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Synthesis and degradation study of graft copolymers of poly(limonene carbonate)†

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The utility of poly(limonene carbonate) (PLimC) for real-world application as an environmentally friendly polymer can be enhanced by improving its brittleness and degradation. In this work, a chemical approach for making graft polymer architecture has been presented for property modification. Grafted polyesters onto PLimC with microphase separation and enhanced hydrophilicity were synthesized and characterized in depth for their structural, thermal, mechanical and morphological properties. The effect of structure on enzymatic and wastewater degradation, assessed by monitoring the production of CO_2 and the mechanism of degradation, is studied by a combination of different analytical methods.

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Introduction

An interesting example of bio-based monomers for subsequent processing is a non-food resource, limonene.[1,2] As a by-product of the orange industry and the primary component of citrus oil, limonene is produced in large quantities (more than 520 000 tons per year)[3] and is therefore a particularly attractive starting material for poly(limonene carbonate) (PLimC) synthesis.[4–6] In the actual polymerization process of PLimC, the *trans*-limonene oxide (*trans*-LO) prepared from limonene is copolymerized with carbon dioxide (CO_2) using a β-diimidate (BDI) Zn(II) complex as a catalyst.[5,7] The synthesis of polycarbonates by reaction of CO_2 and epoxides was pioneered by Inoue *et al.* in 1969.[8,9] Since then, the synthetic route has been expanded to several other epoxides, such as propylene oxide, cyclohexene oxide, limonene diepoxide and functional epoxides.[10–14] Several new catalysts for the reaction were also developed.[15–17] To focus more on the mechanical and optical properties, high molar mass PLimC was targeted. This was obtained in quantitative yields (>90%) by masking hydroxyl functional impurities in the monomer *trans*-LO.[7] The amorphous, high molar mass and completely bio-based polymer PLimC exhibits high optical transmission (94%), high transparency (99.8%), high Young's modulus (E ~0.95 GPa), high tensile strength (40 MPa) and a relatively high T_g (glass transition temperature = 130 °C).[7] The complications regarding the melt processing restrain PLimC from being potentially processed by conventional thermoplastic processing procedures. To overcome this challenge, we introduced the incorporation of readily available, inexpensive, nontoxic, and biobased ethyl oleate as a plasticizer, which makes the biobased PLimC melt-processable and could be pivotal in engineering applications of PLimC.[18] The potential use of PLimC film was shown in gas separation and for energy-saving applications[19] and coatings.[20] Interestingly, the unreacted double-bond in each repeat unit of PLimC can be used for property modification by clicking the appropriate units.[21] Poly(cyclohexene carbonate) (PCHC) unreacted double bonds were used analogously for grafting poly(propylene carbonate).[22–24]

Despite the interesting physical properties and applications of aliphatic polycarbonates, including bio-based PLimC, they are not easily hydrolyzable. This restricts their utility as biodegradable polymers because the polymer chain needs to be fragmented as the first step of biodegradation. The hydrolysis of ester functional groups in the polymer backbone under mild conditions makes aliphatic polyesters biodegradable. The fragmented low molar mass polymer further undergoes bioassimilation, completing the biodegradation process. In our previous study, we aimed at introducing hydrolyzable functional ester linkages onto the PLimC backbone to provide additional functionality (biodegradability) to bio-based PLimC by the simultaneous copolymerization of LO and CO_2 with cyclic esters, such as D,L-lactide (DLLA). Interestingly, the reaction resulted in block copolymers instead of the expected random copolymers.[25] Sequential ring-opening polymerization is the conventional route to making block copolymers, as shown for the block copolymers of PLimC and PCHC.[26] The block copolymers of PLimC and poly(D,L-lactide) (PDLLA)

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proved to be efficient compatibilizers for otherwise incompatible PLimC and PDLLA blends.[25,27]

In the present work, graft copolymers of PLimC with PDLLA and polycaprolactone (PCL) are studied. The question addressed in the present work is whether microphase separation of PLimC with easily hydrolyzable aliphatic polyesters in a graft polymer architecture can be utilized to introduce biodegradability into PLimC. The aliphatic polyesters covalently attached to PLimC are expected to have microphase separation. The working hypothesis was that, with the increased porosity due to the degradation of polyesters by hydrolysis in a microphase-separated copolymer, PLimC degradation might also improve due to the increased surface area and water diffusion through PLimC. Also, reduced surface hydrophobicity due to grafted polyester chains might help in enhancing degradation. Also, grafting might improve the brittleness of PLimC, which is still a bottleneck. Therefore, in the present work, the graft copolymer architecture of PLimC with biodegradable polymers PDLLA and polycaprolactone (PCL) was prepared and structurally, mechanically and thermally characterized. Degradation tests for the polymer films were carried out under controlled conditions using different enzymes for a definite time period and in wastewater followed by a precise characterization by a combination of analytical methods.

