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Fully renewable limonene-derived polycarbonate as a high-performance alkyd resin

Chunliang Li,[a,b] Theo Veldhuis,[c] Bart Reuvers,[c] Rafaël J Sablong[a,d*] and Cor E Koning[a,c,e]

Abstract

Limonene-derived polycarbonate-based alkyd resins (ARs) have been prepared by copolymerization of limonene dioxide with CO_2, catalysed by a β-diiminate zinc–bis(trimethylsilyl)amido complex, and subsequent chemical modification with soybean oil fatty acids using triphenylethylphosphonium bromide as the catalyst. This quantitative partial modification was realized via epoxy–carboxylic acid chemistry, affording ARs with higher oil lengths, lower polydispersities and higher glass transition temperatures (T_g) in comparison to a conventional polyester AR based on phthalic acid, multifunctional polyol pentaerythritol and soybean fatty acid. The novel limonene polycarbonate AR and the conventional polyester AR were evaluated as coatings and both the physical drying (without the presence of the oxidative drying accelerator Borchi® Oxy Coat) and chemical curing (with Borchi® Oxy Coat) processes of these coatings were monitored by measuring the König hardness and complex modulus development with time. A better performance was obtained for the alkyd paint containing polycarbonates modified with fatty acids (FA-PCs), which showed a faster chemical drying, a higher König hardness and a higher T_g in coating evaluation, demonstrating that the fully renewable FA-PCs are promising resins for alkyd paint applications.
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Keywords: alkyd paint; limonene dioxide; renewable polycarbonate; soybean fatty acid

INTRODUCTION

Aliphatic polycarbonates have attracted increasing attention due to their good biodegradability and biocompatibility.[1–7] Potentially, CO_2 can be used as an interesting bio-based building block in preparing aliphatic polycarbonates with low carbon footprints. Among them, conventional aliphatic polycarbonates like poly(cyclohexene carbonate) and poly(propylene carbonate) have limited commercial applications because of their unsatisfactory physical and mechanical properties, like low elongation at break (in the case of poly(cyclohexene carbonate)) and low rigidity (in the case of poly(propylene carbonate)).[8,9] Moreover, the lack of additional functionality in the corresponding epoxides makes it rather difficult to enhance the properties by chemical modification and/or crosslinking. On the other hand, the selective polymerization of functional epoxides, namely epoxy monomers with an extra functionality like an alkenyl, carbonate or hydrophilic group, receives wide attention because the corresponding functional polymers show interesting properties in many applications such as reactive substrates, coating resins and polymeric nanoparticles.[10–17] Recently, we have reported the chemo-selective alternating copolymerization of limonene dioxide and CO_2,[18] leading to a new highly epoxy-functional linear aliphatic epoxy polycarbonate, poly(limonene-8,9-oxide carbonate) (PLOC; carrying a pendent epoxide group in every repeat unit), which can be an interesting polymer precursor for many applications, such as a degradable polymer backbone for alkyd resins (ARs).[19]

Solvent-based alkyd paints typically consist of components such as solvents, binders, pigments, extenders and additives.[20] The binder is a synthetic, highly branched polyester resin called an AR, while pigments and extenders are used to produce the paint colour and improve the mechanical and physical properties of the paint, respectively. Additives typically have various functions in a coating formulation. One important category of additives are metal-based coordination compounds, known as driers, which accelerate paint drying by enhancing the oxidative crosslinking rate of the alkyd binder, thus shortening the drying time.[21,22]

Solvent-based ARs constitute a very versatile and economic group of binders for the paint industry.[23] They usually comprise

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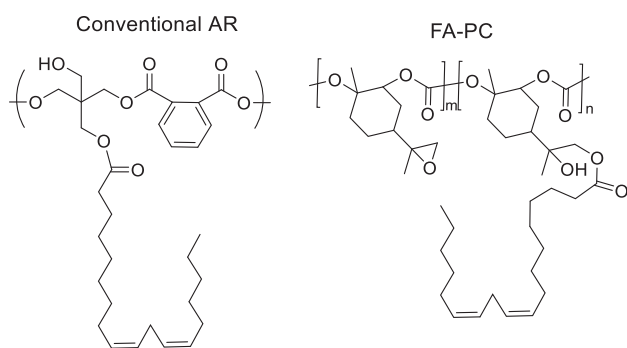
Figure 1. Structures of a typical branched, conventional polyester-based AR and a comb-like limonene polycarbonate-based FA-PC.

