Novel Bio-based Branched Unsaturated Polyester Resins for High-Temperature Applications

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Abstract

Unsaturated polyester resins, one of the most important thermosets, are invariably produced from oil-based monomers. Their application is limited in areas where high thermal stability is required due to their low T_g. Besides, these resins contain 30–40% hazardous styrene as a reactive solvent. Therefore, developing bio-based solventless unsaturated polyester resin with medium to high thermomechanical properties compared to petrochemical-based counterparts is important. In order to achieve this, a series of branched bio-based unsaturated polyester resins were synthesized using bulk polymerization method in two steps. In the first step, four different intermediates were prepared by reacting glycerol (as a core molecule) with either isosorbide (diol), 1,3-propanediol (diol), 2,5-furandicarboxylic acid (saturated diacid), or adipic acid (saturated diacid). In the second step, the branched intermediate was end capped with methacrylic anhydride to introduce reactive sites for cross-linking on the branch ends. The chemical structure of the resins was characterized by ^{13}C-NMR. FT-IR confirmed the poly-condensation reaction in the first step and the end functionalization of the resins with methacrylic anhydride in the second step. The effect of 2,5-furandicarboxylic acid and isosorbide on thermomechanical and thermal properties was investigated using dynamic mechanical analysis, differential scanning calorimetry, and thermo-gravimetric analysis. Results indicated that 2,5-furandicarboxylic acid based resins had superior thermomechanical properties compared to a commercial reference unsaturated polyester resin, making them promising resins for high-temperature composite applications. For example, the resin based on 2,5-furandicarboxylic acid and isosorbide and the resin based on 2,5-furandicarboxylic acid and 1,3-propan-ediol gave glass transition temperatures of 173 °C and 148 °C, respectively. Although the synthesized 2,5-furandicarboxylic acid based resins had higher viscosity (22.7 Pas) than conventional unsaturated polyester (0.4–0.5 Pas) at room temperature, preheated resins can be used for making high-temperature-tolerance fiber-reinforced composite.

Keywords Bio-based unsaturated polyester resins · Isosorbide · 2,5-Furandicarboxylic acid · High-T_g

Introduction

Nowadays, there is growing interest in using bio-based monomers to synthesize polymers. Despite the rather good availability of renewable raw materials, they are more expensive than oil-based alternatives due to the complexity of feedstock production, competition with other industries for resources and policy and regulation. These disparities can result in increased polymer production costs, potentially impacting the price of renewable polymers, market competitiveness, and the adoption of sustainable materials in various industries. However, recent advancements in the knowledge, development of techniques for extracting monomers from bio-based sources and supportive policies provide viable options for sustainable polymer production [1–5]. Unsaturated polyesters (UPE), which are the most common general purpose thermoset resins, are frequently used in the manufacturing of fiber-reinforced composites for marine, construction, and transportation applications and are also used in the coating and adhesives industry [6, 7]. For the synthesis of unsaturated polyester resins, fossil-based monomers such as phthalic anhydride, maleic anhydride, diethylene glycol, and 1,2-propylene glycol are used commercially. Challenges with fossil-based monomers include environmental concerns, resource depletion, price volatility,

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geopolitical dependency, limited sustainability, regulatory pressures, and changing consumer preferences [8–10]. These monomers could be replaced with bio-based alternative monomers such as 2,5-furandicarboxylic acid (FDCA), succinic acid (SA), adipic acid (AD), itaconic acid (IT), lactic acid, various vegetable oils, as well as sugar-based diols such as 1,3-propanediol (PD), ethylene glycol (EG), glycerol (GLY) and isosorbide (IS) [11–14]. However, replacing traditional monomers with bio-based monomers is an immense task. Many commercial thermoset resins contain aromatic components that are difficult to replace with bio-based monomers. Traditional orthophthalic unsaturated polyesters are synthesized from aromatic monomers. Aromatic structures impart stiffness to the resin. They exhibit natural rigidity and planarity. This inherent rigidity hinders the easy bending or rotation of the rings within the polymer chain, effectively rendering them as immobile, inflexible segments in the polymer backbone, consequently leading to increased stiffness. Widespread efforts have been made to find suitable bio-based alternatives for oil-based monomers. For example, Dai et al. synthesized a series of bio-based UPEs based on IT for bio-based coating applications [15]. Bojana et al. produced 100% bio-based UPEs from IT and dialkyl itaconates as a reactive diluent [16]. Thermoset resins made from lactic acid and lactide have also been reported [11, 17–20]. However, finding suitable aromatic structures in nature proves to be quite challenging. For that reason, both FDCA and IS are cyclic, stiff structures which have attracted much attention and several studies have examined the synthesis of thermoplastic resins [21–27]. Although FDCA is still comparatively expensive in the market, there has been a significant decrease in prices in recent years as the production of FDCA as a renewable furan building block has increased and its utilization in plastic manufacturing has grown [28–30]. Besides, integrating FDCA and IS into existing industrial processes and infrastructure may require modifications and adaptations, and addressing these challenges would require research and development efforts.

Unsaturated polyester resins containing FDCA or IS have shown supreme mechanical and thermomechanical properties [12, 28]. Sadler et al. [31] synthesized phthalic anhydride based UPE using IS as a comonomer through the polycondensation reaction with attention to the effects of increasing IS concentration on the properties of resin. They found that increasing the concentration of IS significantly increased the T_g and moduli of the cured resin and also causes an increase in the viscosity of the uncured resin. Xu et al. [32] developed a new UPE and reactive diluent, both based on IS. They found that the resin had better mechanical and thermal properties than commercial and most reported bio-based UPEs. By incorporating IS into both the UPE and RD, they aimed to reinforce the stiffness of the resulting thermosets and alleviate the common

solubility challenges faced by biobased UPEs and styrene. Noordover et al. [33] synthesized polyesters based on succinic acid and isosorbide with T_g values in the appropriate range for coating applications. Lomelí-Rodríguez et al. [25] successfully created coil coatings polyester resins using entirely biomass-derived materials such as IS, FDCA, SA, and 1,5-pentanediol. Rather than extensively detailing the compositions or conducting chemical characterization, the main goal of the project was to examine the practicality of the bio-based coatings. Thus, common mechanical testing methods were employed to assess their performance. The study revealed that incorporating isosorbide into the coil coatings led to improved thermomechanical properties. Sadler et al. [34] used isosorbide as a structural constituent to provide stiffness from the diol component in UPE instead of using oil based aromatic rings such as terephthalic acid and orthophthalic acid. The resins synthesized through the polycondensation of a mixture of diols and diacids. These prepolymers are then blended with styrene. They showed that increased isosorbide content does have a positive effect on T_g and storage modulus. Hofmann et al. [35] developed unsaturated polyester prepolymers based on biobased isosorbide and petroleum-derived phthalic anhydride. In order to make the resin more environmentally friendly and less toxic, it was diluted with a mixture of 2-hydroxyethyl methacrylate and styrene, rather than using only styrene. The resulting crosslinked resins showed similar mechanical and thermomechanical properties as their petrochemical-based counterparts. It had a tensile strength of 62.1 MPa and an elasticity modulus of up to 3.9 GPa. Additionally, the resins had glass transition temperatures reaching 106 °C. Sousa et al. [36] synthesized FDCA-based UPE by noncatalyzed bulk polycondensation. The obtained crosslinked resin was thermally stable up to 230 °C and exhibited relatively high T_g and storage moduli. Additionally, instead of styrene, 2-hydroxyethylmethacrylate was used as the reactive solvent. Dai et al. [37] introduced range of fully biobased UPEs derived from FDCA, IT, SA, and PD were obtained via direct polycondensation. Results showed that the flexural strength, modulus and thermal properties of the cured resins were greatly improved after the introduction of FDCA with the potential to replace oil-based UPE.