Experimental

Materials

Chloroform-*d1* ($CDCl_3$, 99.8%, Deutero GmbH, Germany), disodium phosphate (99%, Grüssing GmbH, Germany), sodium azide (99%, Alfa Aesar), aniline (≥99.5%, Carl Roth) and anisole (Sigma-Aldrich) were used as received. Geneon GmBH, Germany, supplied proteinase K. Tris 1 M buffer solution, pH 8.6, was purchased from the supplier ABCR GmbH, Germany. Molecular sieves 4 Å were purchased from VWR International. Phosphate buffer solution (0.5 M, pH 7.4), tin(II) 2-ethyl hexanoate, azobisisobutyronitrile (AIBN), and lipase from *Pseudomonas cepacia* were obtained from Sigma-Aldrich. D,L-Lactide (DLLA) was bought from Corbion PURAC. β-mercaptoethanol and ε-caprolactone (ε-CL) were purchased from Merck. *trans*-LO was prepared in the laboratory using our previously published procedure. High-purity water (18.2 MΩ cm) prepared from a Milli-Q device was used as the source of water. All solvents (chloroform ($CHCl_3$), dichloromethane (DCM), and methanol (MeOH)) were purchased in technical grade from local suppliers. AIBN was recrystallized three times from MeOH.

Analysis

Nuclear magnetic resonance (NMR) (^{1}H (300 MHz) and ^{13}C $\{^1$H$\}$ (75 MHz)), two-dimensional (2D) heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple-bond correlation (HMBC) spectra were recorded in $CDCl_3$ using an Ultrashield-300 spectrometer (Bruker). The residual peak of the undeuterated component in $CDCl_3$ was used for calibration.

Measurements of the molecular weights (number average molecular weight (M_n) and weight average molecular weight (M_w)) and molar mass distribution ($Đ$) were performed using gel permeation chromatography (GPC). A Waters GPC set equipped with a 515 HPLC pump, a 2707 autosampler, a 2414 refractive index detector, and a 2998 photodiode array detector at 254 nm (Waters GmbH, Eschborn, Germany) was employed. The GPC setup had two separation columns (Agilent PLgel guard mixed-c, 5 × 0.75 cm, particle size 5 μm). Tetrahydrofuran (THF) mixed with 0.25 wt% tetrabutylammonium bromide (TBAB) was used as the mobile phase and calibration was performed using narrow-distributed PS standards. A sample volume of 100 μL (1 mg mL^{-1}) was measured with a flow rate of 0.5 mL min^{-1} at *ca.* 30 °C. 1,2-Dichlorobenzene was used as the internal standard.

The thermal stability of polymers was studied using Netsch-TG 209 F1 Libra instrument in the temperature range of 20–800 °C in synthetic air (80 vol% N_2, 20 vol% O_2).

~5 mg of the polymer was used for differential scanning calorimetry (DSC, 204 F1 Phoenix (Netzsch)) experiments. A heating rate of 10 K min^{-1} and a nitrogen flow rate of 20 mL min^{-1} were used.

Dynamic mechanical analysis (DMA) was performed in a single cantilever mode using the 1 STARe System (Mettler Toledo). The measurements were conducted at a heating rate of 2 K min^{-1} and a frequency of 2 Hz.

An instrument from Elementar Analysensysteme GmbH, Langenselbold, Germany, was used for determining the elemental composition.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements were performed with Zeiss CEM902 (Zeiss Microscopy, Jena/Oberkochen, Germany, operating voltage 80 kV) and LEO 1530 (FE-SEM, Schottky-field-emission cathode; in-lens and SE 2 detector, accelerating voltage 3 kV), respectively.

A Drop Shape Analyzer (Krüss Advance, v1.3.1) was used for contact angle measurements at room temperature (4 μL water drop).

