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Sustainable, rigid imide building blocks as promising substitutes for phthalic anhydride in alkyd resins

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Abstract

New, highly rigid bio-based building blocks were synthesized from renewable raw materials. In a first reaction step, an imide was made from citraconic anhydride and the amino acid glycine. This imide was subsequently reacted with sorbic acid using Diels–Alder chemistry, furnishing a double-ring structure. This new, very rigid renewable building block was then incorporated into alkyd resins by standard polycondensation chemistry and technology. The resulting, >80 wt% renewable, alkyd resins were evaluated as white paints in a preliminary way by solvent casting from xylene. The properties of the renewable coatings look promising, some even outperforming those of standard commercial alkyd resins. For further enhancing the sustainability of the systems discussed, turning these highly bio-based alkyd resins into stable aqueous emulsions is a must.
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Supporting information may be found in the online version of this article.

Keywords: bio-based; imides; glycine; citraconic anhydride; sorbic acid; paint properties

INTRODUCTION

In this paper we discuss renewable, rigid building blocks for alkyd resins. Standard alkyd resins are normally produced from a petro-based, rigid aromatic or cycloaliphatic dicarboxylic acid or anhydride (like phthalic anhydride, hexahydrophthalic anhydride or isophthalic acid), a polyol like petro-based trimethylolpropane or pentaerythritol, one or more bio-based fatty acids and, sometimes, a monofunctional petro-based rigid acid like benzoic acid, fulfilling the role of a chain stopper and glass transition temperature (T_g) booster.[1–3] Whereas fatty acids are fully bio-based, for chemicals like pentaerythritol mass balance certificates are provided by the respective manufacturers (see e.g. the Perstorp site[4]). These certificates indicate the bio-based percentage of the raw materials used for commercial production of these chemicals. However, for developing sustainable alkyd resins with very high bio-based contents, the major challenge is currently to find renewable alternatives for the rigid aromatic and cycloaliphatic mono- and dicarboxylic acids, of which significant amounts are present in commercial alkyd resins. Currently, such rigid renewable diacids are not available on a kiloton scale. Indeed, there are several initiatives for developing renewable, rigid dicarboxylic acids. Although the earlier announced joint venture activity of Avantium and BASF, targeting a 50 000 tons per year plant in Antwerp for the manufacturing of renewable resource-based 2,5-furandicarboxylic acid (FDCA), was cancelled, in January 2020 Avantium announced the construction of a 5 kt FDCA flagship plant at Chemie Park Delfzijl, the Netherlands.[5] Nevertheless, it may take some years before this FDCA plant will be on stream. Also, various methods and processes to produce bio-based

terephthalic acid and phthalic anhydride have been proposed.[6,7] Nevertheless, also the commercial availability of such renewable, 'drop-in' rigid dicarboxylic acids or anhydrides will still take several years, which prompted us to develop our own (partially) renewable rigid dicarboxylic from bio-based building blocks that are currently available on the market in large quantities.

In a recently published paper we reported on bio-based, imide-containing building blocks for incorporation into alkyd resins.[8] These imides were made from fermentation-derived amino acids and either citric acid (furnishing renewable dicarboxylic acids, after imide formation using the amine originating from the amino acid and two of the three carboxylic acid groups of the citric acid) or succinic acid (furnishing renewable monocarboxylic acids, again after imide formation using the amine originating from the amino acid and both carboxylic acid groups of the succinic acid). An example of such a monocarboxylic acid imide is lysine disuccinimide, which is also used in the current paper to replace benzoic acid in the studied alkyd resins. We found that the polycondensation of these aforementioned mono- and dicarboxylic imide acids along with pentaerythritol and fatty acids resulted in oxidative-curing polyesterimide-based alkyd resins with very

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satisfactory coating properties.[8] In addition to our own work, the number of studies concerning esterimide-containing, air-drying alkyd resins is still very limited and we can only cite a few other examples here.[9–13] Probably the most interesting paper is the one by Kishanprasad and Gedam,[11] who synthesized an *N*-(carboxymethyl) trimellitimide from trimellitic anhydride and glycine. This imide monomer was subsequently polymerized with various amounts of linseed oil and glycerol, furnishing polyesterimide resins with various fatty acid contents and oil lengths. These resins produced oxidative-cured alkyd films with interesting properties. However, like the alkyds described by other authors,[9,10,12,13] the trimellitimide structures are not fully bio-based, contrary to the citrimide and succinimide di- and monocarboxylic acids described by Koning *et al.*[8]

In this paper we report a new type of renewable dicarboxylic acid imide building blocks, being potential alternatives for phthalic anhydride, with an even more rigid (and therefore T_g-enhancing) structure than those mentioned in our previous paper.[8] Here we use citraconic anhydride, naturally occurring amino acids and naturally occurring sorbic acid as renewable starting compounds. In a first step, citraconic imide or citraconimide is formed from citraconic anhydride and the amino acid glycine (Fig. 1(a)). Note that the glycine we use in this study was bought from Sigma Aldrich and is actually non-bio-based, because the manufacturing of glycine is more convenient by chemical synthesis. However, bio-based glycine is available and we use it as a model system for amino acids in general, and therefore we will refer to our imide building block as fully bio-based.

In a second step, the citraconic imide is added to the diene structure of sorbic acid using Diels–Alder chemistry, furnishing a rigid double-ring imide structure carrying two carboxylic acid groups and therefore potentially suitable to replace phthalic anhydride in alkyd resins (Fig. 1(b)). At the same time, in the work reported here, petro-based benzoic acid is replaced by the fully bio-based lysine disuccinimide (structure given in Fig. 2).

This paper discusses the synthesis and the molecular characterization of the new renewable, dicyclic imide building block, novel alkyd resins based on these rigid bio-based imide structures and some preliminary properties of alkyd paints based on these unique polycondensation monomers.

