

# Biobased UV-curable coatings based on itaconic acid

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**Abstract** A series of renewable unsaturated polyesters were synthesized from itaconic acid (IA), succinic acid, and 1,4-butanediol by solvent-free polycondensation. Previous studies utilizing IA to make polyesters for coating applications have shown great potential; however, the curing and material properties have not been investigated in detail. The aim of this study was to investigate how the curing is affected by the amount of unsaturations and how well itaconate-based polyesters crosslink without the addition of any other unsaturated monomers or reactive diluents. The chemical structures of the polyesters were confirmed with FTIR, <sup>1</sup>H-NMR, and THF-SEC. The degree of curing was studied with FTIR, and the mechanical properties of the crosslinked polyesters were evaluated with DMA, pendulum hardness, and microindentation. The degree of curing was found to be up to 75%, and furthermore, it was found that the final mechanical properties of the crosslinked coatings could be tuned by modifying the IA content in the monomer composition. The results from DMA showed that there is a clear trend between mechanical properties and crosslinking density.

**Keywords** Biobased, Itaconic acid, UV, Polyester, Coatings

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## Introduction

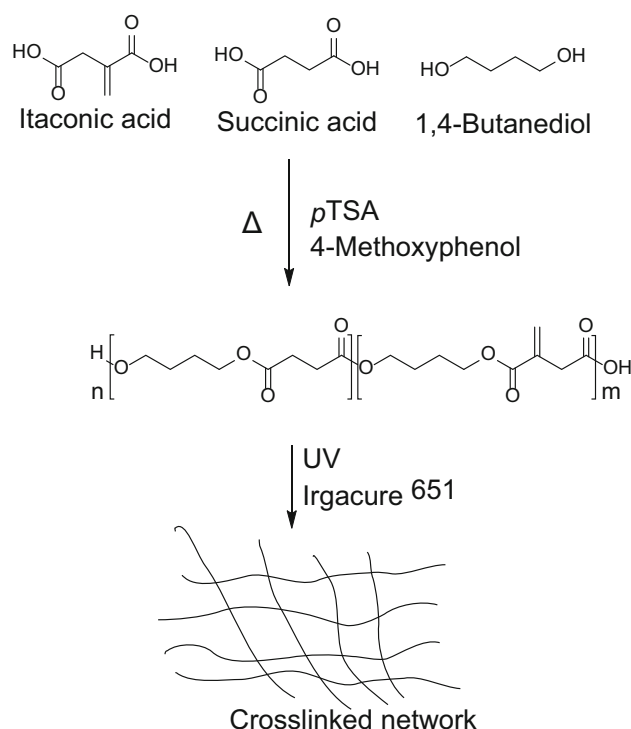
Increased environmental awareness has led to a significant interest in replacing nonrenewable petroleum-based polymeric materials with renewable counterparts.<sup>1–4</sup> Although a renewable feedstock starts to be established in several thermoplastics materials, less progress has been found in other areas such as thermoset coatings.<sup>3,5–9</sup> The number of available monomers having suitable functionalities for crosslinking is still sparse, and both novel crosslinking chemistries and introduction of new monomers need to be further developed. Recent developments include thiol-ene crosslinking of biobased alkenes with intrinsically low reactivity<sup>10</sup> and cationic polymerization of biobased epoxides.<sup>11</sup> Recent developments of renewable coatings have included synthesis of unsaturated polyesters based on the monomer itaconic acid (IA). IA is a renewable, unsaturated, dicarboxylic acid that holds great promise for use in polyester synthesis. This monomer can be made fully biobased at a relatively low cost through fermentation of carbohydrates by the fungi *Aspergillus terreus*.<sup>12</sup> Traditionally, maleic acid has been used to provide the unsaturation in polyesters; however, this double bond is not reactive enough to radically homopolymerize, thus the addition of another monomer, such as styrene, is necessary in the crosslinking step. The 1,1-disubstituted unsaturation in IA makes it homopolymerizable to some degree because the unsaturation is more reactive compared to the double bond in maleate.<sup>13,14</sup>

IA has received significant attention during recent years, most likely due to its interesting dual functionality and the possibility of producing it from renewable resources. There are several recent studies on polymerizing IA with different diols to obtain renewable, unsaturated polyesters for various applications, as recently reviewed by Robert and Friebel.<sup>15</sup> For example, Fonseca et al.<sup>16</sup> synthesized unsaturated polyesters

using IA and copolymerized them with 2-hydroxyethyl methacrylate. Goerz and Ritter<sup>17</sup> made polymeric materials exhibiting a shape-memory effect by thermal curing of polyesters from IA, succinic acid (SA) and isosorbide using dimethyl itaconate as a reactive diluent in the curing step. Chanda and Ramakrishnan<sup>18</sup> obtained unsaturated polyesters from IA and successfully performed Michael addition to the double bond. Farmer et al.<sup>19</sup> synthesized unsaturated polyester resins from various bioderived monomers, including dimethyl itaconate, through bulk polymerization.

An efficient approach to cure thermoset films, e.g., organic coatings, is by the use of UV light that activates the initiator in the system. UV curing provides several advantages such as a low energy consumption, low emission of volatile organic compounds (VOC), and high processing speeds,<sup>20</sup> all relevant for a sustainable production. The development of renewable coating resins that can be crosslinked by means of UV curing is therefore an important step in the progress and development of even more sustainable material solutions. Combining renewable monomers with efficient processing would therefore be ideal when developing sustainable coatings. This has already been explored, for example, by Dai et al.<sup>21</sup>; this group published several studies about renewable polyesters from IA; in one study biobased unsaturated polyesters from IA and different diols were synthesized and subsequently formulated to produce waterborne UV-curable coatings. The cured polyesters exhibited high hardness and good solvent resistance. However, information on the degree of curing as well as some structural information of the resins was lacking. The same group also made thermally cured coatings based on IA and acrylated epoxidized soy bean oil, and in this study, the curing was confirmed with DSC.<sup>7</sup> Finally, it seems the two studies were combined in a project where waterborne UV-curable dispersions were developed based on polyesters from IA and acrylated epoxidized soy bean oil. As seen before the materials had good coating properties and at the same time, the waterborne dispersions provided a good and environmentally friendly method for applying the films.<sup>22</sup>

