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Bio-derived Polymers for Coating Applications: Comparing Poly(limonene carbonate) and Poly(cyclohexadiene carbonate)

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Two fully bio-based polycarbonates, poly(cyclohexadiene carbonate) (PCHDC) and poly(limonene carbonate) (PLC), were synthesised from carbon dioxide and cyclohexadiene oxide and limonene oxide. The low molecular weight polycarbonates were cross-linked by a photoinitiated reaction with trimethylolpropane tris(3-mercaptopropionate), *via* thiol-ene reactions. The cross-linking reactions were monitored using Raman spectroscopy and the reaction temperatures and times were optimised. Kinetic analyses of the cross-linking process suggested diffusion-controlled reactions for both polymers, despite the differences in the nature of alkene moieties (terminal *vs*. internal alkene). The resulting materials were evaluated for coating applications, they showed showed promising solvent resistance and hardness and may be used in the future to prepare scratch-resistant coatings.

Introduction

There is an impetus to develop polymers and materials that are sourced from renewable resources to reduce the dependency on fossil fuels.[1] The use of CO_2 is particularly attractive as it is non-toxic and abundant.[2] Aliphatic polycarbonates (PCs), prepared by ring-opening copolymerisation (ROCOP) of epoxides with insertion of CO_2, are versatile products that add value to captured CO_2 and are of academic and commercial interest.[3] One promising application of these materials is their use as low molecular weight polyols in the synthesis of polyurethanes. Greenhouse gas emissions for such polyols can be reduced by 10-20% compared to existing materials (polyether polyols).[4] There is also a growing interest in using the low molecular weight polycarbonates prepared by ROCOP in coatings applications, either through end-group chain extension (e.g. to make polyurethanes) or by cross-linking of reactive functionalities in the polymer backbone.[4-5] Here, we explore the use of bio-derived epoxides to produce fully renewable, low molecular weight alkene functionalised polycarbonates.

The most commonly employed epoxides in ROCOP are cyclohexene oxide (CHO) and propylene oxide (PO): both are petrochemicals, making the resulting materials only partially renewable.[6] Nonetheless, a few bio-derived epoxides have already been explored including: a) protected glycidyl ethers, derived from glycerine,[7] b) limonene oxide (LO) and limonene dioxide, obtainable from citrus fruits,[8] and c) cyclohexadiene oxide (CHDO), obtained as a by-product from the metathesis of unsaturated plant oils.[9]

In terms of bio-derived coatings materials, there is already a wealth of literature and commercial products using biopolymers or monomers derived from fatty acids, catechols, terpenes, carbohydrates and lignin.[10] Generally, carbon dioxide derived polymers are less explored although poly(limonene carbonate) (PLC) has been studied by several groups for use in coatings applications.[5d-f] Here, the thiol-ene reaction, relevant to producing cross-linked coatings, is compared using polylimonene carbonate (PLC) and poly(cyclohexadiene carbonate) (PCHDC). The polymers differ in terms of the alkene functionality: PLC features a vinyl group whereas PCHDC features an internal alkene within the cyclohexene ring.

Considering more broadly the post-functionalization of unsaturated polycarbonates, produced by ROCOP, three approaches have been explored: a) alkene metathesis,[11] b) chlorination or bromination[12] and c) thiol-ene reaction.[5, 13] The thiol-ene reaction was successfully used to crosslink a copolymer prepared from CHO/vinyl-CHO/CO_2 to produce a new coating[5a] and, in separate work, to transform PCHDC or terpolymers of PO/vinyl-PO/CO_2 into water-soluble polymers.[5c, 13] So far, PCHDC has not been cross-linked or investigated for coatings applications to date.