Finally, resins for fiber-reinforced composites should have appropriate viscosity to guarantee the complete impregnation of the fibers. The conventional approach has largely involved diluting the polyester prepolymer into styrene. Styrene is identified as a hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). Widespread efforts have been made to find suitable bio-based reactive diluents to replace with styrene but one of the less studied ways is a synthesis of solventless UPEs [38–42]. The aim of the current study was to investigate the possibility of producing branched bio-based UPE without using reactive diluent with

thermomechanical properties comparable to the commercial fossil-based UPE used today. Branched low molecular weight polymer intermediates were synthesized with glycerol as a branching point, with FDCA as a rigid skeletal and aromatic structure, and IS as a unique bicyclic rigid structure to increase thermomechanical properties. Methacrylic anhydride (MAAH) was used to end cap the resins and to act as reactive cross-linking sites. To evaluate the effect of FDCA and IS on the mechanical and thermomechanical properties, four different bio-based UPE resins were synthesized: AD as diacid and IS as a glycol, AD as a diacid and PD as a glycol, FDCA as diacid and IS as glycol, and FDCA as diacid and PD as glycol. The synthesized resins were characterized by FT IR, ^{13}C NMR, DMA, TGA, and DSC techniques.

Experimental

Materials

The intermediates in the first step were synthesized from 2,5-furan dicarboxylic acid (Apollo scientific), adipic acid (99%, Sigma-Aldrich), isosorbide (98%, Acros), 1.3-propanediol (98%, Sigma-Aldrich) and glycerol (99%, Sigma-Aldrich). Tin (II)-2-ethyl hexanoate (95%, Sigma-Aldrich) was used as a polyesterification catalyst in this step. End functionalization was performed with methacrylic anhydride ($\geq$ 94%; Sigma-Aldrich). Hydroquinone (99%, Sigma-Aldrich) was used as an inhibitor to prevent crosslinking during the second synthesis step. The reactions were done under an inert nitrogen atmosphere (N$_2$, 99.5%). Acid number titration was performed in a xylene ($\geq$ 98.5%; Sigma-Aldrich) and isopropyl alcohol (99.8%; Sigma-Aldrich) mixture (1:1), with 0.02 M potassium hydroxide ($\geq$ 85%; Sigma-Aldrich) solution in absolute ethanol (VWR Chemicals) as the titrant (standardized with potassium hydrogen phthalate [99.95%; Sigma-Aldrich]) and phenolphthalein (98.5%; Acros), (1% solution in ethanol) as the indicator. Luperox® P (tert-butyl peroxybenzoate, 98%; Sigma-Aldrich) was used as an initiator for the crosslinking of the resins. CRYSTIC 115 NT (Scott Bader), which is a medium reactive orthophthalic polyester resin containing 30–40 wt% styrene, was used as a reference resin.

Synthesis

All unsaturated bio-based polyester resins were synthesized through the bulk polymerization method in two steps. Firstly, 0.033 mol GLY, 0.1 mol FDCA, and 0.11 mol IS were directly introduced into a three-necked round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet, and a thermometer. The flask was heated to 150 °C and tin (II)-2-ethyl hexanoate (0.2% w) was added

to the mixture. The temperature was gradually increased to 200 °C and the reaction was left to proceed under constant nitrogen flux until the complete homogenization of acid and diols (formation of transparent mixture, 15 h after starting the reaction). The reaction progress was then monitored by acid value titration until a constant acid value was reached. This step took 48 h to complete. The same procedure with the same molar ratio for acid and glycol was used to synthesize intermediates from FDCA/PD, AD/IS, and AD/PD with GLY, and the corresponding synthesis steps took 11, 23, and 11 h, respectively.

Figure 1 shows the idealized structures of the synthesized branched intermediates. In the second step of the synthesis, the reaction solution was first cooled to 110 °C. Hydroquinone (0.3 w % of total monomers mass) was then added to the mixture as an inhibitor while stirring. MAAH (0, 11 mol) was added dropwise, and the temperature was kept at 110 °C for 4 h. This step was the same for all resin syntheses. The ideal structure of targeted resins end functionalized with MAAH is presented in Fig. 2.

Curing of the Resins

The resin was mixed with 2.0 wt% of high-temperature-activated peroxide (Luperox® P) and placed in a 130 °C preheated oven for 10 min. Subsequently, the mixture was poured into a Teflon mold and placed in a 150 °C preheated oven for 30 min. The samples were removed from the mold for further property characterization.

Characterization Techniques

Fourier transform infrared (FTIR) spectra of samples from the first and second step of the synthesis and the cured resins were obtained at room temperature on an FTIR (Nicolet i S10 supplied by Themo Fisher) spectrometer. The wavenumber range was 4000–600 cm^{-1} and spectra were recorded after being scanned 64 times. A thermogravimetric analyzer TGA (Q500 from TA Instruments supplied by Waters LLC) instrument was employed to characterize the thermal stability of the cured resins. About 8–15 mg of cured resin was heated from room temperature to 600 °C, at a heat rate of 10 °C/min under a nitrogen environment. Differential scanning calorimetry (DSC) measurements were carried out on a TA Instrument DSC Q 1000 apparatus. Samples of approximately 4–8 mg were put in aluminum pans. Both cured and uncured resins (mixed with 2% peroxide) were analyzed with DSC. Samples were heated from 0 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Dynamic mechanical analysis (DMA) was done on cured samples using a Q800 from TA Instruments (supplied by Waters LLC). Samples of approximately 35 mm length, 5 mm width,
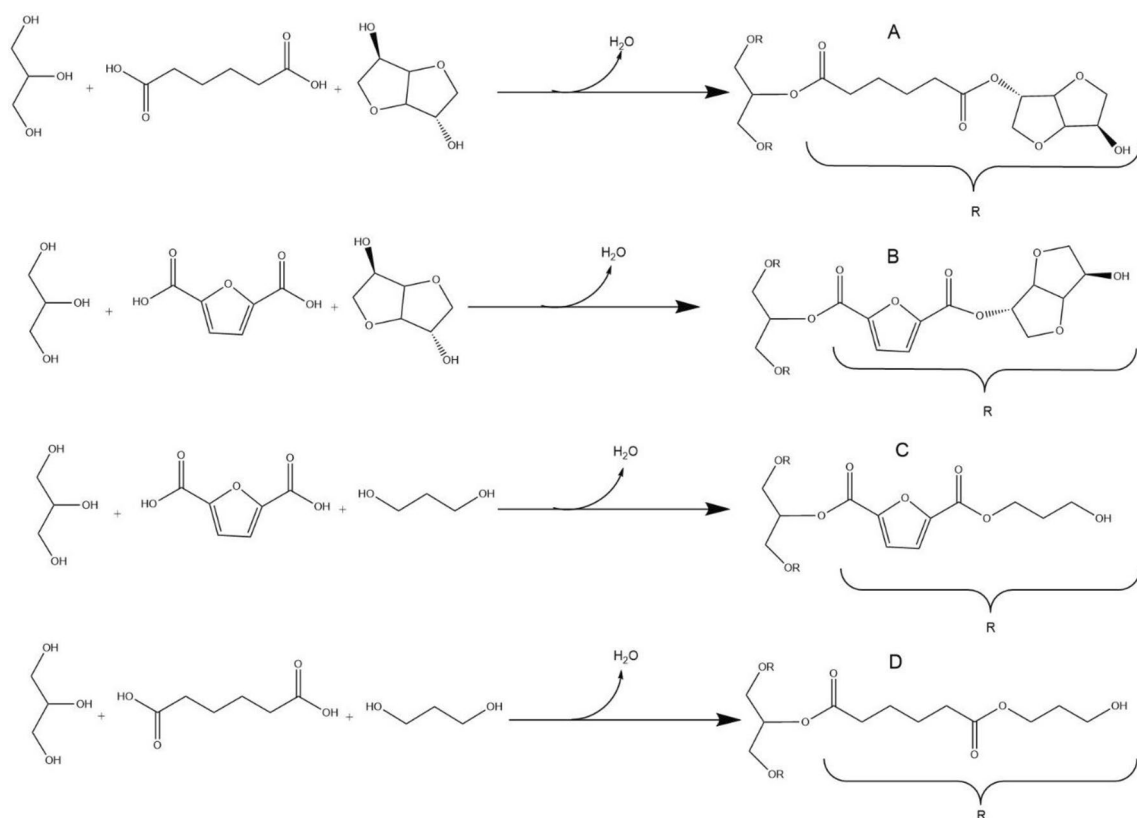
Fig. 1 An idealized structure of synthesized star-shaped intermediates

