. Winne, L. Leibler, F.E. Du Prez, Polym. Chem. 10 (2019) 6091–6108.
[11] M.A. Tasdelen, Polym. Chem. 2 (2011) 2133–2145.
[12] A. Gandini, Prog. Polym. Sci. 38 (2013) 1–29.
[13] R. Wojcieszak, F. Santarelli, S. Paul, F. Dumeignil, F. Cavani, R.V. Gonçalves, Sustain. Chem. Proccess. (2015) 3.
[14] X.K. Li, B. Ho, D.S.W. Lim, Y.G. Zhang, Green Chem 19 (2017) 914–918.
[15] S. Bains, R.M. Pagni, G.W. Kabalka, Tetrahedron Lett. 32 (1991) 5663–5666.
[16] M.G. Silvestri, C.E. Dills, J. Chem. Educ. (1989) 66.
[17] N. Windmon, V. Dragojlovic, Green Chem. Lett. Rev. 1 (2008) 155–163.
[18] T.A. Eggelte, H. de Koning, H.O. Huisman, Tetrahedron 29 (1973) 2491–2493.
[19] V.N. Huynh, M. Leitner, A. Bhattacharyya, L. Uhlstein, P. Kreitmeier, P. Sakrausky, J. Rehbein, O. Reiser, Commun Chem 3 (2020) 158.
[20] D. Wang, S. Chen, J. Zhao, Z. Zhang, Mater. Today Commun. (2020) 23.
[21] A.P. Fradet A, in Comprehensive Polymer Science, Pergamon Press, 1 edn., 1989, vol. 5, ch. 19, pp. 331-334.
[22] S. Paul, Y. Zhu, C. Romain, R. Brooks, P.K. Saini, C.K. Williams, Chem Commun (camb) 51 (2015) 6459–6479.
[23] J.A. Wilson, D. Luong, A.P. Kleinfehn, S. Sallam, C. Wesdemiotis, M.L. Becker, J. Am. Chem. Soc. 140 (2018) 277–284.
[24] L.M. Sridhar, M.O. Oster, D.E. Herr, J.B.D. Gregg, J.A. Wilson, A.T. Slark, Green Chem 22 (2020) 8669–8679.
[25] R.C. Cioc, M. Crockatt, J.C. van der Waal, P.C.A. Bruijnincx, Angew. Chem. Int. Ed. Engl. 61 (2022) e202114720.
[26] B. Ma and Q. Tong, European patent EP0969063B1, 1999.
[27] A.D. Pehere, S. Xu, S.K. Thompson, M.A. Hillmyer, T.R. Hoye, Org. Lett. 18 (2016) 2584–2587.
[28] N.K. Devaraj, M.G. Finn, Chem Rev 121 (2021) 6697–6698.
[29] G.F. Bass, Y. Shin, M.L. Becker, Macromolecules 54 (2021) 1273–1280.