unsaturated vegetable oils or the corresponding fatty acid residues and thus have low values of glass transition temperature (T_g), leading to a low application viscosity after dissolution and subsequent evaporation of the solvent. The unsaturation of the fatty acid moieties also allows ARs to crosslink into a very large network with excellent protective properties. Conventional ARs (Fig. 1) are synthesized via a polycondensation process. First, a polyhydric alcohol, a polycarboxylic acid (anhydride) and a fatty acid or oil are mixed. Very frequently soybean oil or its fatty acids are used. Subsequently, a polycondensation reaction is carried out at elevated temperatures (usually around 220–240 °C), possibly with the use of an appropriate catalyst, resulting in (highly branched) polyesters with very broad molecular weight distribution (polydispersity index (PDI) ∼ 18–25).[24] A careful control over the feeding ratios of the reactants and over the reaction temperature is necessary to produce resins with desired properties. For example, residual hydroxyl and carboxyl groups are necessary for good wetting properties. In comparison, linear polycarbonates modified with fatty acids (FA-PC) with a low PDI can be produced under milder reaction conditions. The structures of a typical, conventional polyester-based AR and FA-PC are shown in Fig. 1. Soybean oil consists of saturated fat (16%), monounsaturated fat (23%) and polyunsaturated fat (58%). The major unsaturated fatty acid derivatives in soybean oil triglycerides are polyunsaturated α-linolenic acid (C-18:3, of which 7–10% is present), polyunsaturated linoleic acid (C-18:2, of which 51% is present) and monounsaturated oleic acid (C-18:1, of which 23% is present). For simplicity, only the structure of linoleic acid as the main component is shown in the structure given in Fig. 1. For oxidative drying (chemical crosslinking) the —C=C—CH$_2$—C=C— sequences present in linoleic and linolenic acid residues are crucial. The CH$_2$ moieties easily lose a hydrogen radical, leaving a carbon radical at the FA residue. This C radical reacts with oxygen to give a —C—O—O— radical, which abstracts a hydrogen radical from another chain part. The resulting —C—O—O—H moiety then is decomposed into —C—O and —OH radicals, for which an earlier mentioned metal coordination complex is the catalyst. Two —C—O radicals present on different alkyd chains can then recombine forming a chemical crosslink. The same crosslinking chemistry can occur for the FA-grafted, comb-like limonene polycarbonate 'alkyds'.

This present paper reports the synthesis of an epoxy FA-PC and its evaluation as a fully bio-based AR. In comparison to conventional classic alkyd paint, FA-PC-based alkyd coatings show a much better performance, like faster chemical drying, higher König hardness and higher T_g.

MATERIALS AND METHODS
Materials
Toluene, tetrahydrofuran, dichloromethane (CH$_2$Cl$_2$) and diethyl ether were purchased from Biosolve and purified using an activated alumina purification system. CO$_2$ with purity of 999 993 vol% was supplied by Linde. (R)-Limonene dioxide (98%, mixture of *cis* and *trans*) was supplied by Nitrochemie Aschau GmbH and was distilled over CaH$_2$ and stored under nitrogen prior to use. Borchi® Oxy Coat (supplied by OMG Borchers) is an organic metal salt (1% (w/w) solution in propanediol) wherein the metal of the metal cation of the organic metal salt is Fe (Borchi® Oxy Coat contains 800–1000 ppm of Fe). The soybean oil fatty acids (SOFAs) were supplied by Oleon (acid value = 201, iodine value = 133). The other chemicals were supplied by Aldrich and were used as received. All reactions involving air- or water-sensitive compounds were carried out under dry nitrogen using MBraun glove boxes or using standard Schlenk line techniques. The reference and more conventional alkyd, a highly branched polyester alkyd based on phthalic anhydride, pentaerythritol and soybean fatty acid, was obtained from DSM Coating Resins. This resin had an M_n value of 3500 Da and a polydispersity (M_w/M_n) value of *ca* 20.

Characterization
The acid value was measured titrimetrically according to ISO 21 14. The acid value is given as the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize 1 g of the test substance and is used as a measure of the concentration of carboxyl groups present. The hydroxyl value was measured titrimetrically according to ISO 4629. The hydroxyl value is given as the mass of KOH in milligrams that is required to neutralize 1 g of the test substance and is used as a measure of the concentration of hydroxyl groups present.