and 2 mm thickness were put in a single cantilever bending clamp and heated from − 25 to 250 °C under inert atmosphere (N_2 gas) with a heating rate of 3 °C/min; the amplitude was 15 µm and the frequency was 1 Hz. A modular compact rheometer (Physica MCR 500) was used to analyze the rheological properties of the resins. The analysis was performed in rotational mode and with a truncated cone plate configuration for measurements. The test was run with shear stress ranging from 0.5 to 2 Pa from room temperature to 120 °C. The acid number titration method was employed to monitor the residual carboxyl groups of the reactants during the progress of the reaction in the first synthesis step. An adequate amount of sample (0.1–0.2 gr) were diluted in 20 mL of 1:1 *v/v* xylene/isopropyl alcohol solutions and titrated with 0.02 M KOH solution in absolute ethanol in the presence of a few drops of 1% phenolphthalein in ethanol as an indicator. The acid number was calculated using the volume of KOH solution that had been used. The synthesized resins were dissolved in $CDCl_3$ and examined using ^{13}C NMR (Bruker Advance III HD Spectrometer) at 850 MHz equipped with a cryogenic probe head. The ^{13}C NMR was recorded using inverse-gated decoupling with 70° excitation pulse and a 30-s relaxation delay. Between 48 and 60 transients were

acquired. These experimental conditions were considered to give approximate quantitative ^{13}C NMR spectra.

Results and Discussion

Viscosity

The processing conditions of thermoset resins depend on their viscosity. Low viscosity is required for most of the industrially used processing methods for composite manufacturing, such as spray and hand lay-up, pultrusion, vacuum infusion, and filament winding. High viscous resins are also challenging to process, as it can result in poor reinforcement impregnation. The viscosity of the resins was monitored using stress viscosimetry from room temperature to 120 °C. Figure 3 represents the viscosity of FDCA/IS, AD/IS, and AD/PD resins. The viscosity of the resins was substantially reduced with increasing temperature. FDCA/IS and AD/IS resins showed approximately similar behavior. Both resins have IS incorporated in the structure, which is a bent molecule with a fused bicyclic ring that is constrained in its conformation. Moreover, the oxolane ring in the fused bicyclic ring can form hydrogen bonds, leading to
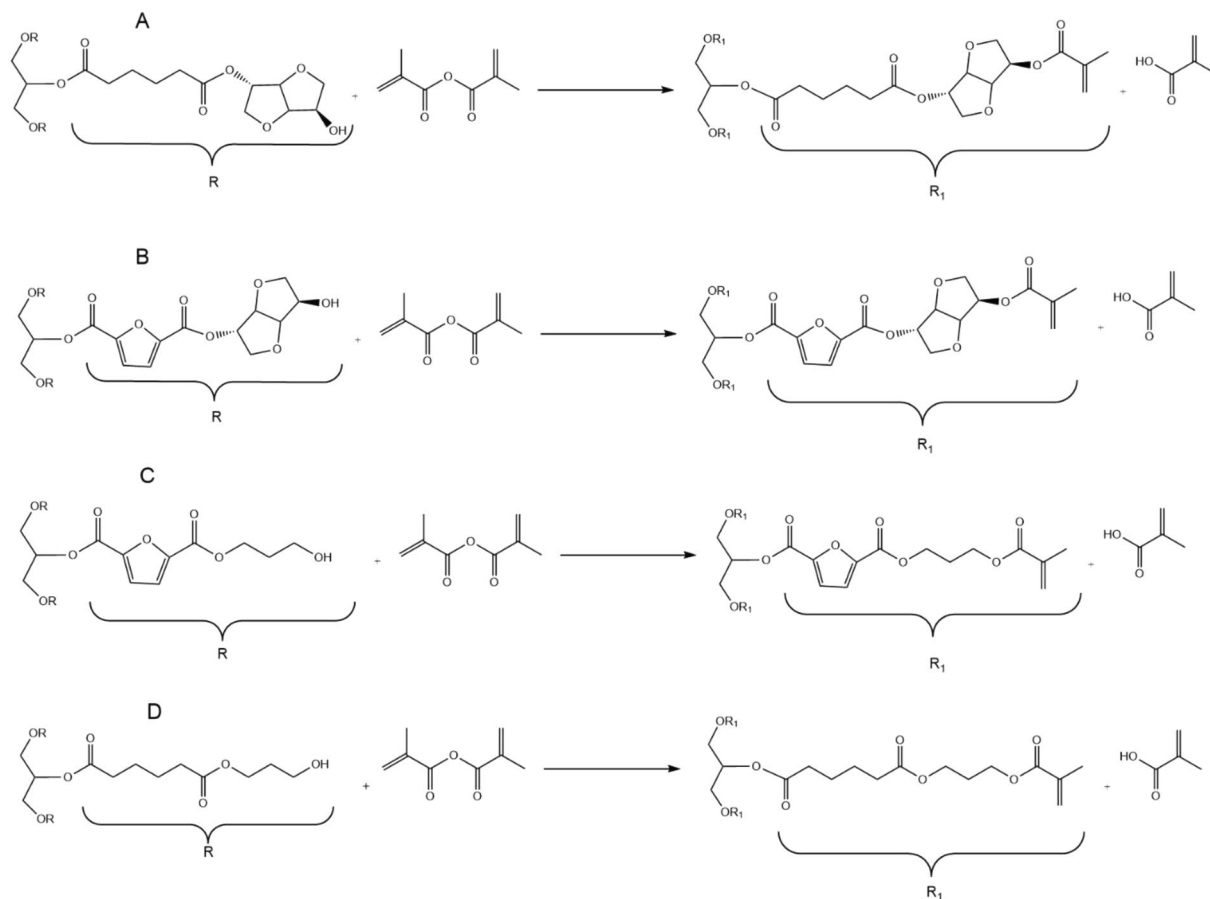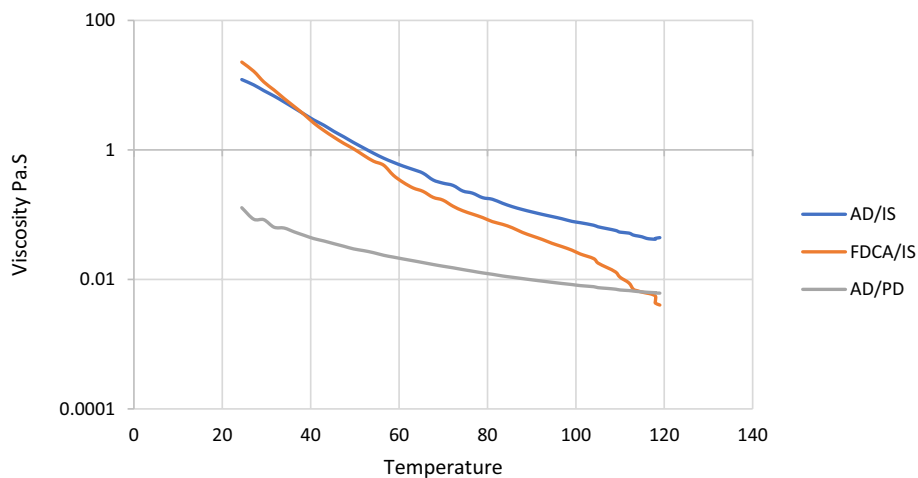
Fig. 2 The idealized structure of obtained resins end functionalized with MAAH