Tensile testing was done by using a Zwick/Roell BT1-FR 0.5TND14 material testing machine equipped with a 500 N KAF-TC load cell at room temperature. The test specimens were prepared according to DIN 5350 S3 A. Tests were performed with a preload of 0.5 cN at a test speed of 10 mm min^{-1} and a grip-to-grip separation of 25 mm. Five specimens were measured for each graft copolymer film.

Enzymatic degradation. The prepared films of poly(limonene carbonate)-*graft*-poly(D,L-lactide) (PLimC-*g*-PDLLA) and poly(limonene carbonate)-*graft*-polycaprolactone (PLimC-*g*-PCL) with 200 μm thickness were used for enzymatic degradation. 0.025 M phosphate buffer solution (pH 7.4), containing sodium azide (0.2 mg mL^{-1}) and enzyme lipase (0.2 mg mL^{-1}), was used for PLimC-*g*-PCL copolymers, and 0.05 M Tris buffer solution (pH 8.6) containing enzyme proteinase K

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(0.25 mg mL^{-1}) with sodium azide (0.2 mg mL^{-1}) was used for PLimC-*g*-PDLLA copolymers. For this test, all films were cut into equal-sized pieces, kept in the solutions prepared at 37 °C, and shaken gently at 60 rpm for different time intervals. After a definite time, samples were taken out in triplicate and each sample was washed first with MeOH, then with Milli-Q water, and again with MeOH. After drying thoroughly in a vacuum at room temperature, the weight of the samples was noted. The samples which were disintegrated after the test were centrifuged at 10 000 rpm and 20 °C for 5 min. After decanting the upper supernatant and following the above-mentioned washing steps, the samples were dried in a high vacuum at room temperature and the weight was noted. All these samples were analyzed by ^{1}H NMR spectroscopy, GPC, and SEM. Also, blank experiments were done under the same conditions without an enzyme.

Degradation test in sludge wastewater. The prepared films were tested for biodegradation in sludge water in an aerobic environment in triplicate for 30 days. The test method was based on DIN ISO 14851:2019. Activated sludge (after nitrification), collected from the wastewater treatment plant at Bayreuth, Germany, was used in the experiment as an inoculum. Around 70 mg of the films were added to 100 mL of the test medium consisting of 95 mL of standard medium and 5 mL of the supernatant of activated sludge. Aniline was used as the positive sample. Activated sludge with the same concentration was used as a blank sample. The Micro-Oxymax Respirometer furnished with an infra-red CO_2 sensor (Columbus Instruments International, USA) was used for this experiment.

The percentage of biodegradation was calculated by monitoring the production of CO_2 using the equation: $\%\text{biodegradation} = \frac{(\text{mg}CO_2)_T - (\text{mg}CO_2)_B}{ThCO_2} \times 100$, where $(\text{mg}CO_2)_T$ is the amount of CO_2 evolved in the test material flask in milligrams and $(\text{mg}CO_2)_B$ is the amount of carbon dioxide evolved in the blank flask between the start of the test and the end of the test, expressed in milligrams. $ThCO_2$ is the theoretical amount of carbon dioxide evolved by the test material, expressed in milligrams, which is calculated using the equation: $ThCO_2 = \text{Specimen (mg)} \times \frac{TOC\,(\%)}{100} \times \frac{44}{12}$, where 44 is the molecular weight of CO_2, 12 is the molecular weight of C, and TOC (%) is the carbon content of the test specimen determined by elemental analysis (EA).

Synthesis of graft copolymers PLimC-*g*-PDLLA and PLimC-*g*-PCL. The synthesis of poly(limonene carbonate) (PLimC) was carried out following the procedure of Neumann *et al.*, described below.[27] The autoclave with a stirring bar was kept overnight at 75 °C in a drying oven under vacuum. Next day the autoclave was taken out of the oven and attached to a CO_2 line to cool it down under vacuum. 73.2 mg (0.152 mmol) of the β-diimidate (BDI) Zn(II) complex [(BDI)Zn(μ-OAc)] catalyst was weighed and placed into the glovebox in a previously prepared Schlenk flask with a stirring bar. Next, freshly distilled 12 mL (73.3 mmol) of masked *trans*-limonene oxide (LO) (previously dried twice with iodomethane and sodium hydride, as well as *n*-butyllithium) was added into the catalyst under protective gas and stirred until the catalyst got dissolved into the LO. Then the mixture of LO and catalyst was injected into the cooled autoclave under a nitrogen counter-flow. Then the autoclave was filled with 20 bar CO_2. The reaction mixture was kept stirring for 48 hours at room temperature. After 48 hours a viscous solid was obtained which was dissolved in DCM and precipitated in MeOH dropwise. From there, a white polymer was obtained. Then the polymer was filtered and kept in a vacuum oven for complete drying before any characterization.