Oil length (OL) of an AR is calculated by dividing the amount of 'oil' in the final alkyd by the total weight of the alkyd solids, expressed as a percentage.

Gel permeation chromatography analyses were carried out using a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector, a Waters 2487 dual absorbance detector and a PSS SDV 5 m guard column followed by two PSS SDV linearXL columns in series of 5 m (8 × 300) at 40 °C. Tetrahydrofuran with 1% (v/v) acetic acid was used as eluent at a flow rate of 1.0 mL min^{-1}. The columns were calibrated using a series of polystyrene standards (Polymer Laboratories, M_p = 580 Da up to 7.1 × 10^6 Da). Before analyses, the samples were filtered through a 0.2 μm polytetrafluoroethylene filter (13 mm, PP housing, Alltech).

^{1}H 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.

Dynamic mechanical thermal analysis (DMTA) was performed using a Physica MCR301 rheometer equipped with an 8 mm diameter plate–plate geometry and a gap size of 0.6 mm. The cooling rate was set at 4 °C min^{-1}. While cooling, the sample was subjected to an oscillatory shear deformation with an amplitude of 0.001 shear units and a frequency of 1 Hz. From this oscillatory deformation and the resulting oscillatory stress, the following rheological characteristics were calculated: (i) the complex shear modulus, G^*, being equal to the ratio of the shear stress amplitude and the amplitude of deformation and (ii) the phase angle, δ, representing the phase lag between the oscillatory shear stress and the

oscillatory deformation. T_g was defined as the temperature corresponding to the maximum value of the loss modulus G'' ($= G^* \sin \delta$) as a function of temperature, at a deformation frequency of 1 Hz and a cooling rate of 4 °C min^{-1}.

Films were prepared from 50 wt% resin solutions in xylene. Borchi® Oxy Coat (0.7 wt%) was added to accelerate the chemical drying due to autoxidation. The solutions were applied on a glass plate using a 100 μm slit applicator. The resin films obtained after evaporation of xylene were characterized by a film thickness of 29 ± 2 μm. The König hardness (reported in seconds) of the coatings was measured according to DIN 53157 using Erichsen hardness equipment. The greater the number of seconds, the greater is the König hardness.

The drying process was monitored according to the standard ASTM D1640 method. Dust-free time was determined by a cotton fibre test. A coating film was applied with a 100 μm slit applicator on a glass plate. An individual absorbent cotton fibre (a loose ball of approximately 0.2 g and a diameter of approximately 3 cm) was dropped from a height of 5 cm. The film was considered to be dust free when the cotton fibres did not stick to the surface when the test film was turned over 180°. Tack-free time was determined following the same procedure, 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 determined.

The water resistance of the paints was evaluated as follows. A 100 μm wet film was cast on a Leneta chart and dried for 24 h under standard conditions. Then three drops of water were placed on the film and one drop of water was removed after 30 min, a further one after 1 h and the final one after 3 h. The water resistance was assessed immediately after removal of the water and after 24 h. The rating for water resistance is as follows: 0 = very poor, dissolved; 3 = acceptable; 5 = excellent, no damage of the coating. The visual damage was examined and the qualification can range from 5 (no visible damage) to 0 (very serious damage).

The colour difference of the coatings was determined following ISO 7724 using a Dr Lange Spectro-pen spectrophotometer. An average of five measurements per sample was taken as $L^* a^* b^*$ colour coordinates. The lightness, L^*, represents the darkest black at $L^* = 0$, and the brightest white at $L^* = 100$. The colour channel a^* represents green at one extremity ($-a$) and red at the other ($+a$), while b^* represents blue at one end ($-b$) and yellow ($+b$) at the other. The colour difference was calculated using the CIE 76 formula with $\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$.