Fig. 3 Viscometry results of the FDCA/IS, AD/IS, and AD/PD resins

more interactions within the chains and ultimately resulting in increased viscosity of the resin [31]. The viscosity of commercial UPE preblended with 38–42% styrene as a reactive diluent is 0.4–0.5 Pas at room temperature based on the supplier's datasheet [43] (the results are 22.7, 12.2 and 0.128 Pas for FDCA/IS, AD/IS and AD/PD respectively)

and at about 50 °C the FDCA/IS and AD/IS resins reach that viscosity. A viscosity range of 0.2–0.6 Pas is commonly used for hand lay-up and spray-up processes. For resin infusion or vacuum infusion processes, a lower viscosity in the range of 0.1–0.2 Pas may be preferred to allow for better impregnation of the reinforcement material. In comparison

to price of styrene and its health and environmental issues, heating the bio-based resin without styrene to 50 °C could be a reasonable option. The viscosity of AD/PD is lower than that of commercial UPE. The possible explanation for that could be the linear structure of AD and PD which leads to lower amount of hydrogen bonds in resin in comparison to FDCA/IS and AD/IS resin. The FDCA/PD resin was very viscous at room temperature and its viscosity could therefore not be measured. FDCA also increases the viscosity of resin [25, 28]. From the geometrical point of view and chain topography, two non linear structure in resin can neutralize each other´s effect. It could be a possible explanation for higher viscosity in FDCA/PD in comparison to FDCA/IS.

Acid Number Titration

Reaction time is a critical factor in all polycondensation reactions. Insufficient reaction time leads to unreacted reactants, whereas excessively long reaction times may result in transesterification reactions and polymer degradation [44]. In this study, the progress of the condensation reaction in the first step was followed by titration according to ASTM D974-12. In this method, the acid number is measured as the quantity of KOH (in mg) which is required to reach the equivalent point when titrating 1 g of the resin dissolved in xylene/isopropyl alcohol solvent. Figure 4 demonstrates the acid number of reaction mixture in the first step for FDCA/

IS, FDCA/PD, AD/IS, and AD/PD resins versus time. The time of reaction in the first step is very high for FDCA/IS and AD/IS resins (48 and 23 h, respectively). The poor reactivity of IS could be assigned to the presence of both exo- and endo-oriented hydroxyl groups in the IS structure. This orientation leads to the formation of intramolecular hydrogen bonds which results in a lower nucleophilicity of the OH groups [31, 45].

Fourier-Transform Infrared Spectroscopy

The polycondensation reaction in the first step, the end functionalization of the resins with methacrylic anhydride in the second step, and the curing reaction of the resins were verified by FT-IR. Figure 5 demonstrates obtained FT-IR spectra for FDCA/PD resin. The peak assigned to the hydroxyl group of the hydroxyl-terminated intermediate produced in the first step, was observed as a broad peak at 3448 cm^{-1}. The large peak at 1725 cm^{-1} is assigned to the carbonyl group of the formed ester (Fig. 5A). Successful production of UPE resin was further confirmed by the emerging peaks at 1635 cm^{-1}, 977 cm^{-1}, and 1785 cm^{-1} (C=C stretching, =CH_2 bending and second formed C=O group of polyester respectively) and the disappearing peak at 3448 cm^{-1} (hydroxyl group) (Fig. 5B). Because the produced resins were cured by a free radical reaction, the carbon–carbon double bond peaks at 1635 cm^{-1} disappeared (Fig. 5C). FDCA/IS, AD/PD, and
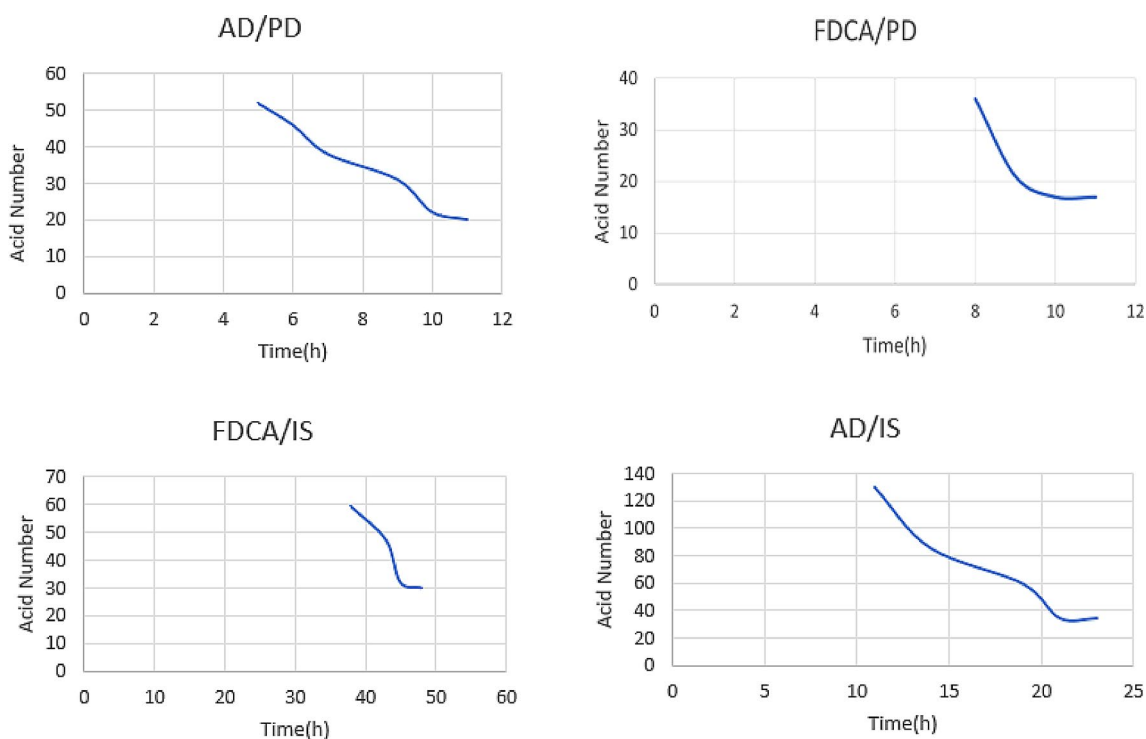