The synthesis of PLimC-OH was carried out according to the thiol–ene click reaction by Zhang *et al.*[28] 56 mL (796 mmol) of β-mercaptoethanol was added under an inert atmosphere in a Schlenk tube to a solution of PLimC (4 g) and AIBN (1.09 g, 6.64 mmol) in $CHCl_3$ (106 mL) and stirred at 70 °C for 24 hours. The resulting solution was poured dropwise in a MeOH : H_2O (1 : 1) mixture and filtered. The filtered white solid was washed several times with MeOH and dried overnight in an oven.

To synthesize PLimC-*g*-PDLLA in a 1 : 1 feed ratio (see Table 1), 3 mg of stannous octoate ($Sn(Oct)_2$) (0.007 mmol) was added to a solution of 0.5 g of DLLA (3.5 mmol) and 1 g of PLimC-OH (3.5 mmol) in 4 mL of anisole in a Schlenk tube and stirred at 120 °C for 4 h. The obtained viscous solution was diluted with a small amount of methylene chloride (CH_2Cl_2) and dropwise precipitated in MeOH. The filtered white solid was washed with more MeOH and dried overnight

Table 1 Graft copolymerization of D,L-lactide onto the PLimC backbone. The copolymerization reactions were carried out for 4 h. The reaction time for preparing PLimC was 48 h

Sample name	Feed ratio (PLimC : DLLA) mol : mol	Copolymer composition (PLimC : PDLLA)mol : mol	Yield (%)	M_p (g mol^{-1})	$Đ^a$	$T_g{}^b$ (°C)	$T_{5\%}{}^c$ (°C)
PLimC	—	—	90	103 200	1.14	128	230
PLimC-*g*-PDLLA (1 : 0.5)	1 : 0.5	1 : 0.4	83	123 283	1.29	25, 120	276
PLimC-*g*-PDLLA (1 : 2)	1 : 2	1 : 1.3	83	163 174	1.34	35, 130	218
PLimC-*g*-PDLLA (1 : 10)	1 : 10	1 : 7	81	200 564	1.31	47, 127	235

[a] Determined by THF-GPC. [b] Determined from the second heating curve (scanning rate 10 K min^{-1} under a N_2 atmosphere) of DSC. [c] Determined at a heating rate of 10 K min^{-1} under a N_2 atmosphere from TGA.

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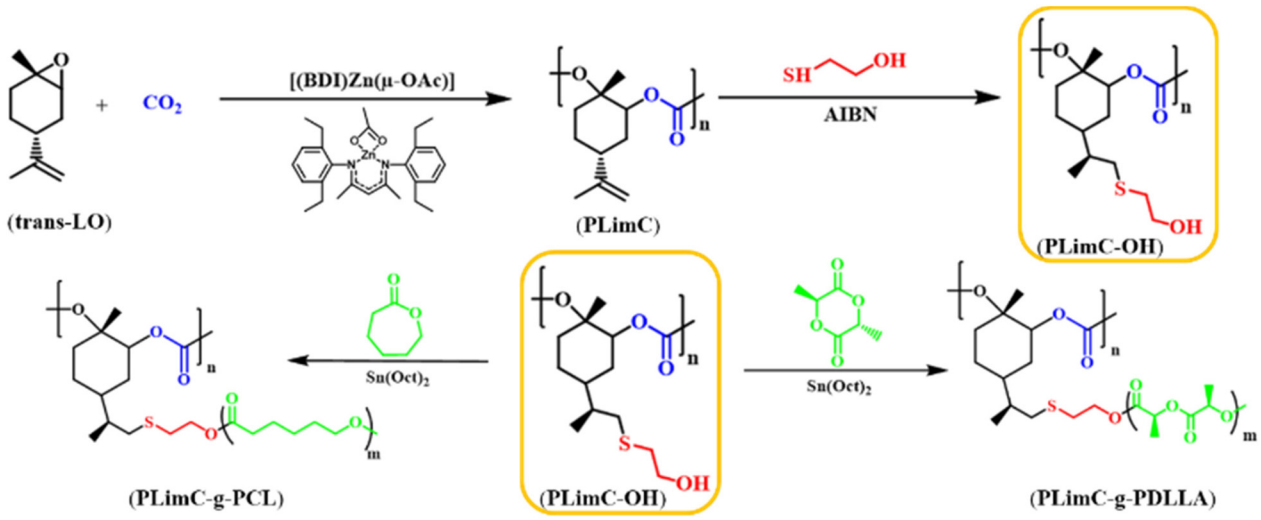
under high vacuum in an oven to obtain the PLimC-*g*-PDLLA copolymer. PLimC-*g*-PCL with different feed ratios was synthesized following a similar procedure (see Table S1†).