This study has been performed to complement the previous work already performed in this field by investigating the performance of itaconate-containing polyesters during the UV-initiated radical crosslinking. Polyesters were synthesized from IA, 1,4-butanediol (BD), and SA (Scheme 1), all of which can be derived from renewable resources. SA is an intermediate in the citric acid cycle and one of the end products in the anaerobic metabolism. It can be made renewably through fermentation with different types of fungi. Hydrogenation of SA is a route to renewable 1,4-BD.<sup>23</sup> Both biobased SA and BD are now commercially available on the market.<sup>24</sup> A series of resins with varied molecular weight and functionality has been synthesized and evaluated with respect to the curing performance and the final structure–property relationship. The possibility to tune the properties of the crosslinked



**Scheme 1: Synthesis and crosslinking of renewable polyesters containing itaconic acid, succinic acid, and 1,4-butanediol**

coatings by varying the molecular weight and amount of SA to IA to was furthermore explored.

## Experimental

### Materials

SA, IA, 1,4-BD, 0.1 M potassium hydroxide solution in ethanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol), and benzoic acid were supplied by Sigma-Aldrich. Toluene and 2-propanol were supplied by VWR Chemicals. 4-Methoxyphenol and *p*-toluene sulfonic acid monohydrate were supplied by Merck. Irgacure 651 was supplied by BASF. Dimethyl (83–85%)–diphenyl (15–17%)–siloxane copolymer, vinyl terminated, was supplied by Hüls Petrarch Systems. Phenolphthalein was purchased from KEBO. All chemicals were used as received.

### Analyses

#### Acid number (AN)

The monomer conversions were monitored by assessing the acid number (mg potassium hydroxide/g polyester). The polyester (ca 0.5 g, known amount) was dissolved in solvent (40 mL, toluene:

2-propanol:distilled water in a 50:50:1 ratio), and the solution was titrated with KOH in ethanol (0.1 M) using phenolphthalein as indicator. The concentration of the potassium hydroxide solution was determined by titrating benzoic acid (0.1 g, known amount) dissolved in distilled water: 2-propanol (40 mL, 1:1).

#### *Proton nuclear magnetic resonance (<sup>1</sup>H-NMR)*

Spectra were obtained at 400 MHz with a Bruker Avance, using deuterated chloroform (CDCl<sub>3</sub>) as the solvent. Spectra were based on 16–40 scans and reported in ppm relative to the solvent residual peak, 7.26 ppm.

#### *Fourier transform infrared spectroscopy (FTIR)*

FTIR analysis was performed with a PerkinElmer Spectrum 2000 FTIR instrument (Norwalk, CT, USA) equipped with a single reflection (attenuated total reflection: ATR) accessory unit (Golden Gate) from Graseby Specac LTD (Kent, England) and a TGS detector using the Golden Gate setup. Each spectrum collected was based on eight scans averaged at 4.0 cm<sup>-1</sup> resolution range of 4000–600 cm<sup>-1</sup>. Data were recorded and processed using the software Spectrum from PerkinElmer.

#### *Size exclusion chromatography (SEC)*

SEC was performed on a Malvern VISCOTEK GPC-max equipped with a refractive index detector and TGuard column followed by two linear mixed bed columns (LT4000L) (35°C). Tetrahydrofuran (THF) stabilized with BHT (1 mL/min) was used as mobile phase. The molecular weights were calculated against polystyrene standards (Polymer Laboratories,  $M_p = 1000$  Da up to  $M = 4.5 \times 10^6$  Da). All samples were filtered through a 0.2- $\mu$ m PTFE filter (13 mm, PP housing, Alltech) before analysis.

#### *Differential scanning calorimetry (DSC)*

Samples (5–15 mg) were placed in 100  $\mu$ L aluminum pans covered by aluminum lids and analyzed with a Mettler Toledo differential scanning calorimeter DSCe 820. Mettler Toledo STARE software V9.2 was used to evaluate the results. Insert temperature was  $-60^\circ\text{C}$ , and end point calibration was set to 5 min. Thereafter samples were heated from  $-60$  to  $150^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  with pure nitrogen (flow rate of 30 mL/min), equilibrated at  $150^\circ\text{C}$  for 5 min, cooled to  $-60^\circ\text{C}$  and equilibrated for 5 min, thereafter heated again to  $150^\circ\text{C}$ .

#### *UV curing*

Curing of films was performed using a Fusion UV curing system of model F300 equipped with Fusion electrodeless bulbs standard type BF<sub>9</sub> with a dose of 6.0 J/cm<sup>2</sup> measured in the wavelength interval 320–390 nm with a UVICURE Plus from Efsen Engineering.

#### *Dynamic mechanical thermal analysis (DMA)*

DMA was performed using a Mettler–Toledo DMA/Q800 with a tensile fixture. All the samples were parts of thin film coatings that had been removed from glass substrate and cut into test specimens, approximate dimensions of 20 mm  $\times$  3.5 mm  $\times$  0.1 mm. Temperature ranged from  $-60$  to  $150^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  at 1 Hz.

#### *Microindentation*

The hardness of the coatings was assessed using a microindentation tester MHT S/N: 02-0134. The coating was indented using a Vickers Pyramid indenter at  $21^\circ\text{C}$  with a maximum load of 1000 mN, a load rate of 2000 mN/min, and equilibration for 5 s. Reported values are average values of triplicates.

#### *Pendulum hardness*

A König pendulum tester was used to measure the surface hardness of the coatings according to ASTM D4366-14. Testing was performed in room temperature on at least three different areas of the films, and the average value was used. König hardness is defined as the time it takes for the amplitude of the pendulum to decrease from  $6^\circ$  to  $3^\circ$ . Samples were analyzed in triplicate. Reported values are the average values from triplicates.