Fig. 4 The acid number curves from acid–base titration for resins
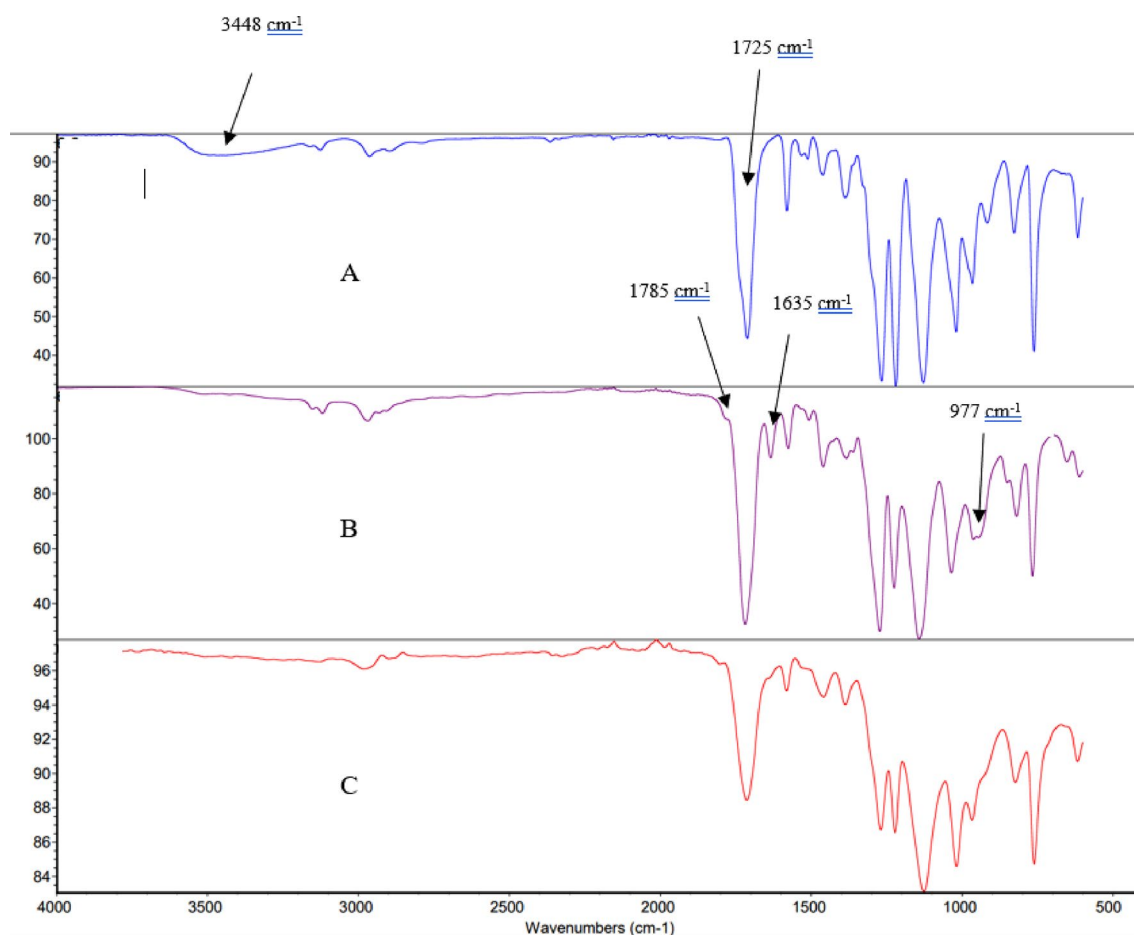
Fig. 5 FTIR results for **A** the first step of the reaction, **B** end-capped resin with MAAH in the uncured state, and **C** final cured FDCA/PD resin

AD/IS resins followed the same pattern and are shown in the Supplementary material.

Nuclear Magnetic Resonance (NMR)

The synthesized resins were characterized by NMR and Fig. 6 shows the quantitative ^{13}C NMR spectra for all four samples. More detailed assignments can be found in the Supplementary material section. From these spectra, the carbonyl area can be used to determine the relative amounts of unreacted MAAH, unreacted methacrylic acid (MA), and reacted MA in each sample (see Supplementary material). It is feasible to ascertain the extent of the reaction of the FDCA and AD acid groups.

In the aliphatic carbon area at 55–85 ppm, detailed assignments of the peaks allow for the determination of how many OH groups have reacted from the IS and PD and also the type of reacted glycerol components formed as a result of the reaction of the three OH groups on the glycerol (see Supplementary material). The results from these calculations are shown in Tables 1, 2, 3, and 4 below.

The number of reacted OH groups from the diols and acid groups from the diacids are fairly consistent throughout the samples and the amount of reacted MA is similar. The ratio of the amounts of residual MA and MAAH varies somewhat.

Conclusions about the distribution of the various reacted glycerol components should be made with caution. Although literature shifts were used as a guide [46], a direct comparison is problematic since the intensities of the glycerol carbon peaks are very weak, there is quite a variation in the type of reacted acyl groups on the glycerol, and it is not completely clear if the literature shifts used here correspond exactly with the shifts observed in the samples analysed.

The figures in Table 4 show that the samples with the FDCA have the most MAG. The higher proportion of glycerol present as MAG could be expected, since after the first FDCA has reacted with the glycerol this might inhibit further FDCA reaction with the glycerol due to steric hindrance. Further work needs to be conducted using simple model systems to check this.

Fig. 6 Quantitative 13C NMR spectra of the AD-IS, AD-PD, FDCA-PD, and FDCA-IS resins. *IS* isosorbide, *PD* propanediol, *G* glycerol
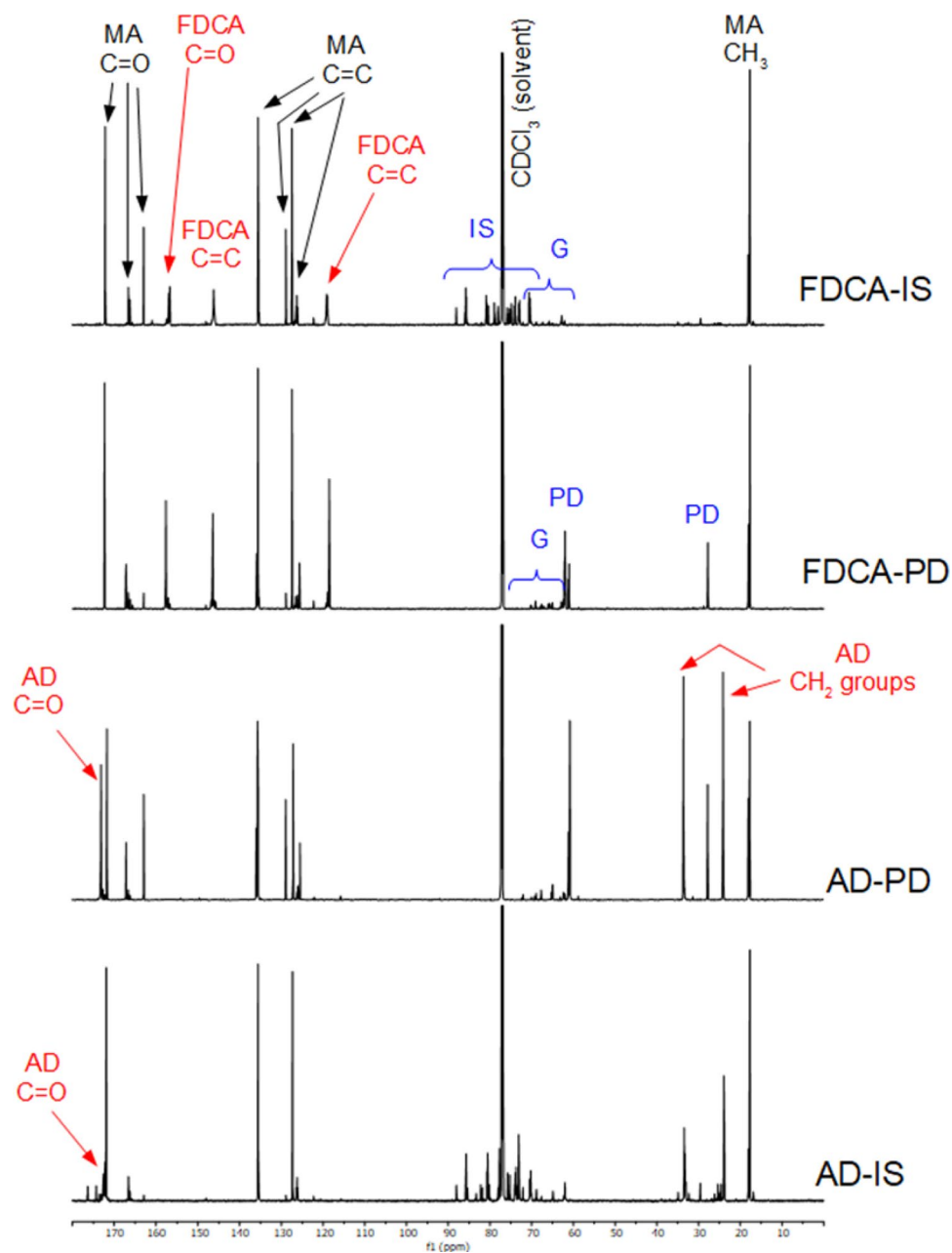