Results and discussion

Reaction sequences for grafting aliphatic polyesters onto the PLimC backbone are depicted in Scheme 1. In the first step, homopolymerization of *trans*-LO was performed in the presence of the catalyst [(BDI)Zn(OAc)] starting from masked *trans*-LO.[7] The reaction was carried out in an autoclave with 20 bar CO_2 pressure and constant stirring for 48 hours. PLimC was structurally characterized by ^{1}H NMR (Fig. 1(a)).[25] A thiol–ene click reaction[28,29] was accomplished with PLimC to convert the double bonds of PLimC to –OH groups. The resulting polycarbonate is designated as PLimC–OH. This thiol–ene click reaction of β-mercaptoethanol and PLimC was achieved using azobisisobutyronitrile (AIBN) as an initiator in pre-dried and freshly distilled chloroform ($CHCl_3$) at 70 °C for 24 hours. To avoid possible cross-linking reactions caused by radical coupling reactions, excess β-mercaptoethanol was added.[28] Therefore, it was necessary to remove β-mercaptoethanol from the products completely as the residual β-mercaptoethanol would initiate the ring-opening polymerization (ROP) of the cyclic ester in the next step. The polymer was fully purified by precipitation in the MeOH : H_2O (1 : 1) mixture several times. Finally, a white polymer was obtained, which was kept under vacuum for drying overnight before further characterization. The synthesized PLimC-OH was further analyzed by ^{1}H NMR (Fig. 1(b)). A triplet peak at around 3.60 ppm ((i), 2H) corresponding to the methylene protons next to the –OH group and another triplet at around 2.65 ppm ((j), 4H) corresponding to the protons adjacent to the S-group in the PLimC-OH structure can be observed (Fig. 1(b)). The peak from the double bond at around 4.68–4.72 ppm (b), observed in the ^{1}H NMR spectra of PLimC (Fig. 1(a)), completely disappeared after the reaction with thiol. This confirms the quantitative conversion of the vinyl group and the formation of PLimC-OH. In the next step, solution ROP of ε-CL and DLLA (see Table 1) initiated by PLimC-OH was performed in anisole as a solvent with different feed ratios of [ε-CL] : [OH] and [DLLA] : [OH] respectively by using stannous octoate ($Sn(Oct)_2$) as the catalyst at 120 °C in a Schlenk tube. The resulting graft copolymers are designated as poly(limonene carbonate)-*graft*-polycaprolactone (1 : *x*) (PLimC-*g*-PCL (1 : *x*)) and poly(limonene carbonate)-*graft*-poly(D,L-lactide) (1 : *x*) (PLimC-*g*-PDLLA (1 : *x*)), where 1 : *x* is the molar ratio of limonene oxide and the cyclic ester in the feed. The chemical structure of the graft copolymers was confirmed by ^{1}H NMR. A compilation of all ^{1}H NMR spectra recorded with different feed ratios of both the PLimC-*g*-PDLLA and PLimC-*g*-PCL graft copolymers has been depicted in Fig. S1 (see the ESI†), which clearly reveals the presence of both DLLA or ε-caprolactone (ε-CL) and LO units in the polymer. Worth mentioning is the shift in the peak position of –S–$CH_2C\mathit{H}_2$–OH (i) of PLimC-OH from 3.78 ppm to 4.2 ppm (i′) as it is now directly attached to a carbonyl carbon. $^{13}C\{^1H\}$ NMR spectra with detailed peak assignment of both graft copolymers are shown in the ESI (Fig. S2†). Heteronuclear multiple quantum coherence (HMQC) NMR has been performed for precise peak assignments. 2D HMQC NMR spectra of PLimC-*g*-PCL (1 : 2) with a copolymer composition of PLimC : PCL as 1 : 1 show relevant cross peaks (Fig. 2(a)). Numbers have been used to represent these cross peaks, that is 3 [i′(^{1}H)–i″(^{13}C)], 4 [j(^{1}H)–j′(^{13}C)], 5 [k(^{1}H)–k′(^{13}C)], 6 [f′(^{1}H)–f″(^{13}C)], 7 [m(^{1}H)–m′(^{13}C)], 8 [e′(^{1}H)–e″(^{13}C)], 9 [a(^{1}H)–a′(^{13}C)], 10 [b(^{1}H)–b′(^{13}C)], 11 [c(^{1}H)–c′(^{13}C)], and 12 [d(^{1}H)–d′(^{13}C)]. Likewise, PLimC-*g*-PDLLA with a copolymer composition of PLimC : PDLLA as 1 : 1.3 also shows relevant cross peaks (Fig. S3(a)):† 1 [q(^{1}H)–q′(^{13}C)], 2 [p(^{1}H)–p′(^{13}C)], 3 [i′(^{1}H)–i″(^{13}C)], 4 [j(^{1}H)–j′(^{13}C)], 5 [k(^{1}H)–k′(^{13}C)], 6 [f′(^{1}H)–f″(^{13}C)], 7 [m(^{1}H)–m′(^{13}C)], and 8 [e′(^{1}H)–e″(^{13}C)]. In order to confirm the attachment of polyester side chains to the