EXPERIMENTAL

Materials

Voxtar™ M100, a partly bio-based pentaerythritol, was bought from Perstorp. Biosuccinium™, a 100% bio-based succinic acid,
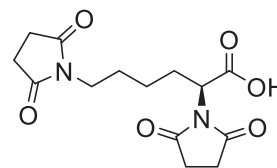
Figure 2 Lysine disuccinimide structure, described previously[8] and used in the work reported in the current paper.

was obtained from Reverdia. Tioxide TR92 was bought from Huntsman, Nuosperse FA601 was bought from Elementis, Borchi OXY-Coat (propyleneglycol-based) and Borchinox M2 were bought from OMG Borchers, Acrysol RM2020 was bought from Dow Chemical and Disperbyk 2015 and Byk 028 were bought from BYK Chemie. Durham Nuodex® Calcium 5 Neutral (calcium drier) was bought from Huntsman Pigments & Additives and Octa Soligen Zr12 (zirconium drier) was bought from OMG Borchers. Soybean fatty acid (Radiacid 0121) was bought from Oleon. L-Lysine (commercially available as Eurolysine LLB-50, being a 53 wt% aqueous solution) was obtained from Ajinomoto. Phthalic anhydride was bought from Arkema and xylene and benzoic acid were obtained from Brenntag. Glycine, citraconic anhydride, sorbic acid, sebacic acid and all solvents were purchased from Aldrich, unless mentioned otherwise. All materials were used as received.

Syntheses of resins
Citraconic acid glycine imide

Citraconic acid glycine imide ('glycine citraconimide') was prepared in a 250 cm³ round-bottomed flask, fitted with a mechanical stirrer, nitrogen inlet, thermocouple and Dean–Stark trap. Citraconic anhydride (76.3 g, 0.681 mol) was added to glycine (53.7 g, 0.715 mol) in a [1:1.05] mole ratio and reacted for 5 h at 145 °C using xylene as an azeotropic agent for water removal. The setup was then changed to a distillation bridge and vacuum distillation was performed to remove the xylene from the reaction mixture. NMR and infrared analyses confirmed that the imide had been formed in high purity.

Glycine citraconimide sorbic acid adduct

In a 700 cm³ pressure reactor, sorbic acid (73.89 g, 0.660 mol) was added to an imide of citraconic anhydride and glycine (111.4 g, 0.660 mol) in a ratio of 1:1. Water (150 g) was then added and the reactor vessel sealed and the reaction proceeded at 150 °C
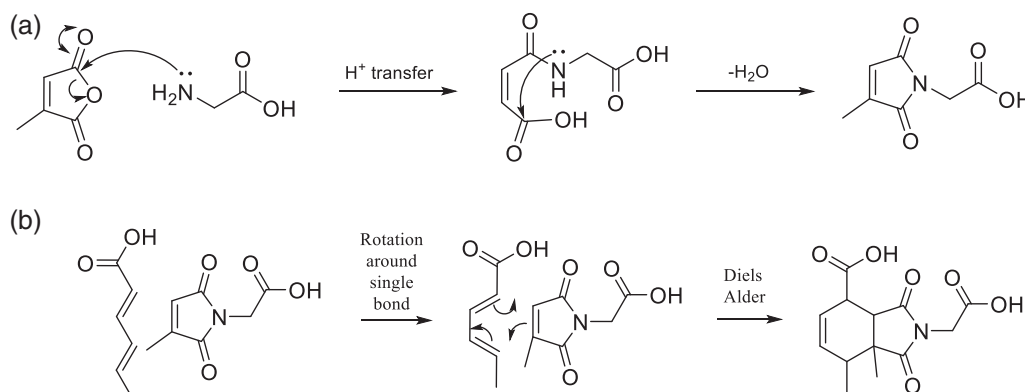
Figure 1 (a) Reaction scheme for step 1: imide formation from citraconic anhydride and (in this case) glycine. (b) Reaction scheme for step 2: formation of Diels–Alder adduct of citraconic imide and sorbic acid. Stereochemistry is not shown here.

Table 1 Composition and M_w and T_g of the prepared imidealkyds and of the reference, standard non-imide alkyd (the amount of soft fatty acids is around 33–34 wt% for all resins)

	Imidealkyd 1 (g or wt%)	Imidealkyd 2 (g or wt%)	Imidealkyd 3 (g or wt%)	Reference alkyd, g (wt%)
Building block				
Soybean oil fatty acids	32.6	33.2	33.7	217.0 (34.1)
Pentaerythritol	18.9	19.2	19.5	155.4 (24.4)
Glycine imide sorbic acid Diels–Alder adduct	28.6	23.2	17.7	
Succinic acid	1.3	1.3	1.3	
Sebacic acid	2.6	6.9	11.2	
Lysine disuccinimide	16.1	16.4	16.6	
Phthalic anhydride				168.2 (26.4)
Benzoic acid				96.2 (15.1)
Total (g)	100.1	100.2	100.0	636.8
Molecular weight and T_g				
M_n (kDa)	2.7	2.2	2.3	3.1
M_w (kDa)	21	12	14	38
T_g (°C)	10	−7	−20	−9

for 5 h. The contents of the reactor vessel were then poured into a round-bottomed flask and left on a rotary evaporator to remove the solvent (water). Subsequent syntheses on larger scale (5 dm³ pressure reactor) involved the same ratio of citraconimide to sorbic acid to water and involved the removal of water performed in a distillation setup instead of a rotary evaporator.

Lysine disuccinimide

Lysine disuccinimide was prepared and characterized as described previously.[8]

Alkyd containing glycine citraconimide sorbic acid adduct ('imidealkyd')

An alkyd resin based on the glycine citraconimide sorbic acid adduct was prepared in a 250 cm³ round-bottomed flask, fitted with a mechanical stirrer, nitrogen inlet, thermocouple and Dean–Stark trap. Amounts of 18.9 g of pentaerythritol, 32.6 g of soybean oil fatty acids, 28.6 g of glycine citraconimide sorbic acid adduct, 16.1 g of lysine disuccinimide, 2.6 g of sebacic acid and 1.3 g of succinic acid were reacted by gradual heating to a maximum temperature of 200 °C using xylene as an azeotropic agent to remove condensation water. After reaction for 8 h a polymer of acid value of 18 mg KOH g⁻¹ was obtained and the mixture was cooled, diluted with xylene and poured out.

All other imidealkyds were synthesized in a similar way. The compositions and weight-average molecular weight (M_w) and T_g values of the three imidealkyd resins are given in Table 1.