#### *Synthesis of unsaturated polyesters*

##### *Synthesis of polyesters with different molecular weights (PIB) (Table 1)*

IA (16.4 g, 126 mmol), 1,4-BD (13.6 g, 151 mmol), *p*-toluene sulfonic acid (100 mg, catalyst), and 4-methoxyphenol (100 mg, radical inhibitor) were added to a three-necked round-bottom flask equipped with a magnetic stirrer, a vigreux column, and a condenser. The flask was placed in a preheated oil bath set to  $160^\circ\text{C}$ , and the polymerization reaction was performed under purging with N<sub>2</sub> (g) until the desired acid number was reached. If the acid number had stopped decreasing before the desired number could be reached, the temperature was increased to  $170^\circ\text{C}$  and

**Table 1: Molar ratios of the monomers used for synthesizing the polyesters and the acid numbers that were reached when the reactions were stopped**

Polyester	Molar composition			Temperature (°C)	Acid number (mg KOH/g)	Reaction time (h)
	Itaconic acid	Succinic acid	1,4-Butanediol			
PIB-90	1.0	–	1.2	160	90	2.0
PIB-70	1.0	–	1.2	160	70	2.5
PIB-60	1.0	–	1.2	160	60	3.0
PIB-40	1.0	–	1.2	160/170	40	4.5
PISB-85	0.85	0.15	1.2	160/170	40	7.0
PISB-75	0.75	0.25	1.2	160	40	6.5
PISB-50	0.50	0.50	1.2	160	40	5.0

Polyesters from itaconic acid and butanediol are denoted PIB-xx, where xx is the acid number that was reached for the synthesis. Polyesters with both IA and SA are denoted PISB-xx where xx corresponds to the ratio of itaconic acid to succinic acid used in the synthesis

the reaction was run until that the desired acid number was reached. This polyester was synthesized four times and terminated at different acid numbers to yield four polyesters with different molecular weights: AN = 90 mg/g, AN = 70 mg/g, AN = 60 mg/g and AN = 40 mg/g. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 6.34 (s, H, =CH<sub>2</sub>), 5.75 (s, H, =CH<sub>2</sub>), 4.12–4.13 (d, 2H, –CO–O–CH<sub>2</sub>–CH<sub>2</sub>–), 4.20–4.21 [d, 2H, –(C=CH<sub>2</sub>)–CO–O–CH<sub>2</sub>–CH<sub>2</sub>–], 3.34 (s, 2H, –CO–CH<sub>2</sub>–CH<sub>2</sub>–), 1.71–1.8 (t, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–). FTIR (KBr, ν/cm<sup>-1</sup>): 2960 (–CH<sub>2</sub>–), 1728 (C=O), 1637 and 819 (C=CH<sub>2</sub>). Polyesters denoted PIB-xx are synthesized from IA and 1,4-BD, where xx corresponds to the respective acid numbers.

#### Synthesis of polyester with different equimolar of itaconic acid and succinic acid (PISB)

Polyesters denoted PISB-xx corresponds to the polyesters synthesized from IA, SA, and 1,4-BD, where xx is the % IA of the diacid content. The stoichiometric ratio between [OH] and [COOH] was kept to 1.2 in all experiments (Table 1).

PISB-50: IA (8.40 g, 64.6 mmol), SA (7.70 g, 64.6 mmol), 1,4-BD (14.0 g, 155 mmol), *p*-toluene sulfonic acid (100 mg, added as catalyst), and 4-methoxyphenol (100 mg, added as radical inhibitor) were placed in a three-necked round-bottom flask. Reaction conditions were otherwise the same as for PIB, and the polymerization was conducted until the acid number measured 40 mg/g. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 6.34 (s, H, =CH<sub>2</sub>), 5.74 (s, H, =CH<sub>2</sub>), 4.12–4.13 (d, 2H, –CO–CH<sub>2</sub>–CH<sub>2</sub>–), 4.20–4.21 [d, 2H, –(C=CH<sub>2</sub>)–CO–O–CH<sub>2</sub>–CH<sub>2</sub>–], 3.35 (s, 2H, O–CO–CH<sub>2</sub>–), 2.64 (s, 4H, CO–CH<sub>2</sub>–CH<sub>2</sub>–OC), 1.71–1.78 (t, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–). FTIR (KBr, ν/cm<sup>-1</sup>): 2960 (–CH<sub>2</sub>–), 1728 (C=O), 1637 and 819 (C=CH<sub>2</sub>).

PISB-75: IA (12.4 g, 95.0 mmol), SA (3.77 g, 32.0 mmol) 1,4-BD (13.8 g, 153 mmol), *p*-toluene

sulfonic acid (100 mg, catalyst), and 4-methoxyphenol (100 mg, radical inhibitor) were added to a three-necked round-bottom flask. Reaction conditions were otherwise the same as for PIB and run until acid number measured 40 mg/g. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 6.34 (s, H, =CH<sub>2</sub>), 5.74 (s, H, =CH<sub>2</sub>), 4.12–4.13 (d, 2H, –CO–CH<sub>2</sub>–CH<sub>2</sub>–), 4.20–4.21 (d, 2H, –(C=CH<sub>2</sub>)–CO–O–CH<sub>2</sub>–CH<sub>2</sub>–), 3.35 (s, 2H, O–CO–CH<sub>2</sub>–), 2.64 (s, 4H, CO–CH<sub>2</sub>–CH<sub>2</sub>–CO), 1.71–1.76 (t, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–). FTIR (KBr, ν/cm<sup>-1</sup>): 2960 (–CH<sub>2</sub>–), 1728 (C=O), 1637 and 819 (C=CH<sub>2</sub>).