Scheme 1 Synthetic pathway of graft copolymers with PLimC as the backbone and PCL and PDLLA as side chains.

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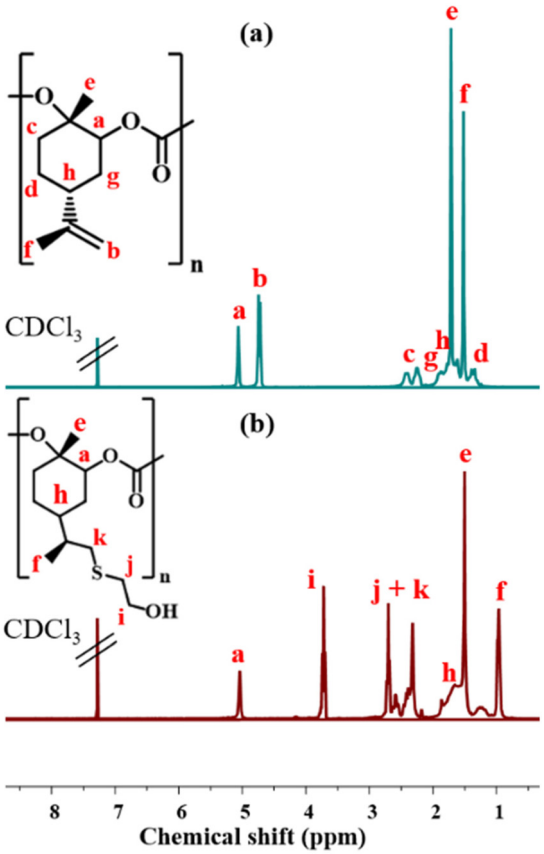

Fig. 1 ^{1}H NMR spectra of (a) PLimC and (b) PLimC-OH recorded in $CDCl_3$.