A comparative 'standard' polyester alkyd resin was prepared by reacting 168.2 g of phthalic anhydride, 155.4 g of pentaerythritol, 96.2 g of benzoic acid and 217 g of soybean fatty acids at a maximum temperature of 230 °C. Esterification was conducted by azeotropic water removal until the acid value was below 15 mg KOH g⁻¹. The resin was cooled, diluted in xylene and poured out. Also for this reference alkyd the M_w and T_g values are given in Table 1.

Resin characterization

Mass spectral analysis was performed with an LCMS (electronspray mass spectrum). Both samples were injected in the UPLC with UV (245 nm) and mass detection (electronspray positive mode, default values). The gradient was a generic one, based on water and methanol, which started with 95% water and was transferred to 95% methanol in 5 min. The column was an HSS C18 column from Waters.

The acid number of the synthesized alkyd resins, given as the mass of potassium hydroxide (KOH) in milligrams required to neutralize 1 g of the tested substance, was used as a measure of the concentration of carboxylic acid groups present. Acid number was determined by titration using the ASTM D974 method.

Gel permeation chromatography analyses for determining M_w were performed using an Alliance Waters 2695 GPC with two consecutive PL-gel columns, type Mixed-C, i.d. = 300/7.5 mm (Polymer Laboratories), size of column particles of 10 μm, using stabilized tetrahydrofuran modified with 0.8% acetic acid (added to prevent interaction of polar groups present in the alkyds with the stationary phase material) as the eluent at 1 mL min⁻¹ at 40 °C and using an Alliance Waters 2414 refractive index detector at 40 °C. A set of polystyrene standards with a molecular weight range from 500 to 7×10^6 Da was used to calibrate the gel permeation chromatography equipment.

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Tensor 27 IR equipped with a Pike GladiATR. ¹H NMR spectra were recorded with a Varian Mercury Vx (400 MHz) spectrometer or a Bruker Advance (400 MHz) spectrometer at 25 °C in chloroform-d_1 unless stated otherwise and referenced *versus* residual solvent shifts.

Usually dynamic mechanical thermal analysis (DMTA) is performed using solid, crosslinked materials, with equipment measuring in tensile mode. Here we aimed to characterize thermomechanical properties both before and after crosslinking of the resins. Before crosslinking, however, it is impossible to measure in tensile mode. But in shear mode DMTA can be performed both before and after crosslinking. Therefore, we chose to measure in shear mode using a Physica MCR301 rheometer equipped with an 8 mm diameter plate–plate geometry.

DMTA was performed (i) on the resins as such and (ii) on 30 μm thick resin films subjected to autoxidation for 24 h. These latter

resin films contained 0.7% Borchi OXY-Coat on solid resin. Borchi OXY-Coat contains 0.09% Fe, acting as a catalyst. The chemically dried films were removed from their substrate using a razor blade. Subsequently, cylindrically shaped samples were created from 16-fold stacked films, with a diameter of 8 mm and a height of 480 ± 50 μm. Samples were positioned between the plates of the measuring geometry, at a temperature of 40 °C. After raising the temperature to 90 °C, the actual DMTA measurement was started while lowering the temperature to −25 °C at a cooling rate of −4 °C min^{-1}. During cooling, the sample was subjected to an oscillatory shear deformation with an amplitude (γ_o) of 0.001 strain units and a frequency of 1 Hz.

As a function of temperature, the complex shear modulus (G^*) was calculated from γ_o and τ_o, the amplitude of the shear stress required for oscillatory deformation:

$$G^* = \tau_o / \gamma_o$$

G^* as a function of temperature can be considered as a measure for the 'hardness' as a function of temperature. Measured at temperatures far above T_g, G^* is related to the density of 'elastically effective' polymer network chains, n:

$$G^*_{T \gg T_g} = G^*_{rubber} = nkT$$

with k and T representing the Boltzmann constant (1.38×10^{-23} J K^{-1}) and the absolute temperature, respectively. The loss modulus (G'') was calculated from γ_o, τ_o and the phase shift (δ) between the oscillatory stress and deformation:

$$G'' = (\tau_o / \gamma_o) \sin \delta$$

T_g is defined as the temperature corresponding to the maximum value of $G''(T)$ as measured for physically dried films.

Paint preparation

Paints were produced by mixing in a Cowles dissolver resin solution (44 g of solid resin), 28 g of Tioxide TR92 (pigment) and 0.30 g of Nuosperse FA601 (dispersant) and milling them into a mill paste. To this paste were added under stirring 0.31 g Borchi OXY-Coat (iron drier), 0.70 g of calcium naphthenate (calcium drier), 1.83 g of Octasoligen Zirconium 12 (zirconium drier), 0.3 g of Borchinox M2 (anti-skinning agent) and xylene to give application viscosity. From these xylene solutions, white pigmented paint films were cast and the xylene was evaporated. The films with drier gave chemically cured films (which can be evidenced by checking the formation of a rubber plateau in the corresponding G^* *versus* T curves) while the ones without drier give only physically dried films without crosslinking (which can be evidenced by checking whether total flow of the material occurs at elevated T in the corresponding G^* *versus* T curves).

Paint characterization

König hardness was determined following DIN 53157 NEN 5319 using Erichsen hardness equipment. The values are given in seconds. The greater the number of seconds, the greater is the König hardness.

Drying properties were determined from the cotton wool dust-free time and tack-free time according to the standard ASTM D 1640 method. A cotton wool adhesion test measures the rate of surface drying of a coating film. The cotton wool adhesion test was conducted on a coating film applied with a 100 μm slit applicator on a glass plate. After applying the coating composition, a swatch of cotton wool (a loose ball of approximately 0.2 g and a diameter of approximately 3 cm) was dropped from a height of 5 cm on the paint film. After 10 s the glass panel was turned over 180° and it was observed if the cotton wool dropped off without

leaving cotton fibers on the surface. When the cotton wool did not stick to the surface, the time was recorded as the dust-free time. For the tack-free time the same procedure was used, but now a weight of 1 kg was placed on the cotton wool. The tack-free time was always determined after dust-free properties were reached.