PISB-85: IA (14.2 g, 109 mmol), SA (2.10 g, 18.0 mmol) 1,4-BD (13.7 g, 153 mmol), *p*-toluene sulfonic acid (100 mg, added as catalyst), and 4-methoxyphenol (100 mg, added as radical inhibitor) were placed in a three-necked round-bottom flask. Reaction conditions were otherwise the same as for poly (IA–BD) and run until acid number measured 40 mg/g. An overview of all the synthesized polyesters is listed in Table 1. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ (ppm): 6.34 (s, H, =CH<sub>2</sub>), 5.74 (s, H, =CH<sub>2</sub>), 4.12–4.13 (d, 2H, –CO–CH<sub>2</sub>–CH<sub>2</sub>–), 4.20–4.22 [d, 2H, –(C=CH<sub>2</sub>)–CO–O–CH<sub>2</sub>–CH<sub>2</sub>–], 3.35 (s, 2H, O–CO–CH<sub>2</sub>–), 2.64 (s, 4H, CO–CH<sub>2</sub>–CH<sub>2</sub>–CO), 1.71–1.79 (t, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–). FTIR (KBr, ν/cm<sup>-1</sup>): 2960 (–CH<sub>2</sub>–), 1728 (C=O), 1637 and 819 (C=CH<sub>2</sub>).

#### UV curing and film formation

Cured films were prepared from all polyesters as follows. Unsaturated polyester (1.5 g) was placed in a vial and heated in an oven preset to 70°C, and a drop of texanol, a drop of dimethyl–diphenyl siloxane and photoinitiator Irgacure 651 (2 wt% Irgacure 651/total resin weight) were added; the formulation was kept at 70°C for 2 h and finally applied onto preheated glass substrates (70°C) using a 150-μm applicator. The UV curing was directly performed thereafter with a total dose of 6.0 J/cm<sup>2</sup>.

## Results and discussion

The present study was designed to investigate the effect of molecular weight and amount of incorporated IA on the curing performance and final properties of the itaconate-functional polyester coatings. Polyesters with different molecular weights with the same concentration of IA (PIB-*xx*) were synthesized from IA and 1,4-BD, where *xx* represent the acid number of the corresponding polyester. A second series of polyesters with different ratios of IA and SA (PISB-*yy*), targeting the same molecular weight, was also synthesized, where *yy* corresponds to the percentage of IA in the feed ratio. IA is prone to undergo isomerization into 2-methylfummaric acid at temperatures around 180°C and higher (Fig. 1).<sup>14</sup> Since the corresponding double bond in 2-methylfummaric acid is substantially less reactive than the one in IA, the reaction conditions for the polycondensation were carefully adjusted to reach the targeted monomer conversion without significant isomerization.

Details on the reaction conditions are presented in Table 1 and data on the formed polyesters in Table 2. For PIB-40 and PISB-85, the reactions slowed down, and therefore, the polymerization temperature was increased to 170°C to push the reaction to higher conversions. In general, more SA resulted in a faster reaction, and therefore, the temperature was not increased for PISB-75 or PISB-50. The seemingly lower reactivity of IA is expected and can be explained by the presence of the conjugated carboxyl group.

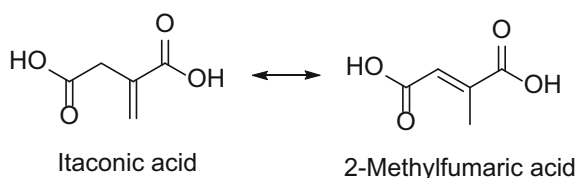


Fig. 1: Rearrangement of IA to 2-methylfummaric acid

### Effect of reaction conditions and monomer composition on the obtained resin structure

The synthesized polyesters were characterized with FTIR and <sup>1</sup>H-NMR to confirm their molecular structures. Figure 2 shows FTIR spectra of PIB-40 and IA as a reference. It can be observed that esters have been formed (1737 cm<sup>-1</sup>) and that the remaining amount of carboxylic acid is low (no detectable peak at 1700 cm<sup>-1</sup>). Furthermore, the ester peak seems to contain two different maxima, which can be explained by the fact that the conjugated ester has a different absorption band than the nonconjugated ester. Peaks at 2960 cm<sup>-1</sup> in the spectrum of IA correspond to the hydroxyl groups in the carboxylic ends, which also has decreased. The absorption bands for the double bond at 1637 and 817 cm<sup>-1</sup> are still present after esterifica-

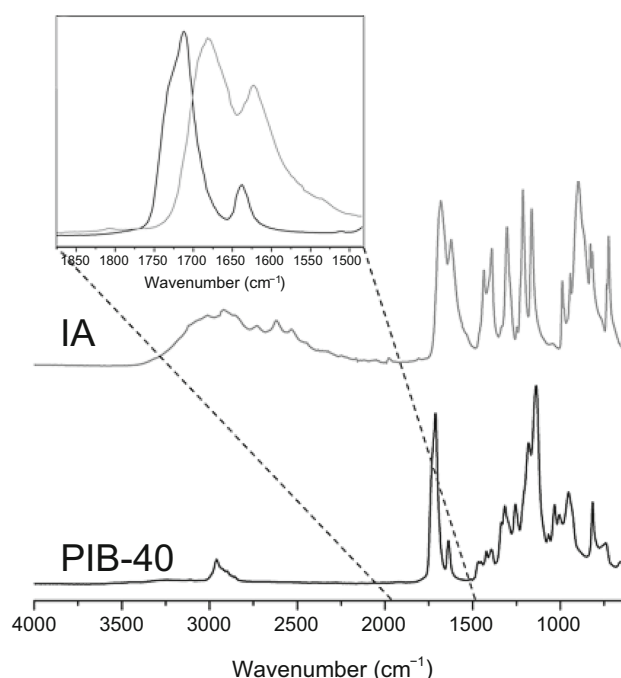


Fig. 2: FTIR spectra of polyester PIB-40 and IA as reference

Table 2: Molecular weights, dispersity, glass transition temperature and crystallization temperature of the synthesized polyesters

Polyester	Acid number (mg/g KOH)	$M_n$ (g/mol) <sup>a</sup>	$M_w$ (g/mol) <sup>a</sup>	$D$ ( $M_w/M_n$ ) <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_m$ (°C) <sup>b</sup>	$\Delta H_m$ (J/g)
PIB-90	90	1800	4500	2.5	-38	–	–
PIB-70	70	3000	4600	1.5	-32	45	7.1
PIB-60	60	4400	32,000	7.3	-31	46	14
PIB-40	40	5600	63,000	6.4	-31	45	33
PISB-85	40	4700	19,000	4.1	-31	40	1.3
PISB-75	40	5300	15,000	2.9	-33	44	11
PISB-50	40	5400	11,000	2.0	-36	46	45

<sup>a</sup> Determined with THF-SEC using polystyrene standards

<sup>b</sup> Determined with DSC

tion, which shows that the double bond is still intact. The double-bond absorption band in IA is furthermore seen to shift slightly when the acid is esterified.