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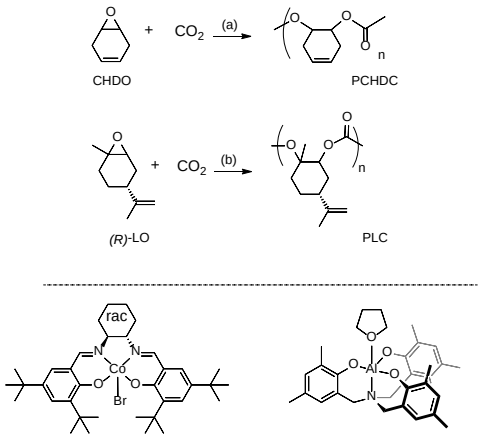
Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

Results and Discussion

The two fully bio-based polycarbonates, PLC and PCHDC, feature either a terminal (PLC) or internal alkene (PCHDC), the differences may be expected to influence the thiol-ene reaction kinetics. Thus, understanding the cross-linking reaction kinetics, using a common multi-functional thiol, is targeted. The study consists of three parts: polymer synthesis, investigation of the cross-linking conditions and the mechanical testing of solvent-casted coatings.

Polymer Synthesis

The two polycarbonates were prepared using literature procedures and catalysts; for each polymer low molecular weights (M_n = 4000) were targeted based on the need to minimize melt viscosity for future coating applications.[5b] Poly(cyclohexadiene carbonate) (PCHDC) was synthesized from cyclohexadiene oxide/CO_2 using a cobalt(III)-salen catalyst system with *n*-propanol added as chain-transfer agent (CTA) (Scheme 1).[13b, 14] The reaction was allowed to proceed until high conversion (79% CHDO conversion) and was purified via the addition of hexanoic acid (to remove catalyst) and the polymer was isolated by re-precipitation (twice) by the addition of methanol to methylene chloride solutions of the polymer. The PCHDC showed a high carbonate-linkage selectivity (>99% carbonate linkages) (Table 1; Fig. S 1 - S 5).[15] The synthesis of PCHDC was repeated three times and showed good reproducibility, with the target molecular weight being obtained in all cases (Fig S3). Poly(limonene carbonate) (PLC) was synthesised from (*R)*-(LO)/CO_2 using an aluminum aminotris(phenolate) catalyst and water as CTA. The reaction proceeded until moderate conversion (67 %) and the polymer purified by precipitation by addition of methanol to a methylene chloride solution of the polymer and by subsequent washing of the polymer with methanol. The PLC also showed a high selectivity for carbonate linkages (>99%) (Table 1; Fig. S 6 - S 8).[8d, 16] The molecular weights of both polycarbonates were compared using SEC with RI detection, calibrated against narrow MW polystyrene (PS), and using SEC with RI, viscosity and multiple-angle-laser light scattering (SEC-MALLS).

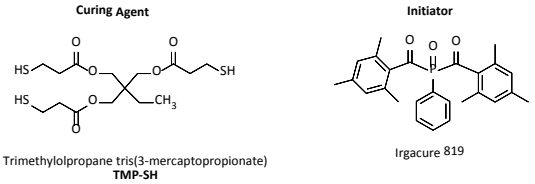


Scheme 1 Synthesis of PCHDC and PLC. Conditions: (a) [Co]:PPNCl:CHDO:*n*-PrOH = 1:1:500:12, 20 bar CO_2, 30 °C, (b) [Al]:PPNCl:LO:H_2O = 1:0.5:200:8, 15 bar CO_2, 45 °C.

For both PCHDC and PLC there was reasonable agreement between experimental and theoretical molecular weights. It is important for the subsequent coating evaluation that the molecular weights of both polycarbonates are similar. The polymer's end-groups were analyzed using MALDI-ToF mass spectrometry, for PCHDC chains are terminated by n-propyl alkoxide and hydroxyl groups (consistent with the addition of n-propanol as CTA), whilst for PLC chains are terminated with a,ω-dihydroxyl groups (consistent with the use of water as CTA) (Fig. S 4 and S 8). Additionally, for PCHDC end-group analysis was conducted by ^{31}P NMR spectroscopy, after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane and using Bis(phenol)A as an internal standard. The chemical shift of the resulting phosphorus species was similar to that of the poly(cyclohexylene phthalate) counterpart (146.7 *vs.* 147.1 *ppm*), indicating the presence of a secondary alcohol as an end group (Fig. S 5).[17] It is important to emphasise that although the PCHDC and PLC end-groups differ, this is not expected to exert any influence over the cross-linking reaction which involves reaction of the alkene functional groups.