The color change due to yellowing was measured according to CieLab. A coating film was applied with a 100 μm slit applicator on a glass plate and dried for one week at room temperature. Then the initial color according to CieLab (L^*, a^*, b^* values) was measured and the b^* value recorded. Next the film was stored in an oven at 50 °C for one week or for three weeks. Again, the color was measured and the change in b^* value was recorded as Δb^*. The higher the Δb^* value, the stronger was the yellowing.

Gloss measurements were carried out with a BYK Gardner micro TRI gloss 20 60 85 glossmeter in accordance with ASTM D523 89.

RESULTS AND DISCUSSION

Synthesis and characterization of fully bio-based citraconimide based on citraconic anhydride and glycine ('glycine citraconimide')

Glycine citraconimide was synthesized as described in the Experimental section and the reaction pathway is illustrated in Fig. 1. Whereas the FTIR spectrum of the bio-based citraconic anhydride shows the typical anhydride carbonyl bands at 1770 and 1830 cm^{-1} and a clear C=C bond absorption at 1650 cm^{-1}, that of the fully bio-based reaction product shows the typical imide carbonyl bands at 1705 and 1770 cm^{-1} (Fig. 3). The alkene band is retained at around 1650 cm^{-1} (Fig. 3). In Fig. SI1 in the supporting information, it is shown that the calculated and the recorded ^{1}H NMR spectra of the glycine citraconimide are almost identical. This is supportive evidence for the formation of the imide, in addition to the FTIR data discussed above. It can also be seen in the ^{1}H NMR spectrum that xylene and traces of other impurities are also present. The presence of traces of xylene, used as an azeotrope to remove the reaction water resulting from imide formation, is not an issue since the reaction product will be used as a monomer in an alkyd resin synthesis, for which xylene will again be added as an azeotropic agent. The other impurities make up such a small amount that this is insignificant. Neither the FTIR spectrum nor the ^{1}H NMR spectrum point to the occurrence of Michael addition of the glycine amine group to the methyl-substituted carbon–carbon double bond, which is a well-known side reaction occurring during the imidization of maleic anhydride.[14]

Synthesis and characterization of fully bio-based Diels–Alder adduct of glycine citraconimide and sorbic acid

The renewable glycine citraconimide was reacted with sorbic acid, a naturally occurring substance used as a food preservative,[15] using Diels–Alder chemistry as described in the Experimental section and the reaction pathway is illustrated in Fig. 2. A ^{1}H NMR spectrum of this crude reaction product consists of many signals, corresponding to many regiochemical, optical and stereoisomers (supporting information, Fig. SI2). In Fig. SI3 in the supporting information, eight different isomers are presented. Realizing that for each of the drawn isomers both the exo- as well as the endo-stereoisomers can be present, at least 16 different isomers can be present in the reaction mixture, apart from some impurities. This in itself already explains the complicated character of the ^{1}H NMR spectrum of the equimolar Diels–Alder reaction product of sorbic acid and glycine citraconimide. A rough estimation of the
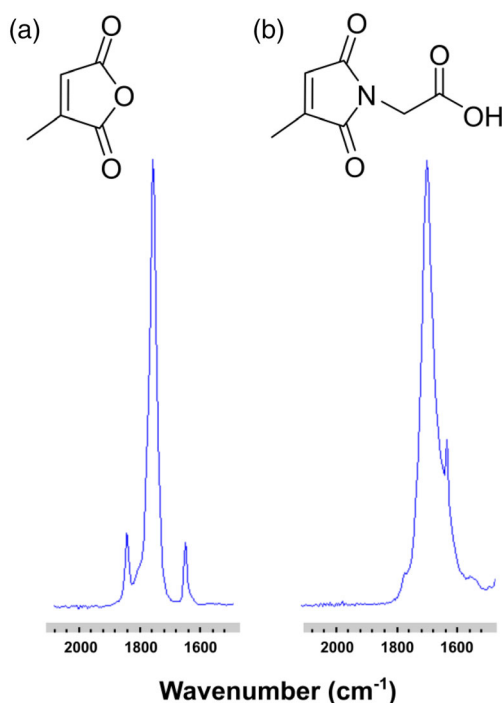
Figure 3 Relevant parts (a) of the FTIR spectrum of citraconic anhydride, showing typical anhydride carbonyl bands at 1770 and 1830 cm^{-1} and a clear C=C bond absorption at 1650 cm^{-1}, and (b) of the FTIR spectrum of glycine citraconimide, showing typical imide carbonyl bands at 1705 and 1770 cm^{-1} and the retained C=C absorption at around 1650 cm^{-1}.

composition of this crude Diels–Alder adduct, based on the integrated spectrum, is as follows: $84 \pm 1\%$ desired Diels–Alder adduct, $5 \pm 1\%$ unreacted sorbic acid and $11 \pm 1\%$ dimerized sorbic acid. The latter impurities further complicate the spectrum. Remarkably, although expected because of the presence of unreacted and even dimerized sorbic acid and the initial equimolar ratio of sorbic acid and glycine citraconimide, no traces of unreacted glycine citraconamide were detected, possibly because of radical oligomerization of the reactive C=C bond of the citraconimide.

The Diels–Alder adduct was purified by crystallization from the crude reaction mixture in a refrigerator at 7–8 °C. The crystals were formed in a yield of *ca* 35 wt%. Figure 4 shows the ^{1}H NMR spectrum of the formed crystals. This spectrum is markedly cleaner than that of the crude reaction product. For integration of the spectrum, the peak at 4.0–4.3 ppm was set as the reference of two protons, as this peak represents the two protons attached to the carbon adjacent to the nitrogen atom of the imide. The relatively large integration value of the peaks between 7 and 7.5 ppm in the spectrum indicates that two of the eight isomers shown in Fig. SI3, namely isomers 6 and 2, are most likely the predominant isomers in the mixture. The spectrum also shows traces of unconjugated isomers and free sorbic acid, which makes it challenging to quantitatively describe the isomer composition with high accuracy, as well as to understand peak multiplicity. Despite this, the relatively large integration value of the peak at *ca* 7.11 ppm compared to the peak at *ca* 7.25 ppm (even after taking into account the contribution of sorbic acid to the peak) indicates that isomer 6 is more prominent than isomer 2. (Note that it is possible that not all isomers crystallized out.) The preference for the formation of regioisomer 6 over regioisomer 2 is

understandable from the orbital theory in view of LUMO and HOMO orbital effects, illustrated in Fig. SI4.