The  $^1\text{H-NMR}$  spectra were also in accordance with the expected polyester structures (Fig. 3). Unexpected-

edly, there appears to be fewer end groups in the  $^1\text{H-NMR}$  spectra than what were expected. This indicates that the molecular weight is higher than the targeted molecular weight, probably due to evaporation of 1,4-BD which has affected the stoichiometric ratio. Since

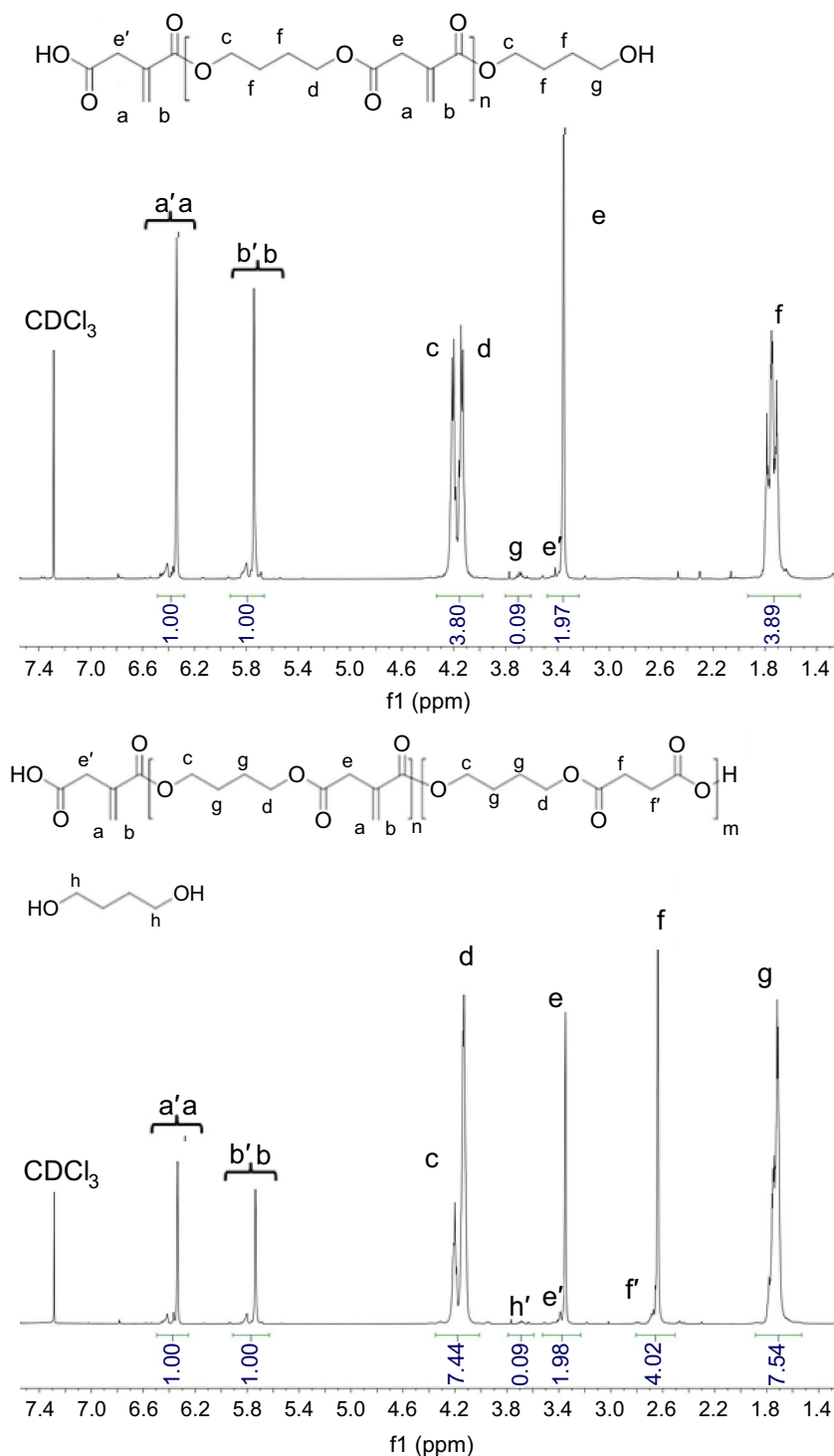


Fig. 3:  $^1\text{H-NMR}$  spectra of PIB-40 (top) and PISB-50 (bottom). The satellites around 5.4–6.6 ppm correspond to the unsaturations of IA which have not been fully incorporated into the polymer (a' and b')

BD was used in excess, the evaporation will make the stoichiometric imbalance less so that the molecular weight can become higher. Because 1,4-BD was used, the loss of diol can also be explained by the formation of THF.<sup>25</sup> If rearrangement of itaconate to 2-methylfumarate occurs, it should have been encompassed with the appearance of peaks around 2.3 ppm and around 6.8 ppm. There is a small peak around 6.8 which indicates that rearrangements may have occurred; however, the peaks corresponding to the pendant methylene group are significantly larger so it can be assumed that the extent of rearrangement is very low.<sup>14</sup> Furthermore, there is no significant sign of the Ordel reaction saturating the double bonds by the addition of the diol which gives rise to a methylene peak at 3.16 ppm.<sup>19</sup> All FTIR and <sup>1</sup>H-NMR spectra can be found in the supporting information (SI).