Cross-linking studies

The cross-linking of both polymers by the thiol-ene reaction was investigated using a commercial multi-functional thiol (trimethylolpropane tris(3-mercaptopropionate), TMP-SH) in the presence of a photo initiator (Irgacure 819, Scheme 2). It is relevant to note that the thiol cross-linking agent is not bio-derived, but was selected to allow comparison with recently published coatings based on related polycarbonates and methacrylates.[5a, 18] The thiol conversion was monitored by Raman spectroscopy as this technique had previously been successfully used to monitor other polymer cross-linking reactions using thiol-ene chemistry.[19] For both polymers, different molar ratios between the alkene functionality and the curing agent were studied, namely (C=C):(SH) = 1:1, 2:1 and 4:1.



Scheme 2 Curing agent (left) and initiator (right) used in this study.

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Table 1 Epoxy/CO_2 copolymerisation results[a]

Entry	Polymer	Conversion [%][b]	Selectivity [%][b]	$M_{n,\,theo}$ [g mol^{-1}][c]	$M_{n,\,SEC\text{-}PS}$ [g mol^{-1} (Đ)][d]	$M_{n,\,SEC\text{-}MALLS}$ [g mol^{-1} (Đ)][e]
1	PCHDC	79	99	4,610	3,340 (1.06)	4,200 (1.05)
2	PLC	67	99	4,900	4,160 (1.21)	2,960 (1.18)

[a] For conditions: see Scheme 1; [b] polycarbonate *vs.* polyether linkages, determined by ^{1}H NMR (Fig. S 1 and S 2); [c] Based on (MW(CHDO) + MW(CO_2)) x (conversion of monomer) x (Ratio monomer/CTA); [d] Determined by SEC in THF using narrow MW PS as a calibration standard (Fig. S 3, S 7); [e] Determined by SEC-MALLS.

Table 2 Glass transition temperatures of different unreacted polymer-thiol mixtures and optimal curing temperatures

Entry	Polymer	(C=C):(SH)[a]	T_g[b] [°C]	ΔT[c] [°C]
1	PLC	100% PLC	92.1	-
2	PLC	4:1	58.8	30
3	PLC	2:1	51.0	30
4	PLC	1:1	30.1	110
5	PCHDC	100% PCHDC	98.3	-
6	PCHDC	4:1	54.2	30
7	PCHDC	2:1	47.5	30
8	PCHDC	1:1	7.6	90
9	-	100% TMP-SH	-	

[a] Molar ratio; [b] Determined by DSC (Fig. S 9 – S 12); [c] Temperature above T_g (ΔT) at which maximum conversion was determined by Raman spectroscopy (see Fig. S 16 for spectra).

1. Temperature Optimisation

The glass transition temperatures (T_g values) of the unreacted polycarbonate/thiol mixtures, in which TMP-SH acted only as a plasticiser, were used as a starting point for the temperature optimisation of the curing process (Table 2). The curing temperature was increased stepwise and each film was cured for 30 minutes, under UV-irradiation. The resulting films were then analysed based on the decrease of the Raman signal for thiols (~ 2580 cm^{-1}, Fig. 1) after normalisation of the carbonyl signal (~ 1750 cm^{-1}). For both polymers, the optimal consumption of sub-stoichiometric amounts of curing agent ((C=C):(SH) = 2:1 and 4:1) was observed at a temperature of 30 °C above the glass transition values of the unreacted mixtures.