In addition to the FTIR and NMR characterization, the crude Diels–Alder reaction product was also submitted to liquid chromatography–mass spectrometry analysis. In addition to some unidentified compounds that were present in minor quantities, five dominant compounds were present: (i) sorbic acid (with *m/z* 112), also identified in the ^{1}H NMR spectrum of the crude adduct (see above); (ii) dimerized sorbic acid (with *m/z* 224), also identified in the ^{1}H NMR spectrum of the crude adduct (see above); (iii) the desired Diels–Alder adduct (with *m/z* 281); (iv) the anhydride of the Diels–Alder adduct (with *m/z* 263, being 281 minus a water molecule); and (v) the amic acid of the Diels–Alder adduct, which is the non-ring-closed imide (with *m/z* 299, being 281 plus a water molecule). Compounds 3–5 will all react in the same way in a polyester synthesis at elevated temperature, namely as a dicarboxylic acid. The dimerized sorbic acid will also react as a dicarboxylic acid, whereas the sorbic acid would react as a chain stopper if it does not leave the polymerization mixture by sublimation during the polyester synthesis. Interestingly, we also noticed that two structures with *m/z* 281 passed through the liquid chromatography column at different times. This is evidence towards the endo and exo stereoisomerism we expect for these Diels–Alder adducts.

Synthesis and characterization of imidealkyds and of standard reference alkyd

TGA measurements of the Diels–Alder adduct of glycine citraconimide and sorbic acid pointed to significant retro Diels–Alder reaction, followed by sublimation of the released sorbic acid, at temperatures above 200 °C (Fig. SI5). Therefore, during the polymerizations for making alkyd resins from the mentioned crude and non-crystallized Diels–Alder adduct, the temperature was gradually raised and kept below 200 °C. For comparison with the imidealkyds, a standard non-imidealkyd with standard composition was synthesized from phthalic anhydride, pentaerythritol, soybean fatty acids and benzoic acid. For the three different synthesized imidealkyds, the compositions and the number-average molecular weight (M_n), M_w and T_g values are given in Table 1. Additionally, the molecular weight distributions are shown in Fig. SI6. With respect to the standard alkyd formulation, in the imidealkyds the Diels–Alder adduct of the glycine citraconimide and sorbic acid, a dicarboxylic acid, was used as a substituent for phthalic anhydride and the lysine disuccinimide (described previously[8]) was used as a fully bio-based substituent for monofunctional benzoic acid. A standard, small amount of succinic acid and various amounts of sebacic acid were added to the polymerizing mixture to enhance the compatibility of the nonpolar fatty acids and the relatively polar glycine citraconimide sorbic acid adduct. Without addition of these monomers, phase separation was observed during synthesis whereas the compositions listed in Table 1 all showed a homogeneous polymerization mixture. Note that in a standard alkyd composition only the fatty acid residues are bio-based, whereas for both the imidealkyds and the reference alkyd, the pentaerythritol can be prepared from a mixture of renewable and petro-based raw materials, for which a so-called mass balance certificate for the percentage bio-based raw materials can be obtained from the manufacturer.[4] The phthalic anhydride and benzoic acid are completely petro-based. On the other hand, in the imidealkyds 1, 2 and 3 described in this paper, the fatty acids, the glycine imide sorbic acid adduct, the succinic acid, the sebacic acid and the lysine disuccinimide are
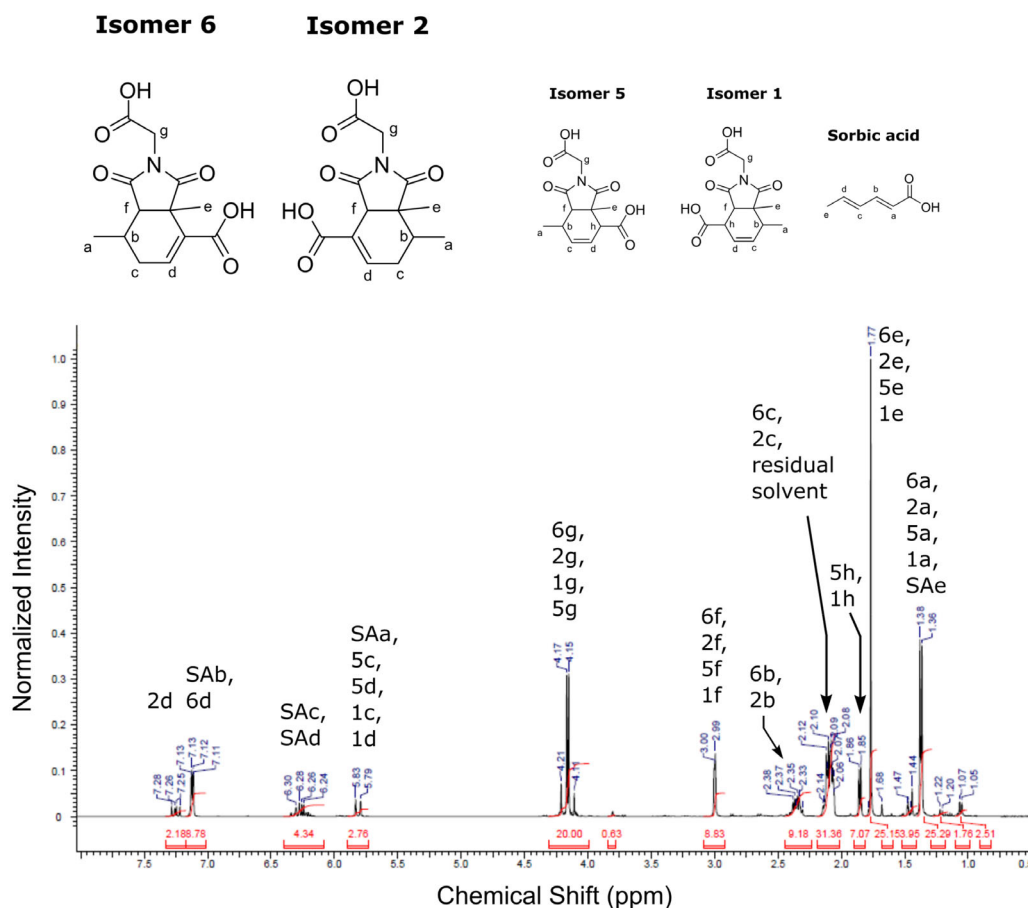
Figure 4 ^{1}H NMR spectrum of the crystallized Diels–Alder reaction product of sorbic acid and glycine citraconimide with structural identification. At the top of the figure, the proton environments are labelled a to g and shown for isomers 6, 2, 5, 1 (as defined in Fig. SI3), and sorbic acid. The spectrum shows labelled peaks, where '6a' refers to isomer 6, proton environment a, and so on. 'SAc' refers to sorbic acid environment, etc. Peaks are labelled with the most significantly contributing proton environments. Further characterization is in the supporting information.