Table 1 Percentage of reacted and unreacted MA and residual MAAH (the MAAH is counted as two MA units)

Sample	% of total MA		
	Free MA	MAAH	Reacted MA
FDCA-IS	45.5	17.7	36.7
FDCA-PD	55.0	3.6	41.5
AD-PD	38.6	25.5	36.0
AD-IS	67.9	1.8	30.3

Table 2 Percentage of reacted and unreacted OH groups on the diols

Sample	% of total OH groups on diol		
	Diol	Reacted OH	Unreacted OH
FDCA-IS	IS	78.5	21.5
FDCA-PD	PD	75.9	24.1
AD-PD	PD	76.5	23.5
AD-IS	IS	77.0	23.0

Table 3 Percentage of reacted and unreacted acid groups on the diacids

Sample	% of total acid groups on diacid		
	Diacid	Reacted	Unreacted
FDCA-IS	FDCA	93.5	6.5
FDCA-PD	FDCA	100	0
AD-PD	AD	100	0
AD-IS	AD	94.9	5.1

Table 4 Distribution of the glycerol into the different reacted glycerol species.

Sample	% glycerol as total in each species			
	MAG[a]	1,2-DAG[a]	1,3-DAG	TAG[a]
FDCA-IS	42.4	9.0	30.7	17.9
FDCA-PD	26.7	0.0	36.7	36.5
AD-PD	7.4	18.0	43.2	31.3
AD-IS	0.0	13.9	21.6	65.5

[a]*MAG* monoacylglycerol, *DAG* diacylglycerol, *TAG* triacylglycerol

Dynamic Mechanical Analysis

Viscoelastic properties of cured UPEs were evaluated with DMA. Tan δ, storage modulus, *G,* and loss modulus, *G″,* were recorded as a function of the temperature. The polymer chain-packing density in the glassy state and glass transition temperature of the polymer are given by storage modulus and tan δ respectively [11, 18]. Higher *G* indicates higher stiffness as well as better flexural elastic modulus of the polymer due to an increase in crosslinking density [44]. Typically, high performance composites' resins have a T_g in the range of 115–250 °C and moduli in the range of 2–3 GPa at room temperature [47, 48]. Commercially available UPEs have a T_g of about 100 °C and a modulus of 3 GPa [49]. Figure 7A indicates the storage modulus for the resins. The commercial fossil-based UPE is shown as a reference as a comparison with synthesized resins. *G* was 4807, 4036, 2901, 278, and 3126 MPa for FDCA/IS, FDCA/PD, AD/IS, AD/PD, and UPE, respectively at 25 °C. As expected, the two UPE resins with FDCA showed the highest storage modulus owing to their highly rigid structure. This applies to the rubbery plateau region too. They show a significant difference to UPE. FDCA/IS resin also showed superior *G* to the FDCA/PD resin due to the bicyclic rigid structure of IS. AD/IS resin's storage modulus is the same as UPE but AD/PD resin represented lower *G* than the other resins used in this study. The peaks of tan δ for all resins are shown in Fig. 7B. Glass transition temperatures were recorded as 173, 148, 104, 58, and 92 for FDCA/IS, FDCA/PD, AD/IS, AD/PD, and UPE resins, respectively. All synthesized resins except AD/PD

showed better or similar T_g to commercial counterparts. T_g for FDCA-based resins is approximately twice that of UPE, making them promising resins for high-temperature applications. Besides, resins containing IS as a "stiffening agent" show higher T_g. In fact, IS provides increased stiffness in the final crosslinked polymer. Compared to other reported bio-based UPEs, both FDCA/IS and FDCA/PD show relatively high T_g and *G*. Sousa et al. and Dai et al. synthesized resins based on FDCA have T_g of 104.4 and 127.6 °C and *G* of 613.7 and 2391 MPa, respectively [36, 37]. The main reason for this could be the difference in the structure of resin. Both resins synthesized by Sousa et al. and Dai et al. contain soft aliphatic moieties—SA and PD—in their structure. Using diols like PD leads to a linear structure (two branched) resin, while using GLY as a three-functional glycol leads to a star-shaped structure which increases the crosslinking density, thus increasing thermomechanical properties such as T_g and *G.* This structure is formed by the reaction of all three hydroxyl groups in GLY with acid, which is also confirmed by the NMR. Esmaeili et al. and Bakare et al. also reported star-shaped bio-based UPEs based on glycerol as a core glycol with lactide or lactic acid as a monomer with a T_g of 66.11 and 97 °C and a *G* of 3478 and 4314 MPa, respectively [4, 19]. Jahandideh et al. synthesized UPE based on glycerol and IT with a T_g of 122 °C and a *G* of 3109 MPa [44]. All these star-shaped UPE have a similar structure to FDCA/IS and FDCA/PD resins due to the presence of GLY but a lower T_g and *G*, which confirm the FDCA and IS effect in the improvement of thermomechanical properties. Table 5 summarizes the results of the DMA test. SD refers to the Standard Deviation in tables.

Differential Scanning Calorimetry

The curing behavior of the resins was investigated by detecting any residual exothermal heat in the DSC thermograms of cured specimens. As shown in Fig. 8, there are no remaining unreacted double bonds in the cured resins and the resins can therefore be verified as completely cured. Resins containing FDCA in the structure showed significantly higher exothermic heat evolved at 222 J/g and 189.2 J/g, respectively, than the AD/IS and AD/PD resins (Fig. 9). Several factors such as the composition of the resins and the reactivity of the different double bonds influence the heat exotherm. The composition of the resins is not identical. The amount of free MA, MAAH, and reacted MA varies between the four resins (see Table 1). However, the differences are probably not significant enough to explain the difference in the heat exotherm. Another possible explanation could be that part of the double bonds of FDCA had somehow reacted during synthesis. However, an inspection of the NMR spectrum, which shows the signals at 120 and 146 ppm