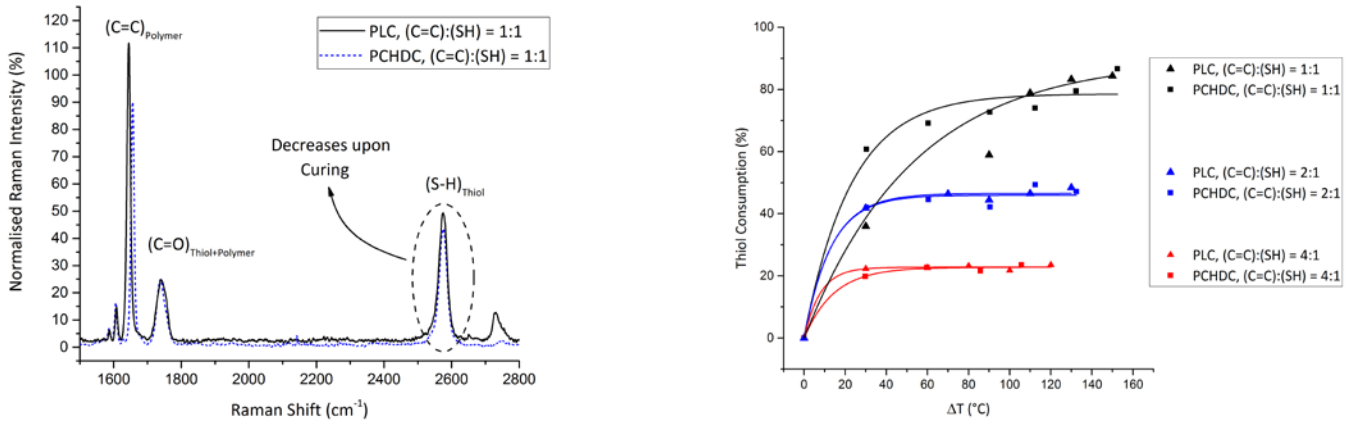

Fig. 1 Raman spectra of the uncured PCHDC (blue) and PLC (black) films (left, for 1:1 mixtures) and temperature optimisation (right, see Fig. S 16 for individual spectra). ΔT refers to the curing temperature above T_g ($\Delta T = T_{curing} - T_g$).

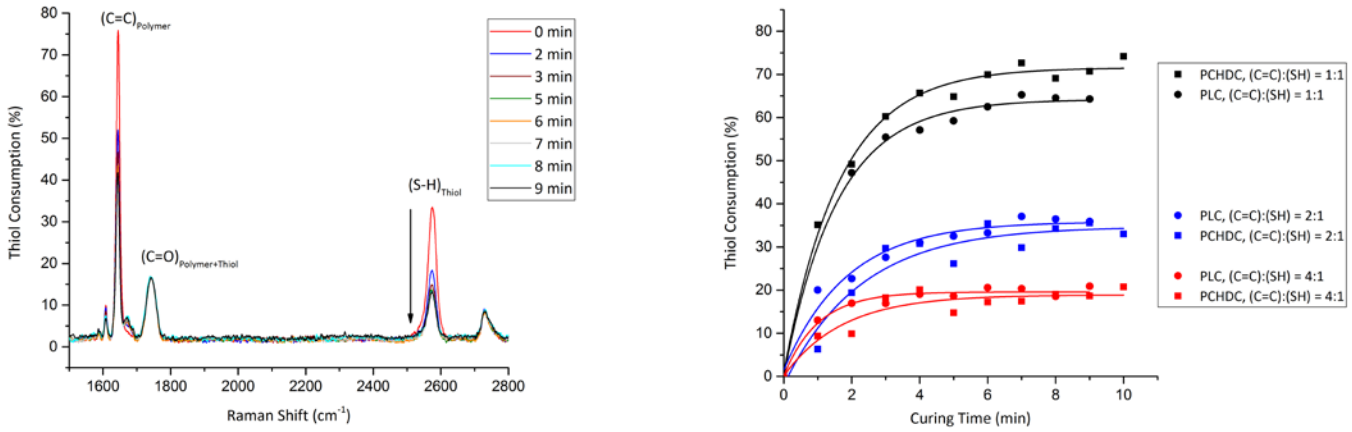

Fig. 2 Raman spectra for the curing of PLC (molar ratio (C=C):(SH) = 1:1, left) and kinetic analysis for the curing of PLC and PCHDC films (right) (for individual spectra see Fig. S 17 and S 18).