all fully bio-based, making these imidealkyds at least 80 wt% bio-based (calculated from the weight percentages given in Table 1, ignoring the bio-based content of pentaerythritol which is unknown to us) and even more if the pentaerythritol is indeed partly bio-based. Using the same approach, the reference alkyd is *ca* 34 wt% bio-based.

The as-prepared reference alkyd and the three imidealkyds listed in Table 1 were all studied using DMTA. The T_g values measured for the physically dried and non-cured alkyds are listed in Table 1. These T_g values correspond to the temperatures at which the maximum of the $G''(T)$ curves were measured (Fig. SI7). The G^* *versus T* curves for these resins are shown in Fig. 5(a); no catalyst for the oxidative chemical curing was added and the non-cured resins flow at elevated temperature. These data clearly show that, for very similar weight percentages of soft fatty acid residues, imidealkyd 1 based on *ca* 29 wt% of the very rigid, double-ring glycine imide sorbic acid adduct has a significantly higher T_g than the reference alkyd based on 26–27 wt% phthalic anhydride, even though M_w of the imidealkyd is lower. Higher contents of the compatibilizing mixture of flexible sebacic and succinic acids reduce T_g and cause lower G^* values over a wide temperature range, including room temperature. Imidealkyd 2 has T_g very close to that of the reference alkyd, even though M_w of imidealkyd 2 is significantly lower. Upon addition of the catalyst mixture to the resin solutions, chemical oxidative curing of the fatty acid

residues takes place, which is reflected by both an increase of T_g (Fig. SI7) and the formation of a rubber plateau at temperatures above T_g (Fig. 5(b)). The height of the rubber plateau corresponds to the crosslink density of the cured alkyd films. From Fig. 5(b) it can be concluded that crosslinking of the imidealkyd resins is at least equal to or even better than that of the reference alkyd, pointing to higher resistance against blocking, imprinting and mechanical impact. At room temperature, the temperature at which normally the hardness of coatings and paints is measured, imidealkyd 1 with the highest dicyclic imide content has a significantly higher G value than the reference alkyd. Imidealkyd 2 containing *ca* 7 wt% of sebacic acid shows a G *versus T* curve very similar to the corresponding curve for the reference alkyd. At room temperature, imidealkyd 3 containing *ca* 11 wt% of flexible sebacic acid has a lower modulus than the reference alkyd.

Characterization of white paints
From the three imidealkyd resins and the non-imide reference alkyd, white paints were made as described in the Experimental section. For these white alkyd-based paints four important properties were determined: the König pendulum hardness, the drying speed (by performing a cotton wool test), the yellowing in the dark (alkyd resins tend to yellow in the dark due the oxidative drying process) and the gloss measured one day after application of the paints.
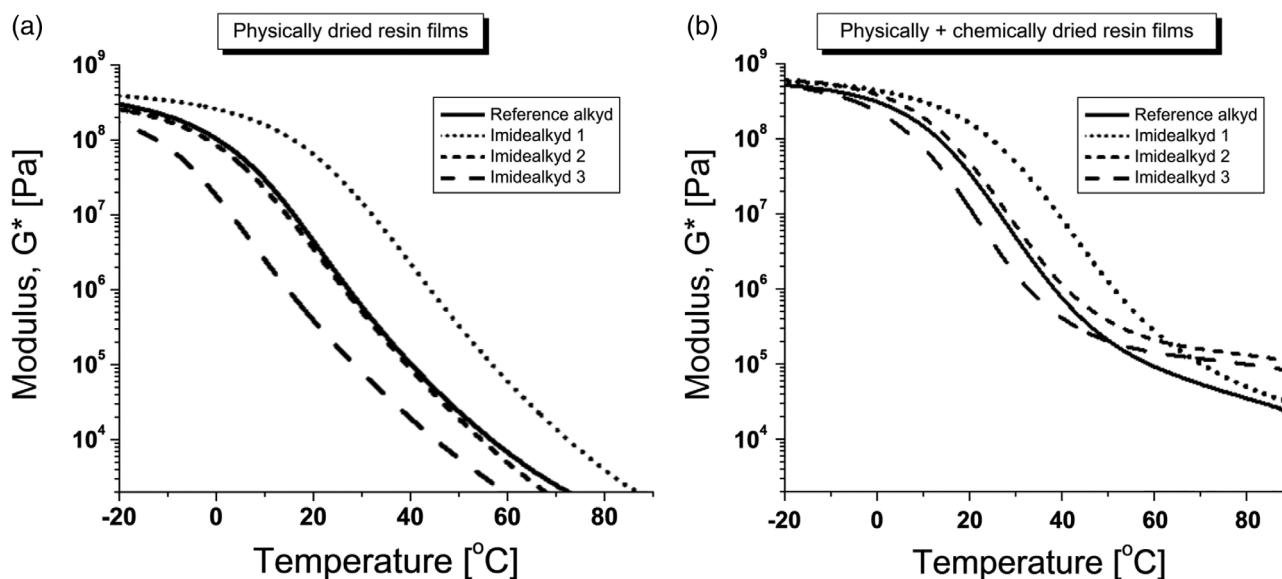
Figure 5 DMTA profiles of (a) physically dried and (b) oxidatively cured non-pigmented resin films of the reference alkyd and the three imidealkyds listed in Table 1. The curves in (b) were measured after 24 h drying of 30 μm thick films.