Synthesis of PLOC

The polymerization was performed at 25 °C in bulk. An amount of 1.18 g of (Et-BDI)Zn[N(SiMe$_3$)$_2$][18] was dissolved in 100.9 g of (R)-limonene dioxide (600 mmol) and the solution was transferred into a 250 mL stainless steel Büchi reactor and flushed five times with CO_2 (0.5 MPa). The reactor was sealed, pressurized with 10 MPa CO_2 and the monomers were allowed to react for 12 h.
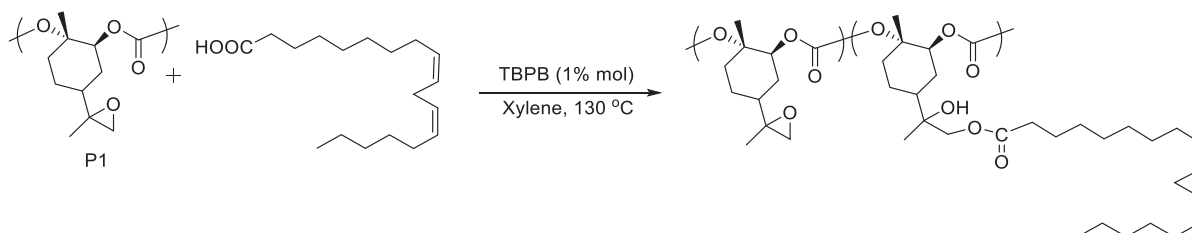
The final (R)-limonene dioxide conversion was determined to be 36% using ^{1}H NMR analysis. The reaction mixture was dissolved in an appropriate amount of dichloromethane and precipitated with a large excess of methanol. The polymer was washed with methanol to remove the catalyst and any unreacted monomers and dried in vacuum. The analyses were performed on crude samples (M_n = 20 kDa; PDI = 1.2; T_g = 139 °C.)

Synthesis of fatty-acid modified PLOC (FA-PC)

Amounts of 17.5 g of PLOC polymer (82.4 mmol of oxirane groups), 19.9 g of SOFA (71.1 mmol) and 0.25 g of triphenylethylphosphonium bromide (TPEPB) dissolved in 10 g xylene were stirred for several hours at 130 °C under a nitrogen atmosphere (Scheme 1). The progress of the reaction was followed by monitoring the acid value and the reaction was continued until an acid value of 3 mg KOH g^{-1} was reached. Once the desired acid value was achieved, xylene was removed under vacuum and the polymer was discharged from the reaction vessel and collected. The polymer had an OL of 59%, calculated by dividing the amount of 'oil' in the final alkyd by the total weight of the alkyd solids, M_n of 29 kDa and PDI of 5.5.

RESULTS AND DISCUSSION

Modification of PLOC with fatty acids

The high epoxy functionality of PLOC allows the relatively easy post-modification with high amounts of fatty acids via epoxy–carboxylic acid chemistry. Due to its low polarity and high T_g (139 °C), PLOC could be modified with a very high weight percentage of T_g-lowering fatty acid, while still achieving a rapid physical drying, which is related to the still relatively high T_g of the PLOC-FA reaction product. Remarkably, T_g of the PLOC-FA comb polymer having a high OL of 59% is just as high as T_g of the reference, a polyester-based alkyd having an intermediate OL of 39%. The high incorporation of fatty acid is also expected to induce excellent and fast chemical drying by autoxidation (related to the high OL). The pendant epoxy groups were efficiently modified by SOFA at 130 °C in the presence of TPEPB as a catalyst. An acid value of around 3 mg KOH g^{-1} was reached within *ca* 5 h, indicating a rapid and complete modification. The high OL of the resulting FA-PC (59%) suggests a high incorporation of SOFA, which is also confirmed by the almost complete disappearance of the peaks at 2.55–2.65 ppm (Fig. 2), assigned to the epoxy protons in the ^{1}H NMR spectrum of FA-PC.

Although the molecular weight distribution of the polymer became much broader after the modification, as shown in Fig. 3, it was still much narrower than that of the conventional resins. The bimodal peak of the parent PLOC polymer is caused by the side reactions like chain coupling and/or chain transfer during the polymerization, which have been well studied in the epoxide/CO_2 copolymerization system catalysed by β-diiminate