However, higher curing temperatures were necessary for equimolar mixtures (90 °C and 110 °C for PCHDC and PLC, respectively). This observation was in agreement with the formation of highly cross-linked networks when using high amounts of curing agent, as the degree of cross-linking should increase the glass transition temperature of the (partially) cured films.[20] No significant formation of disulfide bridges was observed during these experiments as no $\nu_{S\text{-}S}$ peak could be detected (expected at 498 – 511 cm^{-1}).[21] In addition, the intensities of the peaks arising from the carbon-sulfur bonds, $\nu_{C\text{-}S}$ and $\nu_{C\text{-}S,S\text{-}C}$ at 622 and 621 cm^{-1}, were very low (Fig. S 21 - 22).[22] This observation was consistent with the limited formation of disulfide bonds observed previously in thiol-ene reactions between limonene and TMP-SH.[19e] It is worth mentioning that the conversions of the thiol were below 100% for stoichiometric amounts of curing agent. This may be explained by rapid formation of a highly cross-linked network at high curing agent ratios (molar ratio (C=C):(SH) = 1:1). It is proposed that at this point the mobility of the network was limited and the rate of reaction of the remaining SH groups with the available unsaturated bonds was significantly hampered. Nonetheless, the conversions are sufficient that at least one of the three thiol groups on the cross-linker is covalently bonded in the resin and, therefore, leaching should not occur.

2. Kinetics

The thiol consumption was monitored by Raman spectroscopy for ten minutes, once the optimised curing temperatures were determined (Fig. 2, left). In most cases, exponential trends were observed and the thiol conversion reached a maximum within five minutes, generally close to the values determined during the temperature optimisation study, and small differences (ca. 15%) were detected only for large amounts of curing agent (molar ratio (C=C):(SH) = 1:1). This might result from longer reaction times in the temperature optimisation (10 *vs.* 30 min). Rather similar kinetics for both polymers (Fig. 2, right) suggested that the cross-linking was not determined by the chemical reactivity of the alkenes (terminal *vs.* less reactive internal olefin), but was diffusion-controlled.

3. Evaluation of Coatings

Aluminum substrates (*ca*. 10 x 5 cm) were coated with a mixture of the polymer, crosslinking agent and photo initiator and cured under optimised conditions for 30 minutes. Aluminum was selected as the model substrate as it is commonly applied in the paint industry as it is not subjected to corrosion and is lighter than steel. Additionally, aluminum is incorporated in many standards used for the mechanical testing of new coatings.[23] All coatings were transparent (Fig. S 24 – 25) and had an excellent degree of adhesion (Gitterschnitt test revealed a value of 0 on a scale of 0 to 5 with 0-best (no detachment) and 5-poorest, see ASTM D 3359). The coatings were also evaluated with a range of tests, including acetone resistance, pencil hardness, König hardness and reverse impact test (Table 3). For the samples cured with lower amounts of curing agent, a moderate acetone resistance was observed, in agreement with a low amount of cross-links present in the films. All the other samples exhibited a good acetone resistance, as expected from sufficiently cross-linked materials. In all cases, no significant changes in pencil hardness were measured and a high scratch-resistance of H-2H could be noted. Compared to non-crosslinked high MW PLC (> 100 kDa), an improvement from B to 2H clearly shows the benefit of the cross-linking.[8e] Moreover, when performing the König hardness tests, a decrease was observed with higher amounts of curing agent, which could be ascribed to unreacted, plasticising thiol groups. In a direct comparison between PLC and PCHDC, a higher hardness based on the König test was noticed for PCHDC. This can most probably be ascribed to its higher intrinsic stiffness (compare T_g values for neat polymers in Table 2, entries 1 and 5) because of the absence of pending, bulky isopropenyl groups. In the case of PLC, this might result in a somewhat enhanced free volume between the polycarbonate chains. In addition, the cross-linker becomes directly attached to a moiety present in the main chain in the case of PCHDC, whereas for PLC the cross-linker is connected to the pendant isopropenyl groups, which might lead to a less rigid cross-linked network.

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Table 3 Mechanical testing of cured PLC and PCHDC films

Sample, molar ratio (C=C):(SH)	Acetone Resistance	Thickness (µm)	Pencil hardness	König hardness (s)	Impact
PLC, 1:1	+	40	H	103	-
PLC, 2:1	+	36	2H	110	-
PLC, 4:1	+/-	32	2H	114	-
PCHDC, 1:1	+	60	2H	123	-
PCHDC, 2:1	+	40	2H	151	-
PCHDC, 4:1	+/-	38	H	159	-
Carvone methacrylate[18, a]	+	64	2B	185	-
PCHC/PVCHC (50/50)[5a, a]	+	30	6-8H	n. r.	+

[a] Reported films prepared by powder coating; n. r. = not reported.