Figure 6 shows that the König hardness of the oxidatively cured alkyds decreases with increasing sebacic acid and decreasing imide content. Compared to the reference, it can be seen that imidealkyd 1 exhibits a higher hardness, but the other resins containing relatively high sebacic acid contents show significantly lower hardness levels. These observations are approximately in agreement with the rheological data given in Fig. 5(b). Note that replacing benzoic acid by lysine disuccinimide in itself also enhances the hardness.[9] We believe, however, that the contribution of the very rigid dicyclic imide to the hardness is more important.

Figure 7 shows the dust-free and tack-free drying times of the imidealkyds and the reference alkyd. The results show that the hardest paint, based on the alkyd containing the highest percentage of rigid dicyclic imide and the lowest sebacic acid content, shows a significantly faster drying than the standard alkyd. The high T_g value of the resin means that the physical drying is extremely fast in this case (T_g is higher than room temperature, whereas T_g of the reference alkyd resin is lower than room temperature and some chemical drying seems to be required to make the coating non-sticky; note that during the test the chemical drying will start). Higher sebacic acid contents, and accordingly lower T_g, give longer drying times. The resin containing *ca* 7 wt% sebacic acid shows drying times comparable to that of the reference alkyd.

A known and important feature of alkyd resins is the yellowing in the dark, related to the oxidative drying process.[3,16,17] Normally, yellowing in the dark is more pronounced for higher fatty acid contents. Within 1.5 wt%, the fatty acid contents of all studied resins are the same, the reference alkyd even having the highest content. Nevertheless this reference alkyd shows the lowest yellowing after 21 days in the dark (Fig. 8). We believe that this is caused by the presence of imide functionalities in the imidealkyds, which also causes the somewhat higher initial yellowness. All in all, the initial yellowness and the yellowing after 21 days of the imidealkyds are *ca* 0.4–0.5, respectively 0.4–0.6 '*b**-value units' higher than the corresponding values of the reference alkyd. This is a disadvantage of these sustainable alkyd resins with enhanced renewable content.
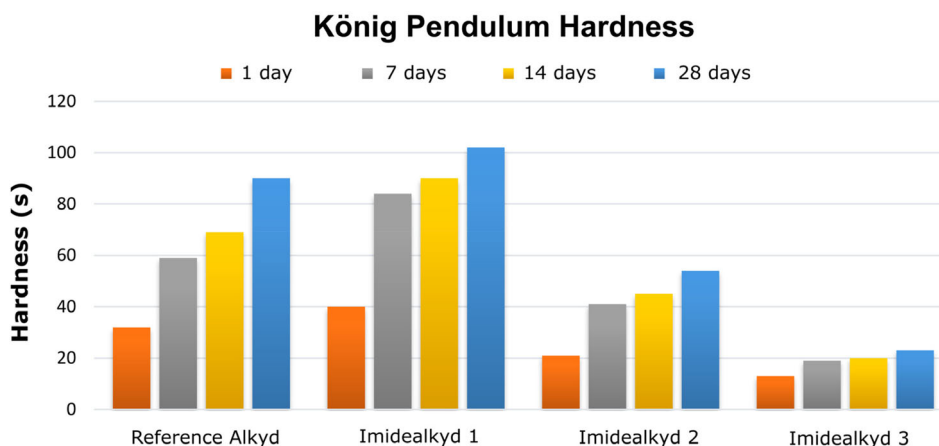
Figure 6 Chart showing the König hardness levels of white paints of the oxidatively cured reference alkyd and the three imidealkyds listed in Table 1 after drying times of 1, 7, 14 and 28 days at 21 °C and 54–55% humidity.
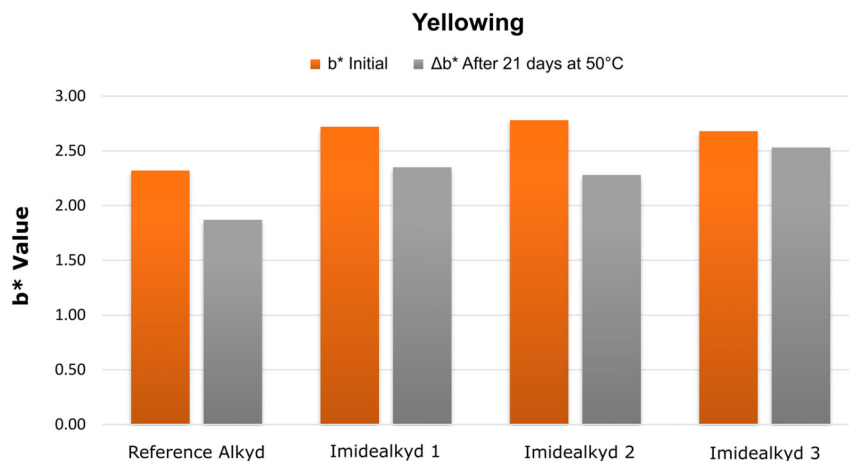
Drying: Cotton Wool Test
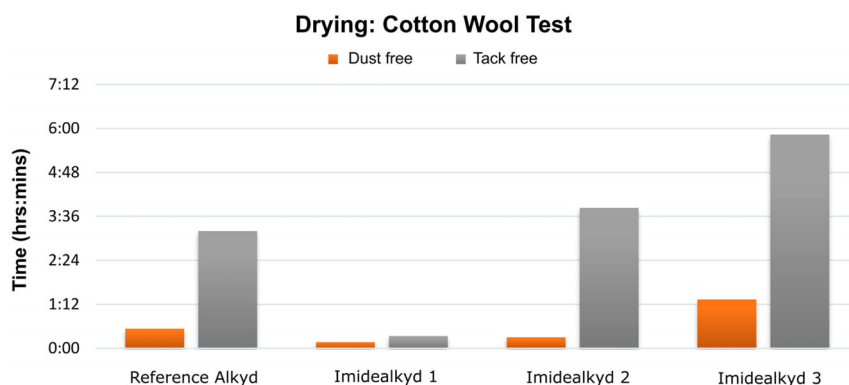
Figure 7 Chart showing the drying times of white paints of the oxidatively cured reference alkyd and the three imidealkyds listed in Table 1.