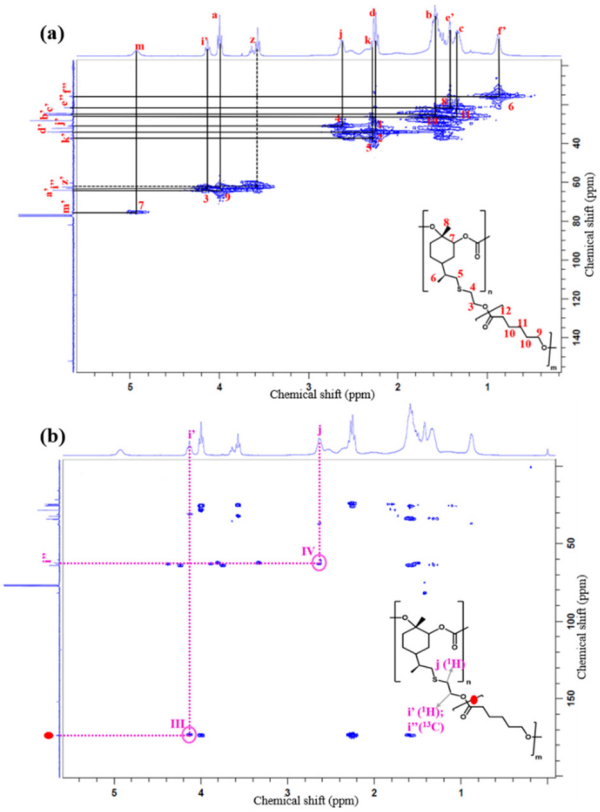

Fig. 2 (a) HMQC and (b) HMBC NMR spectra of PLimC-*g*-PCL with a feed ratio of 1 : 2 recorded in $CDCl_3$.

PLimC backbone and therefore the formation of a graft copolymer, heteronuclear multiple-bond correlation (HMBC) NMR was performed (Fig. 2(b) and Fig. S3(b)†). The 2D HMBC NMR spectra of PLimC-*g*-PCL (1 : 2) with a copolymer composition (determined as mol%) of 1 : 1 (PLimC : PCL) show cross-peaks between [j (^{1}H) and i″(^{13}C); IV] and [i′(^{1}H) and the ester of PCL; III]. The observation of cross peaks is a strong hint for the bonding of both PLimC and PCL units. The 2D HMBC NMR spectra of PLimC-*g*-PDLLA (1 : 2) with a copolymer composition (determined as mol%) of 1 : 1.3 (PLimC : PDLLA) show cross-peaks between [j (^{1}H) and i″(^{13}C); II] and [i′(^{1}H) and the ester of PDLLA; I]. The representative NMR spectra of the copolymers prepared from a starting feed molar ratio of 1 : 2 are shown in Fig. 3 as a representative example. The copolymer composition was determined by taking the peak area under the representative peaks of PCL (4.1 ppm (d), see Fig. 3(a)), PDLLA (5.20 ppm (p), see Fig. 3(b)) and PLimC (5.06 ppm (a), see Fig. 1(a)).

An increase in the feed ratios of DLLA or ε-CL increased the corresponding amount of DLLA or ε-CL ring-opened units in the copolymer (see Table 1 and Table S1 (see the ESI†)). GPC analysis shows that almost all the polymer compositions show a small shoulder at a higher molecular weight. This behavior is known for GPC curves of homo PLimC in the literature.[25] In our previous work, we discussed the mechanism of polymerization in which although the catalyst exists in the form of a dimer, the acetate ligand from only one catalyst molecule coordinates with the LO monomer due to its steric hindrance.[7] The reaction between the two separate Zn coordinated monomers followed by CO_2 insertion leads to chain propagation. According to this mechanism, the two propagating chains are always coupled due to the catalyst dimer at the active chain end. During polymer processing when the catalyst is not completely removed, an additional peak in the high molecular weight region can be observed in the GPC curves. The shoulder in the GPC curves was also observed by Jutz *et al.* during the copolymerization of CO_2 and cyclohexane oxide.[30] Due to the presence of the shoulder in the GPC curves, implying two overlapping peaks, the number average molecular weight (M_n) could not be reported, and therefore, the peak molecular weights (M_p) are given in Table 1. As the amount of PCL or PDLLA increased in the copolymers, the molecular weight of the graft polymer shifted to higher values (Table 1 and Fig. 3(c and d)). Furthermore, the copolymers were thermally characterized by thermogravimetric analysis (TGA) and the study discloses a degradation temperature above 200 °C for all copolymers. No trend in the change in degradation temperature was observed on changing the copolymer composition. In the case of the TGA of PLimC-*g*-PCL (see ESI Fig. S4(a)†), an increase in the degradation temperature from 226 °C to 293 °C can be