Scheme 1. Post-modification of PLOC with SOFA. Note: only one of the three fatty acid residues of SOFA is shown for clarity.
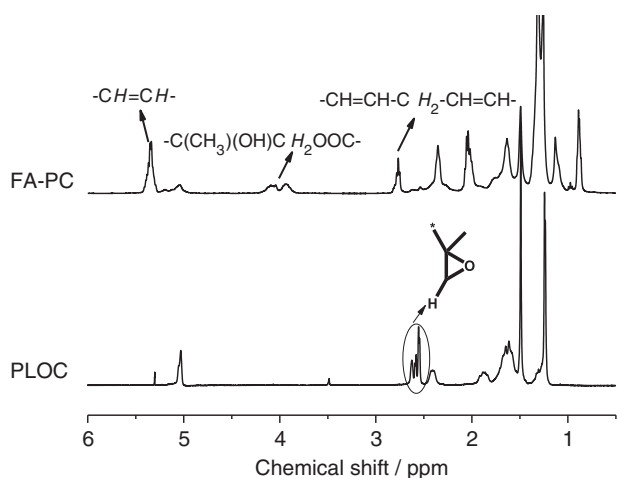
Figure 2. ^{1}H NMR spectra of PLOC and of FA-PC.
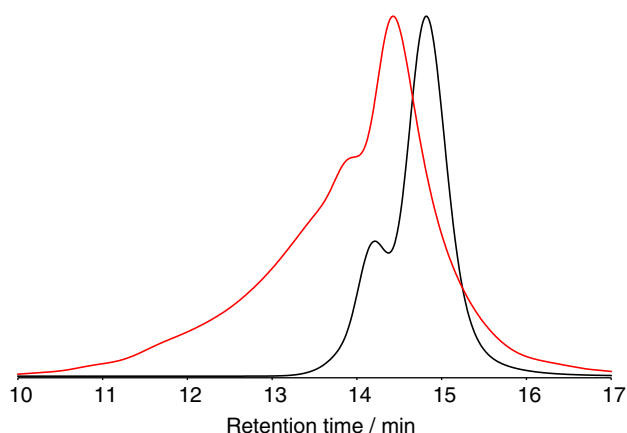
Figure 3. Gel permeation chromatograms of PLOC starting material (black curve) and FA-PC (red curve).

Table 1. Properties of resins

Sample	M_n (kDa)	M_w/M_n	T_g[a] (°C)	Oil length (%)
PLOC	20.0	1.2	139	0
FA-PC	29	5.5	−1	59
Branched polyester alkyd	3.5	*ca* 20	−10	39

[a] Determined by DMTA.

Table 2. Properties of alkyd paints containing different binders (FA-PC and branched polyester alkyd)

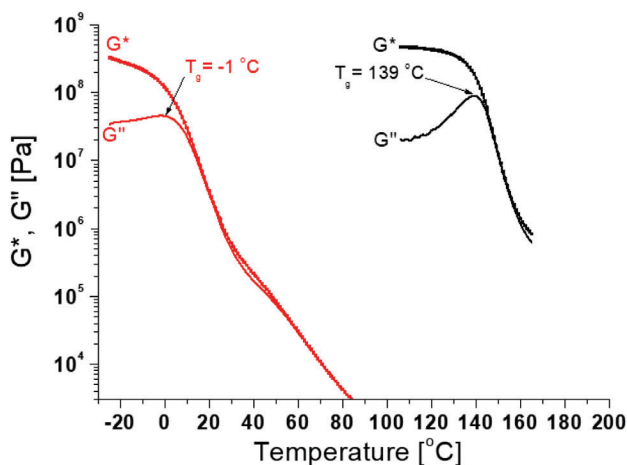| Binder	FA-PC	Branched polyester alkyd
Viscosity (Pa s, at 70 °C)	1750	410
Oil length (%)	59	39
Dust-free time (min)	10	10
Tack-free time (h)	3.3	3.0
Water resistance	5	5
Colour difference (ΔE) by CIE74 (1 week/3 weeks)	4.96/8.07	2.76/4.88

Figure 4. Complex modulus G^* and shear loss modulus G'' as a function of temperature for PLOC (black symbols) and FA-PC (red symbols).

zinc complexes.[25] During the post-modification, the higher molecular weight PLOC chains contain more epoxide functionalities per chain than the lower molecular weight PLOC ones, leading to a more significant molecular weight increase than the lower molecular weight PLOC chains. This causes the broadening of the molecular weight distribution.