For all the films, impact tests resulted in delamination and brittle fracture of the sample. It is worth mentioning that many commercially available coating systems lack toughness as well. Depending on the demands for their specific applications, this does not need to be prohibitive for future applications.

When compared to recently published results on coatings based on carvone methacrylate[18] and a copolymer of cyclohexene oxide/vinyl-cyclohexene oxide (CHO/VCHO)/CO_2,[5a] all films showed a good solvent resistance. With respect to the pencil hardness test, PLC and PCHDC were more scratch-resistant than the methacrylate (2H *vs.* 2B) and less than the polycarbonate (2H *vs.* 6H). The König hardness of the PLC and PCHDC films were lower than that of films based on carvone methacrylate, which was probably a consequence of the selected coating technique. In particular, solvent casting was used in this study and powder coating for the methacrylate. As residual amounts of solvent may have a plasticising effect and powder coatings are performed under neat, solvent-free conditions, the latter is expected to yield a higher hardness. With respect to impact strength, the polycarbonate (CHO/VCHO/CO_2) showed superior properties. This may be ascribed to the low thickness of the films investigated in that specific study in combination with a lower glass transition temperature in comparison to the PCHDC- and PLC-based coatings. It is well known that the toughness of films is related to their thickness.[24] Overall, the investigated polymers showed characteristics of hard but brittle resins.

Direct comparisons to other commercial systems were not made as the investigated coatings were two-component systems and commercial coatings typically contain additives, including pigments, thickening agents, anti-foaming and levelling agents. In general, commercial coatings are highly target-specific and each may suffer individual drawbacks, such as adhesion problems (elastomer polyurethane/polyurea and polyesters), poor exterior durability (epoxy and polyester systems) or moderate chemical resistance (acrylic coatings). The preliminary work here demonstrates the potential for novel coatings based on PLC and PCHDC which showed good adhesion to metal, good chemical resistance and high hardness. These features are compatible with future investigations targeting use as a primer coating.

The thermomechanical properties of the cured films were analysed by dynamic-mechanical thermal analysis (DMTA, see Fig. 3). Nearly full thiol-conversion could be noted on both sides of the free-standing films (Fig. S 19). Based on the storage modulus, a glassy modulus of ca. 1.0 GPa was measured in all cases, which is typical for polymer films.[19b] The stiffness below T_g of the cured PCHDC samples was somewhat higher than that of cured PLCs with similar (C=C):(SH) ratios, in agreement with the earlier mentioned higher König hardness values for PCHDC. With an increasing content of curing agent, higher T_g values were detected. Within each series, the glass transition was visible as a significant drop in the storage modulus. The observed rubbery plateaus of the storage modulus curves at temperatures exceeding T_g indicate highly cross-linked networks, which was further confirmed by higher cross-link densities with more curing agent present (Table S 2). The tan δ curves were consistent with this finding and an increase in T_g with the amount of curing agent was clearly visible as a shift of the global maximum towards higher temperature. In the direct comparison between the two polymers, higher T_g values were detected for PCHDC than for PLC for molar ratios of (C=C):(SH) = 1:1, which was in agreement with better mechanical properties of PCHDC. Interestingly, the reverse was found for a 2:1 ratio (i. e. T_g of the PLC film was higher than the PCHDC film). In addition, peak analysis revealed the highest full-width at half maximum of all samples for the PLC cured film with a molar ratio of (C=C):(SH) = 2:1, which suggested a less homogeneous sample in that case (Fig. S 23).