Polymerizations were also performed separately at 150 and 180°C, in order to determine the suitable processing window for this esterification process. Temperatures below 160°C were found to be too low as it was not possible to reach the targeted acid numbers (the acid number stopped decreasing after a couple of hours). We propose that this is due to the fact that the conjugated acid in IA is not reactive enough under these conditions. Furthermore, lower temperatures mean that the viscosity becomes higher with subsequent difficulties in removing the formed water.

Analysis with THF-SEC was performed to assess the molecular weights, and the SEC traces are found in supporting information. Molecular weights and dispersities are presented in Table 2. PIB synthesized to different conversions were found to have different molecular weights, whereas the PISBs with different ratios of IA and SA had similar molecular weights ( $M_n$ ). As seen in the <sup>1</sup>H-NMR spectra, the molecular weights are larger than expected for all polyesters. The theoretical molecular weights have been calculated and are presented in supporting information.

The higher molecular weight polyesters PIB-60 and PIB-40 had higher dispersities than the lower molecular weight counterparts. This is in accordance with the fundamental theory on stepwise polymerization. DSC analysis was performed on the polyesters to assess their morphologies as summarized in Table 2. Almost all

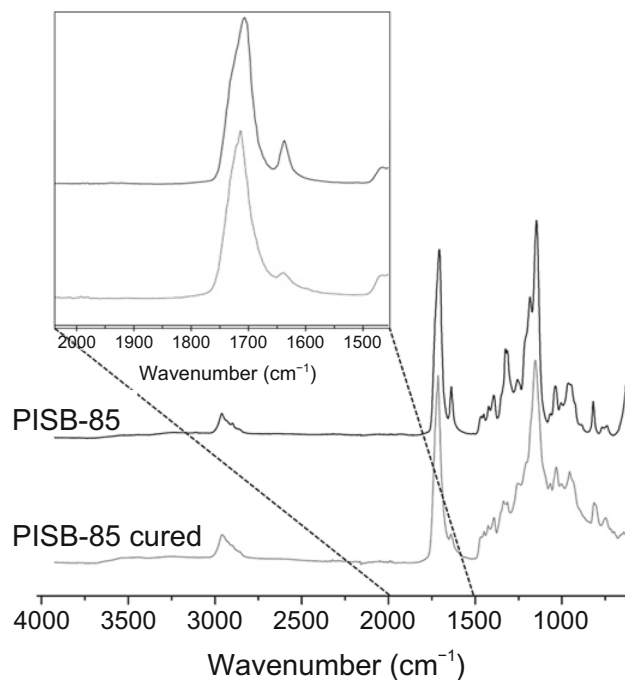
polyesters exhibited glass transition temperatures ( $T_g$ ) close to  $-30^\circ\text{C}$  and were found to be semicrystalline to varying degrees, with melting temperatures close to  $45^\circ\text{C}$ , except PIB-90, which did not show any crystallinity, possibly due to the low molecular weight. Of the samples containing both IA and SA, it was found that the sample containing the least IA (PISB-50) had the highest degree of crystallinity corroborating the hypothesis that IA is more efficient to restrict the crystallization than SA.

### Curing performance and final coating properties

The IA-based polyester resins were heated to allow mixing with the photoinitiator without the use of solvent. Films were then applied onto glass substrates and cured with UV light. The resulting dry films were characterized with FTIR to study the degree of curing,  $X$ , which was calculated according to equation (1), where  $A$  is the area of the peaks corresponding to the carbonyl ( $1713\text{ cm}^{-1}$ ) and the double bonds ( $1637\text{ cm}^{-1}$ ) prior to curing ( $t = 0$ ) and after curing ( $t$ ). The results are found in Table 3. Peak intensities were normalized against the carbonyl peak. The double-bond conversion was calculated by normalizing the absorbance bands of the unsaturation against the absorbance band of the carbonyl group. However, it should be noted that the absorptivity of the carbonyl is also affected by the curing as it decreases when no longer conjugated with a double bond; however, it is not significantly affected. As a consequence though,

**Table 3: Degree of curing of films made from unsaturated polyesters, as assessed by RT-FTIR**

Polyester	Degree of curing (%)
PIB-90	28
PIB-70	34
PIB-60	56
PIB-40	61
PISB-85	75
PISB-75	58
PISB-50	50



**Fig. 4: FTIR of PISB-85 before and after curing**

the amount of residual unsaturations is slightly over-estimated.<sup>26,27</sup>

$$X(\%) = \frac{(A_{1637}/A_{1713})_{t=0} - (A_{1637}/A_{1713})_t}{(A_{1637}/A_{1713})_{t=0}} \times 100\% \quad (1)$$

As given in Table 3, relatively high conversions can be obtained when homopolymerizing the itaconate esters although the unsaturation is 1,1-disubstituted and situated within the chain structure. Monomer conversions as high as 75% can be achieved although the crosslinking will lead to restricted molecular mobility in the system. Furthermore, a trend can be seen; polyesters with a higher molecular weight had a higher degree of curing, and replacing IA with SA results in a decrease in the degree of curing. This could be explained by the fact that as IA reacts and forms an ester on the conjugated side, the double bond becomes more reactive toward radical polymerization. In the case of the lower molecular weight polyesters, less IA has been incorporated which is why the degree of curing is lower. The same theory can be fitted into the PISB series; replacing some of the IA with SA leads to more unreacted IA since SA is more reactive in condensation polymerization.<sup>17</sup>