Properties of alkyd paints using FA-PC as binder

To evaluate the performance of FA-PC as an AR, a highly branched polyester-based binder with a chemical composition close to that of commercial standard ARs and an OL of 39% was tested as a reference. Some of its properties are presented in Table 1. The FA-PC and the polyester-based branched alkyd were dissolved in xylene with and without the Fe-based drier Borchi Oxy Coat (oxidative curing catalyst) and applied on glass plates to study chemical and physical drying, respectively. Physical drying usually involves merely the evaporation of solvent and film formation without notable chemical drying or oxidative crosslinking, yielding a composition of specific T_g. FA-PC-based alkyd paint had a much higher viscosity due to its higher molecular weight. In spite of a significantly higher OL (59% *versus* 39%), FA-PC showed the same dust-free time and only a slightly longer tack-free time compared to the reference polyester alkyd, indicating a comparable physical drying rate (Table 2). This similar physical drying speed is related to

the very similar T_g values (Table 1). Physical drying can be accompanied by chemical oxidative crosslinking, causing chemical drying, particularly in the presence of a drier. After this curing procedure, no visible damage was observed in the water resistance test of FA-PC, as for the reference material, suggesting a perfect water resistance, most likely arising from a strong hydrophobicity.

The yellowing of the coatings was studied by measuring the colour difference during the drying of the films in the dark at 50 °C. A more significant change was observed for FA-PC coatings than for the branched polyester-based alkyd. Yellowing in the dark is a well-known phenomenon for alkyd-based coatings and paints and is related to the chemistry of the oxidative curing of the fatty acid residues.[26] The stronger coloration of the FA-PC is therefore fully in line with its higher OL.

A critical aspect of an alkyd paint film is its mechanical behaviour immediately after completion of evaporation of solvent, before the
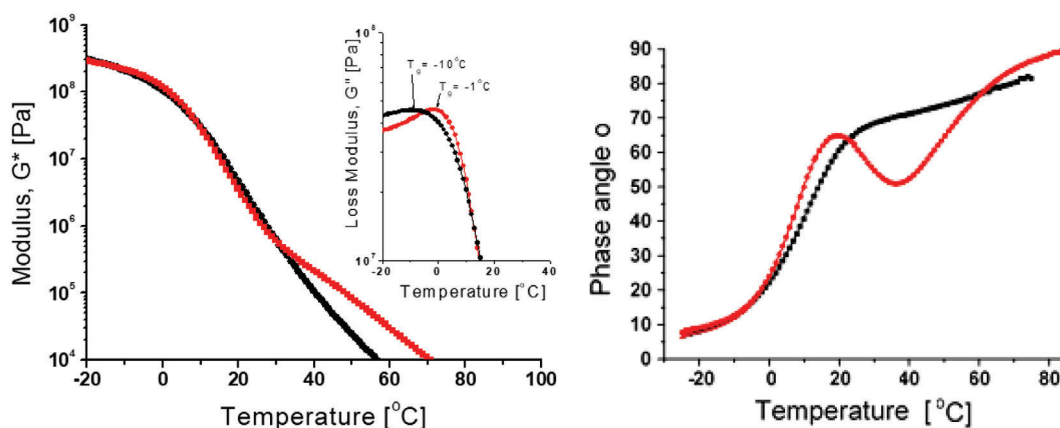
Figure 5. Complex modulus and phase angle as a function of temperature for FA-PC (red symbols) and branched polyester alkyd (black symbols) coatings after physical drying of film cast from xylene solution.

initiation of autoxidation. At this stage, alkyd films might be too soft and tacky due to the SOFA modification required for autoxidation. In order to determine the relationship between the thermomechanical properties and the performance of the coatings, DMTA was performed on films dried during different times. First, the samples were measured before being dissolved in xylene. T_g of PLOC was significantly reduced by the SOFA modification, from 139 to $-1\,°C$ (Fig. 4), which is still higher than T_g ($-10\,°C$) of the branched polyester resin modified with only 39% SOFA. Apparently, the rigid PLOC backbone facilitates modification with a significantly higher SOFA concentration (59%) than the traditional alkyd (39%), while still attaining acceptable mechanical properties at the beginning of the autoxidation process. The similarity between the T_g values of physically dried FA-PC and branched polyester-based alkyd films, in spite of the very significant difference in OLs (see the overlapping DMTA curves; Fig. 5), correlated well with the similar dust-free and tack-free-times, which are in fact reflections of the physical and chemical drying rates (Table 2). A second transition is observed in the shear modulus profile, probably caused by an

uneven distribution of the fatty acid over the PLOC backbone. In particular, T_g of the modified PLOC (OL = 59%) can be simply increased by reducing the OL (by tailoring the amount of grafted FA), leading to faster physical drying and to less pronounced yellowing.