The gloss, also an important property of alkyd paints, was determined one day after applying paint on a substrate. Figure 9 shows that the gloss levels, measured at angles of both 20° and 60°, are somewhat lower than the corresponding values for the reference alkyd. Nevertheless, these gloss values are still at an acceptable level and the qualification of high gloss paints is still valid for the highly renewable paint binder systems, where the binders have over 80 wt % bio-based contents and where for the remaining 19–20 wt% a mass balance certificate for 1–100% bio-based character can be bought.

Summarizing and critically evaluating the obtained results, we can say that the novel imidealkyds, with bio-based contents of over 80 wt%, show advantages as well as disadvantages when compared to a standard alkyd with only *ca* 34 wt% bio-based content. Some of the presented imidealkyds for sure show potential as sustainable, renewable alkyds. Imidealkyds with high dicyclic imide contents show higher hardness, faster drying, a slightly lower gloss but more pronounced yellowing in the dark compared to the reference alkyd. For imidealkyds with lower amounts of dicyclic imide contents, no real advantages with respect to a reference alkyd are observed, with the exception of a higher sustainability.

One should realize that the preliminary results reported here concern xylene-cast white paints, which are obviously less sustainable than waterborne alkyds because of the harmful nature of the organic solvent. Nevertheless, in view of their high bio-based content, the 'solvent-borne' alkyds described in this paper are expected to be more sustainable than the currently commercially available solvent-borne alkyds (note that a full life-cycle analysis would be required to confirm this statement, which is beyond the scope of this paper). Since transferring alkyds into stable water-based emulsions is a very challenging and time-consuming exercise, in industry frequently the intrinsic properties of novel alkyd resins are first determined after casting paints from xylene. The benefits of the xylene-cast resins with high contents of the Diels–Alder adduct of citraconimide and sorbic acid would justify efforts to turn these imidealkyds into emulsions. For this, two standard technologies are available: the so-called phase-inversion process[18] and the solvent-assisted dispersion process.[19] In the first process, separate surfactants are added to the pure alkyd melt and in the presence of water under stirring phase inversion takes place. In the second process, in a low-boiling solvent like acetone, dimethylolpropionic acid is chemically connected to the OH-functionalized resin via urethane chemistry using a diisocyanate. After neutralization of the tertiary COOH group of dimethylolpropionic acid with a strong base, and addition of water and emulsification by stirring, the acetone is evaporated and an emulsion of the resin in water remains, stabilized by internal dispersants, all chemically connected to the resin. This solvent-assisted dispersion process enables the dispersion of highly viscous, high-T_g resins into water, as is the case for the most interesting imidealkyd with the highest dicyclic imide content, and seems to be the preferred emulsification route. The evaporated acetone is trapped and is not released in the environment

Yellowing

Figure 8 Chart showing the yellowing levels of white paints of the oxidatively cured reference alkyd and the three imidealkyds listed in Table 1 after 21 days.

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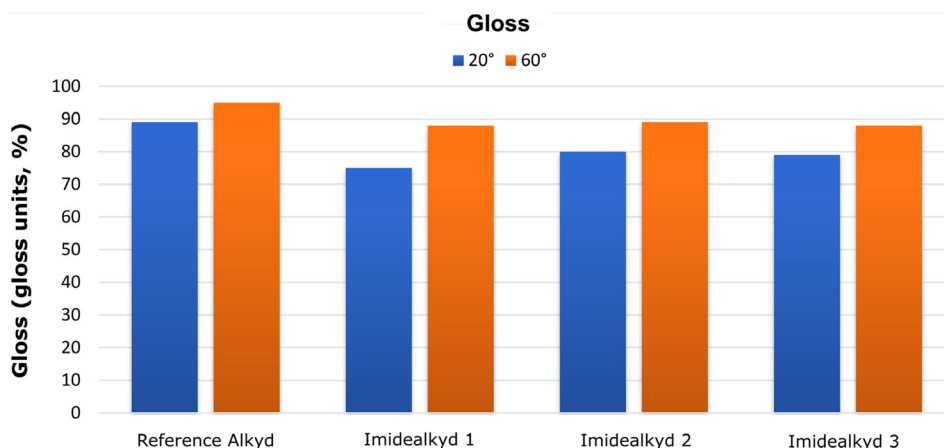
Figure 9 Chart showing the gloss levels (at angles of 20° and 60°) of white paints of the oxidatively cured reference alkyd and the three imidealkyds listed in Table 1 after 1 day.

during the industrial emulsification process, as would be the case for xylene-based paint systems, releasing a harmful organic solvent in the environment after paint application by the painter. Therefore, emulsification using the solvent-assisted dispersion process would render a sustainable paint system. The emulsification is a study in itself and falls beyond the scope of this paper.

CONCLUSIONS

New, highly rigid bio-based building blocks were synthesized from renewable raw materials. In a first reaction step, an imide was made from citraconic anhydride and the amino acid glycine. This imide was subsequently reacted with sorbic acid using Diels–Alder chemistry, furnishing a double-ring structure. This new, very rigid renewable building block was then incorporated into alkyd resins by standard polycondensation chemistry and technology. The resulting, >80 wt% renewable, alkyd resins were evaluated as white paints in a preliminary way by solvent casting from xylene. The properties of the renewable coating based on the highest citraconimide sorbic acid adduct look promising, the König hardness and the drying speed even outperforming those of standard commercial alkyd resins, while the imidealkyds containing lower contents of the fully renewable Diels–Alder adduct do not have much to offer, besides their enhanced bio-based content, with respect to a standard reference alkyd. For further enhancing the sustainability of the systems discussed, turning these highly bio-based alkyd resins into stable aqueous emulsions is a must. We believe that the only feasible approach towards preparing stable aqueous emulsions of the high-T_g and highly viscous imidealkyd with the highest bio-based Diels–Alder adduct content is via the solvent-assisted dispersion process.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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