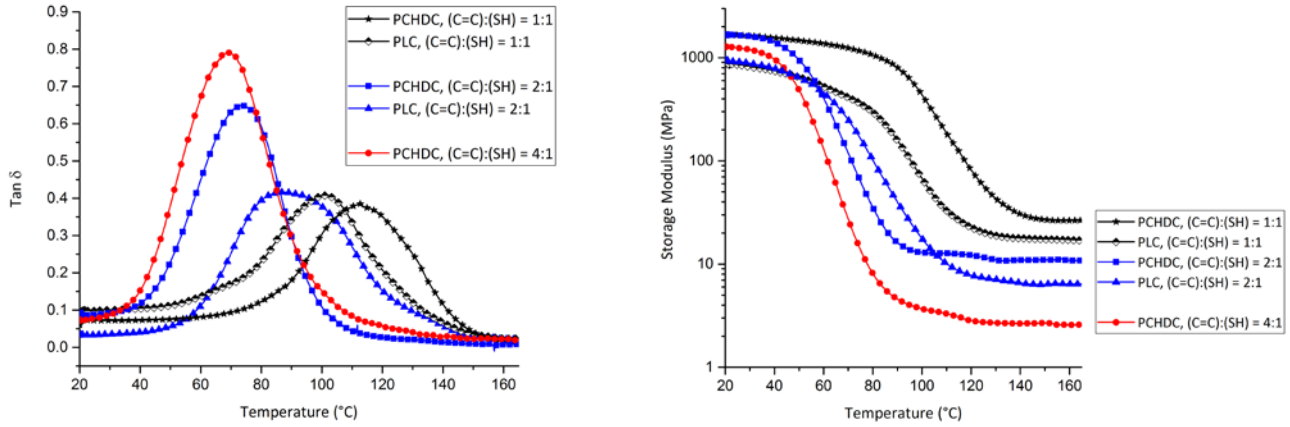

Fig. 3 DMTA results for cured films (a free standing film for PLC 4:1 could not be obtained due to insufficient physical properties).

We attribute this to thicker films required for the DMTA measurement. Under these conditions, the thickness and the homogeneity of the samples were not well controlled and a doctor blade could not be used.

During these tests, we noted differences depending on how PLC films were dried before curing. If the films were dried under air, ATR-IR spectroscopy indicated low thiol conversions in the fingerprint region due to oxygen inhibition (a similar signal was overlaid for PCHDC; Fig. S 21). This was in contrast to Raman measurements, which showed high consumptions (Fig. S 22). We ascribe this behaviour to higher penetration depth of Raman spectroscopy over ATR-IR (*ca*. 3 µm *vs.* 1 µm).[25] The low conversions in ATR-IR were greatly improved when the films were dried under nitrogen. This suggested that, during the drying process, oxygen was incorporated in the surface of the film and consequently, initiation was inhibited near the interface. Further away from the surface, the oxygen concentration was too low to affect the curing reactions significantly. This influence of oxygen on radical-mediated thiol-ene reactions was recently studied for light activated polymers.[26] This hypothesis was further supported by better mechanical properties when the samples were dried under nitrogen (see Table S 1).

Conclusions

Two fully bio-based polycarbonates, namely poly(cyclohexadiene carbonate) and poly(limonene carbonate), were cross-linked using a tri-functional thiol (trimethylolpropane tris(3-mercaptopropionate), *via* the thiol-ene reaction, to obtain coatings materials. The cross-linking reaction was investigated using different amounts of curing agent (molar ratios of (C=C):(SH) = 1:1, 2:1 and 4:1): firstly, optimal curing temperatures were determined; secondly, kinetics were measured; and thirdly, coatings on aluminum substrates were subjected to mechanical testing. Overall, the optimised temperatures and kinetics were similar for the two polymers suggesting that the cross-linking process is diffusion controlled, under the conditions tested. The resulting coatings showed promising properties with respect to solvent and scratch resistance. Further coating material evaluations, including optimization of formulations are recommended future developments using these materials.

Acknowledgements

We are grateful to Prof. M. S. P. Shaffer and Dr. A. Clancy for help with the Raman measurements. The authors gratefully acknowledge Climate KIC (Project EnCO_2re (T. S.)), the Grantham Institute and EPSRC (EP/K035274/1 and EP/L017393/1) for funding (J. U. and P. K. S.). This work forms also part of the research program of the Dutch Polymer Institute (DPI), project #796p (C. L.) and received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No. 289253 (C. L.).

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Graphical Abstract

Tim Stößer, Chunliang Li, Junjuda Unruangsri, Prabhjot K. Saini, Rafaël J. Sablong, Michael A. R. Meier, Charlotte K. Williams and Cor Koning

Bio-derived Polymers for Coating Applications: Comparing Poly(limonene carbonate) and Poly(cyclohexadiene carbonate)

Two fully bio-based polycarbonates, poly(limonene carbonate) and poly(cylcohexadiene carbonate), were post-functionalized *via* thiol-ene reactions and tested as future coating materials.