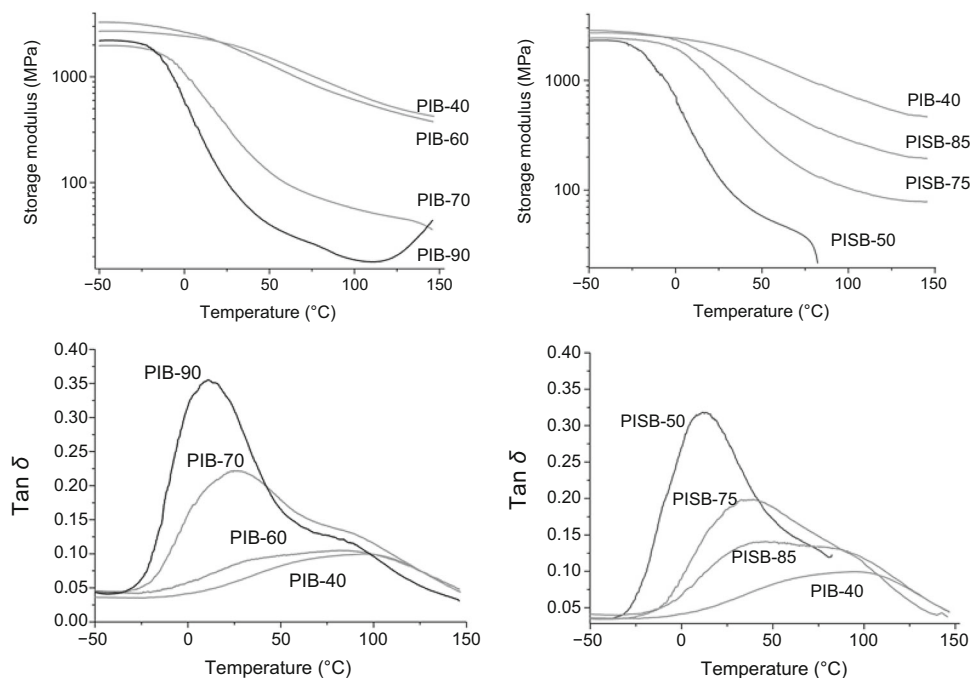
Traditional unsaturated polyesters are based on maleate or fumarate, which have 1,2-disubstituted unsaturations. These are not very reactive to homopolymerization and need to be copolymerized with, for example, styrene, in order to achieve efficient

curing.<sup>28</sup> The 1,1-disubstituted unsaturation in IA is significantly more reactive than the double bond in traditional unsaturated polyesters and makes homopolymerization possible. FTIR spectra of PISB-85 before and after curing are shown in Fig. 3. The alkene group at 1637 cm<sup>-1</sup> decreases significantly; however, a minor amount is still present after curing.

DMA was used to measure the storage modulus and the glass transition temperature of the cured films. Figure 4 shows that the modulus is significantly lower for the films obtained from the lower molecular weights PIB. It can also be seen that the incorporation of SA decreases the storage modulus. When plotting the storage modulus as a function of temperature, it is possible to observe a plateau region above the *T<sub>g</sub>*. The modulus in this region is related to the average molecular weight, *M<sub>c</sub>*, between crosslinks according to equation (2), where  $\rho$  is the density (g/m<sup>3</sup>), R is the ideal gas constant (J/mol/K), T is the temperature (K), and the *E'* is the storage modulus (MPa) in the plateau region above *T<sub>g</sub>*.<sup>29</sup>

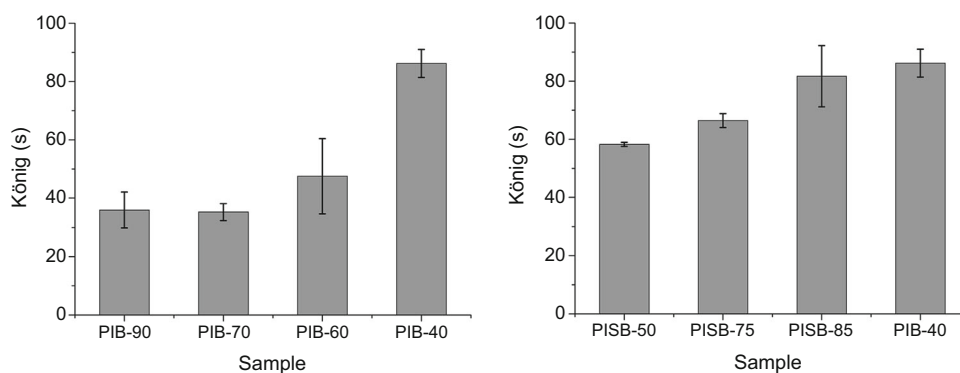
$$M_c = \frac{3\rho RT}{E'} \quad (2)$$

In this case, the DMA data did not allow for the calculation of *M<sub>c</sub>* because the rubber plateau was never reached; however, a trend can still be observed; higher molecular weight PIB gave rise to a higher storage modulus in the plateau region which means that it has a higher concentration of crosslinks. Increasing the amount of SA decreases the modulus, and thus, the

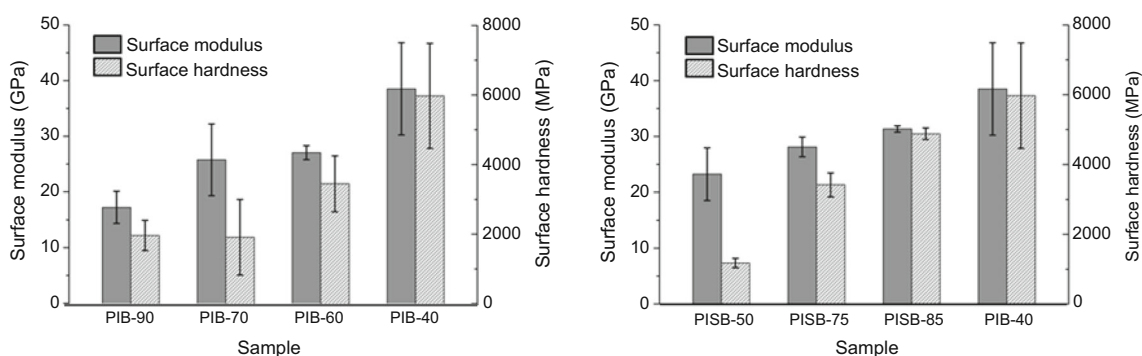


**Fig. 5: Storage modulus and tan  $\delta$  measured with DMA. The glass transition temperatures of the crosslinked materials are defined as tan  $\delta$  maximum**