The change in thermomechanical properties of FA-PC and branched polyester alkyd coatings during 24 h of drying was measured by DMTA and shown in Fig. 6. The shift of the loss modulus curves towards higher temperature indicates an increase of T_g by 18 and 16 °C for FA-PC and the branched polyester alkyd coatings, respectively. Meanwhile, in both cases a higher crosslink density due to the autoxidation process is reflected by an increase of the rubber modulus, G_{rubber}, defined as $G*(T_g + 70\,°C)$, which is proportional to the number of elastically active network chains.[27] After 24 h of drying, G_{rubber} of FA-PC increased to 1.6 MPa, while that of branched polyester alkyd coating was only 0.06 MPa, suggesting a much faster crosslinking of the FA-PC coating. Such fast crosslinking is very favourable, since it is required for rapid development of both blocking and water resistance of a coating.
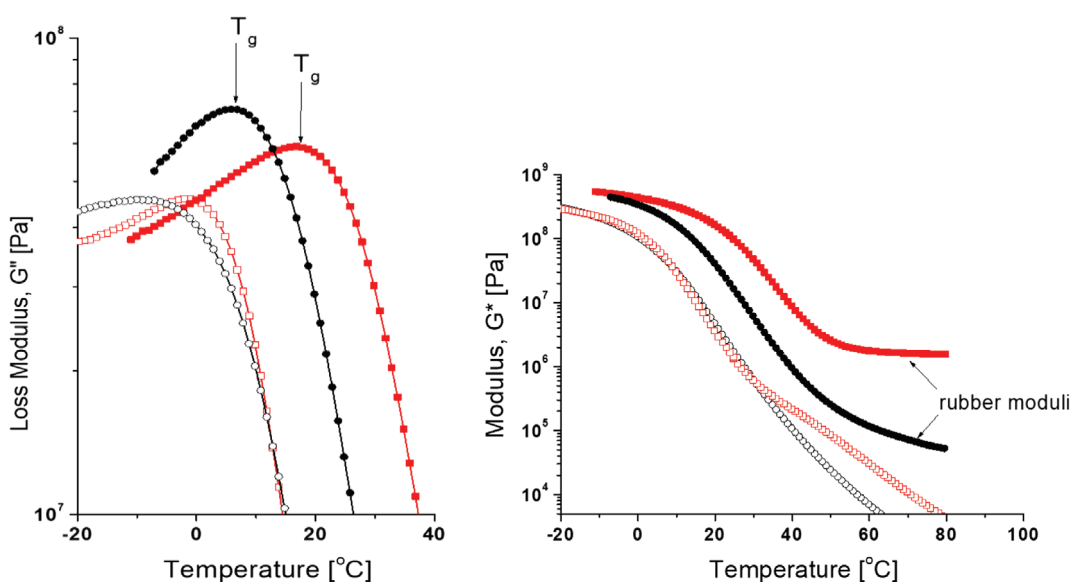

Figure 6. Impact of 24 h autoxidation on loss modulus and complex modulus for FA-PC (red symbols) and branched polyester alkyd (black symbols) coatings. Curves with open symbols were measured for 100% resin. Curves with filled symbols were determined after 24 h autoxidation of 29 μm thick films.
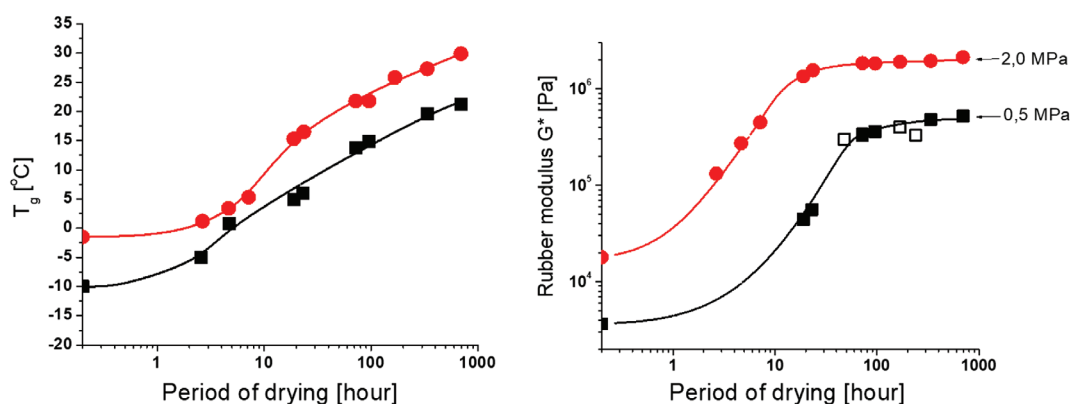
Figure 7. Rubber modulus and T_g as a function of time for FA-PC (red symbols) and branched polyester-based alkyd (black symbols) coatings dried during different times.