Fig. 7 The DMA curves for cured samples of FDCA/IS, FDCA/PD, AD/IS, AD/PD, and UPE resins. **A** Storage Modulus, **B** Tan d
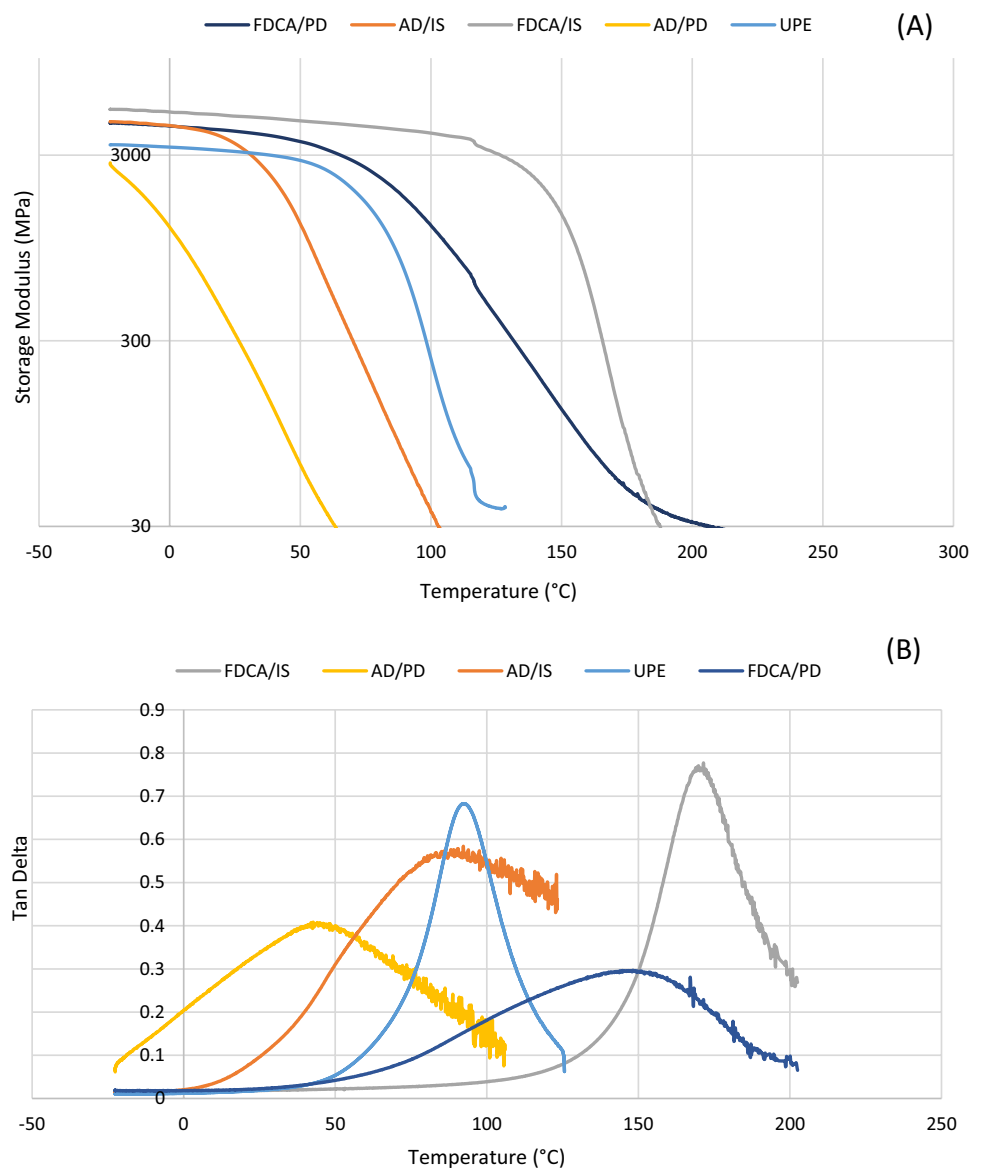

(A)

(B)

Table 5 The storage modulus and the glass transition temperatures of different resins

Resin type	Storage modulus at 25 °C (MPa)/(SD)	Tan δ peak (T$_g$ °C)/(SD)
FDCA/IS	4807 (63)	173 (1.65)
FDCA/PD	4036 (99.37)	148 (0.5711)
AD/IS	2901 (134.32)	104 (2.339)
AD/PD	278 (17.11)	58 (0.425)
CPUS	3126 (57)	92 (0.645)

(the double bond carbons of FDCA), does not support this explanation. Another possible explanation could be that part of the double bonds of FDCA reacted during curing. An inspection of the FTIR spectra (Figs. 5, 6), reveals the
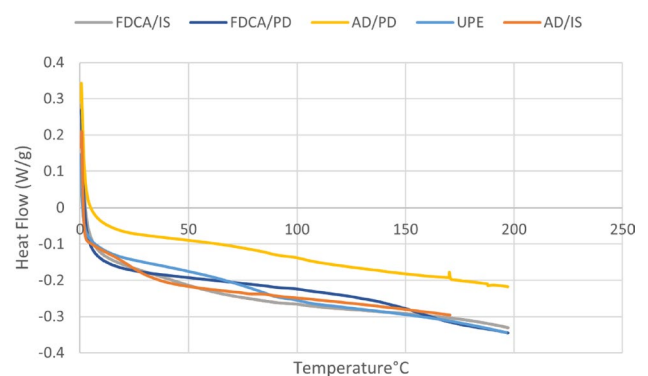
Fig. 8 DSC curve for cured resins

Fig. 9 DSC curve for uncured resins
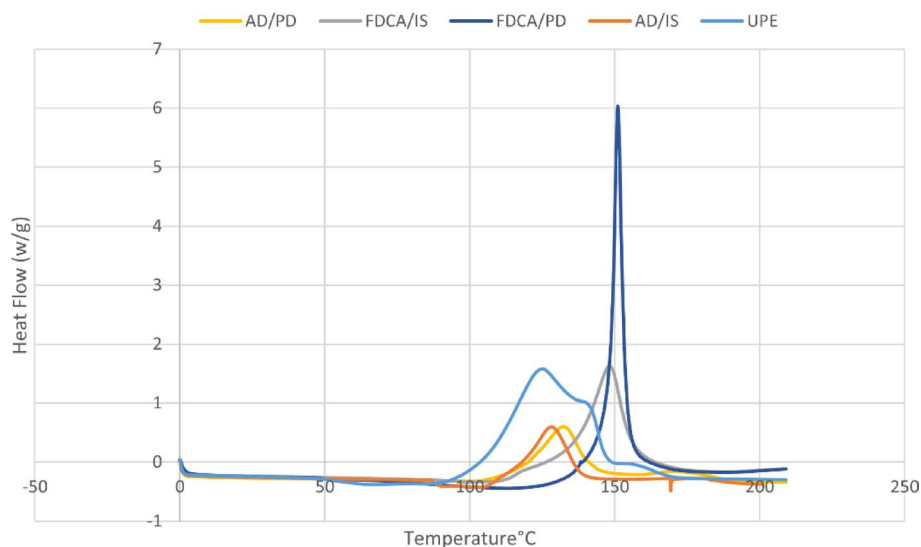
peak of the double bonds of FDCA to be at 1580 cm^{-1}. The peaks can actually be seen both before and after curing but it is possible that part of the double bonds reacted during the curing of the resins. There are several studies proving that furan-based monomers can participate in Diels–Alder (DA) reactions. Sain et al. synthesized a polymer from tung oil and furfuryl methacrylate. They confirmed the cross-linking of the conjugated trienes of tung oil through free radical polymerization with the acrylate group of furfuryl methacrylate, followed by a DA reaction between the furfuryl moiety of furfuryl methacrylate and the remaining unreacted double bonds of tung oil [50]. Froidevaux et al. and Gandini studied the DA reaction between furan derivatives and maleimide [51, 52]. Zhang et al. investigated the DA reaction of furan with maleic anhydride [53].