**Fig. 6: Pendulum hardness of samples with different molecular weights (left) and samples synthesized using different amounts of succinic acid (right)**



**Fig. 7: Surface modulus and surface hardness measured with microindentation for samples to different molecular weights (left) and samples synthesized from different amounts of succinic acid (right)**

crosslinking density is also decreased. When cutting pieces for DMA from the films (made on glass substrates), it was observed that PIB-40 was very hard, which correlates with the results from DMA. However, the material was also very brittle. In that sense PISB-85, which also had a high storage modulus and evidently a well-formed network, was less brittle and easier to work with. Incorporating more SA resulted in very soft materials, since SA residues introduce more flexibility than IA with its pendant methylene group.

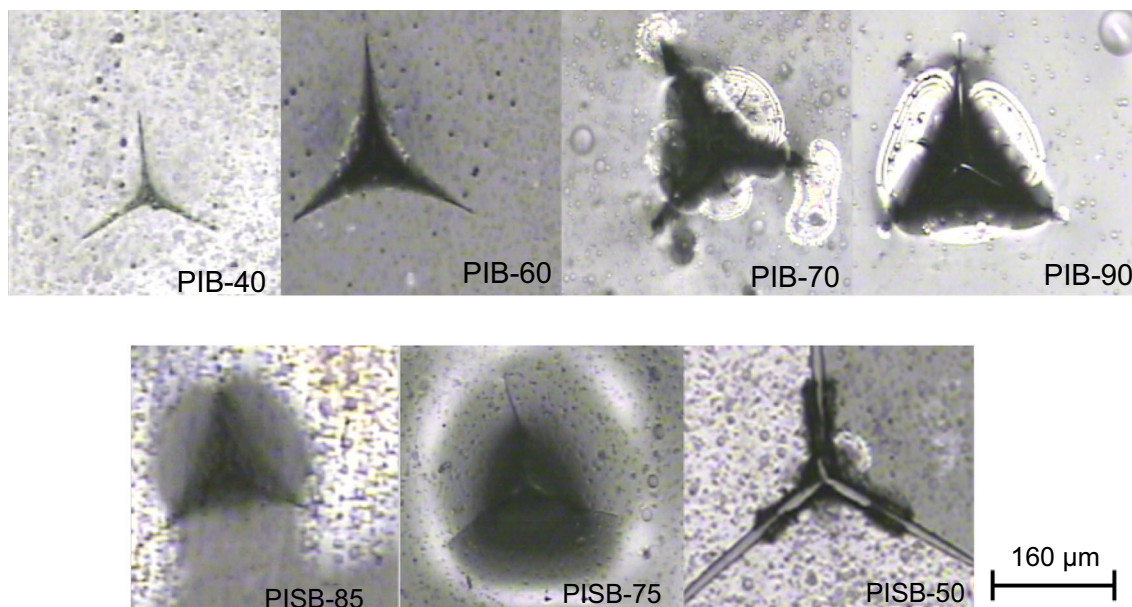
The maximum in  $\tan \delta$ , corresponding to the  $T_g$  of the materials, is affected by the molecular weight as well as the amount of SA (Fig. 5), as expected. Furthermore, the higher molecular weight samples (PIB-60, PIB-40) and the samples containing the lower amounts of SA (PIB-75 and PIB-85) appear to have a broader  $\tan \delta$  maximum.

Broadening of the  $\tan \delta$  maximum occurs when multifunctional monomers produce networks and form highly crosslinked regions as well as less densely crosslinked regions.<sup>30</sup> In this case, it can be explained by the fact that the crosslinked polyesters with a broad  $\tan \delta$  all had a high dispersity prior to the crosslinking,

as given in Table 1. Thus, the network constitutes a wider range of polyesters with different molecular weights, and as shown in Fig. 5, the crosslinking density decreases with decreasing molecular weight.

Pendulum hardness was measured for all films, and the results are presented in Fig. 6. In accordance with the results from DMA, higher molecular weights give higher pendulum hardness and higher incorporation of SA decreases the hardness. Moreover, the surface hardness and surface modulus, as assessed by microindentation, also show the same trend as other mechanical properties (Fig. 7); higher molecular weight gives higher surface hardness and higher pendulum hardness, as well as a higher storage modulus and surface modulus. This is an effect of the higher molecular weight polymers, resulting in more chain entanglements and a more efficient curing. As predicted, incorporation of SA decreases the surface hardness and pendulum hardness and decreases the surface modulus and storage modulus.

Microscope images of the indentations are shown in Fig. 8. Interestingly PIB-40, which had the highest surface modulus and hardness, barely has an indentation.



**Fig. 8:** Indentations from microindentation, using a force of 250 mN, micrographs were obtained with a  $\times 5$  microscope

## Conclusions

Green unsaturated polyesters, well suited for coating applications, were successfully synthesized from renewable monomers, including IA. By optimizing the reaction conditions, it was shown that IA could be incorporated into a polyester without significant amount of double-bond rearrangement. All polyesters were UV-cured, and the material properties of the resulting films were studied with DMA, pendulum hardness, and microindentation. The results showed that the storage modulus and surface modulus were significantly increased with increasing molecular weight of the polyester. The surface hardness and pendulum hardness also increased with increasing molecular weight. This suggests that the molecular weight of unsaturated polyesters based on IA does affect the final coating properties, and by controlling it, the final material properties can also be tailored. It was also verified that the itaconate double bond could be free radically homopolymerized to high conversions. Replacing IA with SA to various degrees resulted in softer materials, with lower modulus and hardness with increasing SA content, as seen by all characterization methods. In conclusion, it is thus possible to make fully biobased, solvent-free, UV-curable polyester resins and tailor the material properties under the presented reaction conditions.

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