Continuous monitoring of the rubber modulus (G_{rubber}) and T_g development during chemical oxidative drying in the presence of the iron-based drier revealed a much faster chemical drying of the FA-PC coatings (OL = 59%) compared to the branched polyester alkyd (Fig. 7). G_{rubber} of the FA-PC system increased rapidly with prolonged drying time, which reached 0.1 MPa in 2.5 h while it took 20–30 h for the branched polyester alkyd (OL = 39%) to reach the same modulus value. G_{rubber} further increased to 2.0 MPa in 20 h and remained constant, indicating the complete build-up of the network, whereas the branched polyester-based alkyd exhibits a much lower final G_{rubber} of 0.5 MPa. T_g of the FA-PC paint dried for 20 h reached 40 °C, while that of the branched polyester-based alkyd coating reached only 30 °C. The gradual development of T_g, even after 1000 h, demonstrated the impact of a process other than the crosslinking since G_{rubber} reached its maximum value at *ca* 20 h. This trend was most likely caused by the emission of the residual solvent trapped in the coatings, and particularly volatile aldehydes formed by side reactions like β-scission of the unsaturated groups in the autoxidation process.[28] Overall, these results suggests a higher crosslink density and faster drying of the FA-PC coating, unfortunately at the cost of a higher yellowing.

The König hardness of the coatings was also monitored to follow the development of the chemical crosslinking in time (Fig. 8). The König hardness increased rapidly with chemical drying. After 1 day, the FA-PC coating showed a König hardness of 63 s, which is much higher than that of most commercial alkyds (42 s; Fig. 8). The hardness of the FA-PC coating revealed a gradual increase with drying time, up to 133 s in 4 weeks, consistent with the T_g development curve. In general, the FA-PC coating presented a much higher König hardness than the branched polyester alkyd-based one after the same drying times, a phenomenon which is due to the significantly higher OL of FA-PC, while drying times are still comparable.

Figure 8. König hardness development of FA-PC coatings compared to branched polyester-based coatings.

the branched polyester alkyd, very likely due to the higher fatty acid content, FA-PC showed a much better performance like faster chemical drying, higher König hardness and higher T_g. In view of the mild and low-energy-consuming modification conditions, low-polydispersity FA-PC can be a good and very sustainable alternative for conventional, largely polyester-based ARs.

ACKNOWLEDGEMENTS

CONCLUSIONS
We have reported the chemo-selective copolymerization of (R)-limonene dioxide with CO_2, followed by catalysed epoxide ring-opening reactions with SOFAs. The resulting FA-PC was further evaluated as a fully sustainable and fully renewable AR. Particularly, an OL of 59% was reached for FA-PC, much higher than that of a binder with a close-to-commercial chemical composition, namely a branched polyester-based alkyd with an OL of 39% and a 39% bio-based content. Although the yellowing of the FA-PC coatings was slightly more pronounced than that of
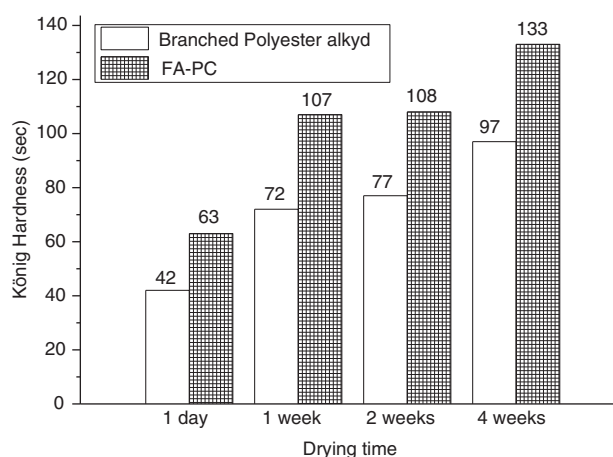
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