The exotherm heat of the commercial UPE was 296 J/g, which is higher than for the four synthesized resins. This is related to the presence of styrene as a reactive diluent in the resin. The double bond in styrene reacts with the unsaturated carbon–carbon bond in the polyester backbone to form a complex three-dimensional network.

DSC data are represented in Table 6.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to characterize the cured samples for evaluating their thermal stability. The results are shown in Fig. 10 and summarized in Table 7. All synthesized resins showed high thermal stability compared with the commercial UPE, with 10% weight loss at temperatures above 300 °C. A possible explanation could be that commercial orthophtalic polyester resins are typically linear structures, but the synthesized resins all have branched structures which may lead to higher cross-linking densities. This may explain the higher thermal stability of the synthesized resins. The maximum degradation temperature for the commercial resin was 380 °C while the other resins displayed higher temperatures. For example, FDCA/IS gave a maximum degradation temperature of 403 °C. Sousa et al. synthesized series of resins containing different percentages of FDCA. They concluded that increasing the percentage of FDCA did not lead to a significant increase in the thermal stability of the cured resins [36]. Comparing the four resins, it is difficult to see a clear pattern. Replacing FDCA with AD (AD-IS) actually increased the maximum degradation temperature from 403 to 435 °C. However, in contrast to that, replacing IS (of FDCA-IS) with PD (FDCA-PD) decreased

Table 6 DSC results for cured and uncured resins

Resin type	Heat of exotherm for uncured resin (J g^{-1}) (SD)	Peak temperature for the uncured resin (°C)	Heat of exotherm for cured resin (J g^{-1})
FDCA/IS	222 (15)	148	0
FDCA/PD	189.2 (5.15)	151	0
AD/IS	147 (3.61)	128	0
AD/PD	135.35 (0.35)	130	0
UPE	296.3 (2.595)	106	0

Fig. 10 TGA curve for the cured resins. **A** Weight reduction curves, **B** Derivative weight change curves
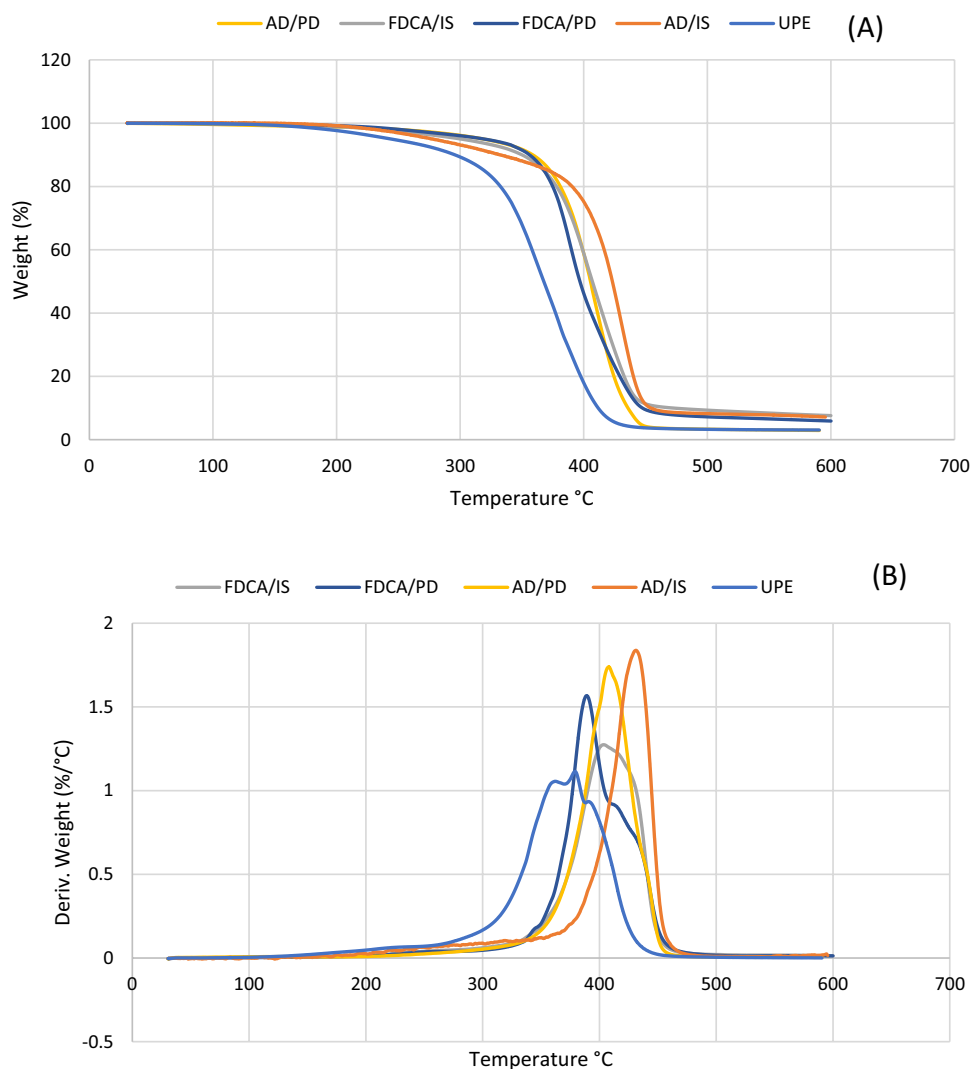

Table 7 TGA results for cured resins

Resin type	Degradation temperature at 10 wt% loss (°C) (SD)	Maximum degradation (°C) (SD)	Solid residue at 600 °C (%) (SD)
FDCA/IS	347 (3)	403 (2.5)	7.6 (0.2)
FDCA/PD	351 (4.5)	390 (1)	5.9 (0.1)
AD/IS	312 (5)	435 (8)	5.4 (0.15)
AD/PD	361 (1.63)	409 (2)	2.9 (0.22)
UPE	294 (2.2)	380 (1.5)	3.05 (0.17)

the maximum degradation temperature. A possible explanation is that the thermal properties of the synthesized resins are not only related to the idealized structures; it must also be considered that the resins reacted differently. Characterization by NMR clearly revealed that the composition of the resins differed. For example, FDCA-IS had a high content of MAG while AD-IS had a high content of TAG (see Table 4).

Also, the amount of free MA, reacted MA, and MAAH varies between the resins (see Table 1). It is therefore not easy to directly correlate the chemical structure with the thermal properties.

Conclusions

Four bio-based branched unsaturated polyester resins with reactive end groups were successfully synthesized and characterized in two steps using bulk polymerization. This study proved that resins containing FDCA and IS have good thermomechanical properties due to their structure. For example, FDCA/IS showed a T_g of 175 °C, making it a promising resin for high temperature applications. As expected, the viscosities of the resins (except AD/PD) were high because of the absence of a diluent but preheated resins at 50 °C have similar viscosity to the commercial reference UPE containing 30–40% styrene. Hence, they are suitable for common fiber

impregnation processing techniques such as bulk molding compounding, sheet molding compounding, and manual lamination. Regarding the thermogravimetric results, the thermal stability of synthesized resins was higher than that of UPE. Among the four synthesized resins, the FDCA/IS resin could have strong potential for producing composite used in storage tanks for maintaining solvents at high temperatures, and AD/IS is a promising substitute for UPE because of its similar thermomechanical properties. The synthesized resins, especially FDCA/IS and AD/IS, show promising thermosmechanical properties and could potentially be used for composite applications. This may be evaluated in future studies.

Declarations

Competing interests The authors declare no competing interests.

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