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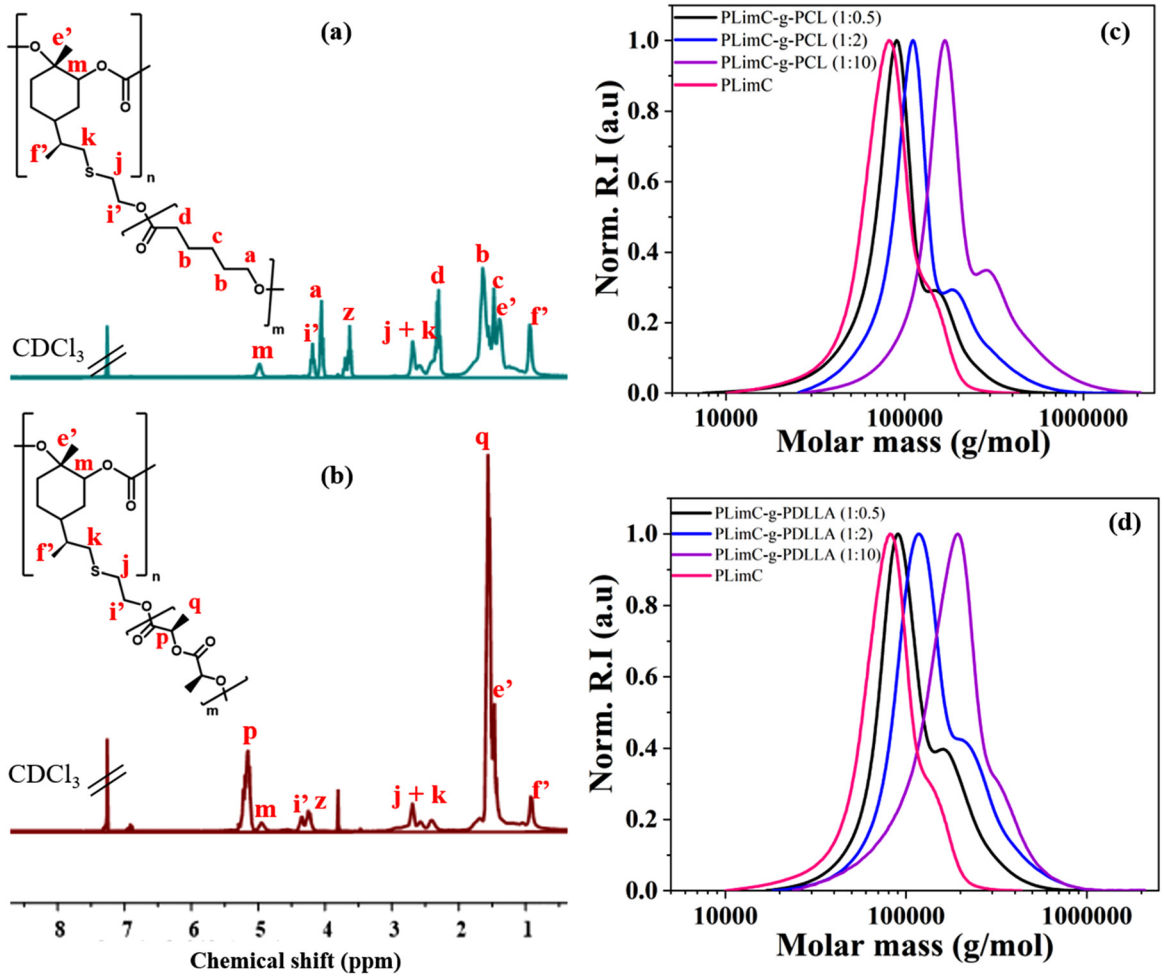

Fig. 3 ^{1}H NMR spectra of graft copolymers (a) PLimC-*g*-PCL and (b) PLimC-*g*-PDLLA with a 1 : 2 feed ratio recorded in $CDCl_3$. THF-GPC curves of graft copolymers (c) PLimC-*g*-PCL and (d) PLimC-*g*-PDLLA with different feed ratios.

clearly noted as the composition of the ε-CL block in PLimC-*g*-PCL varies from a lower to a higher value. Differential scanning calorimetry (DSC) measurements with different feed ratios assess the melting and crystallization behaviour of the polymers. DSC assessment of the graft copolymer PLimC-*g*-PDLLA has been performed, and T_g values close to 128 °C and 50 °C for pure PLimC and pure PDLLA, respectively, have been noticed. All copolymers show two distinct T_g values (Fig. S4,† and Table 1). Further dynamic mechanical analysis (DMA) measurements were carried out to unambiguously study the T_g values. The DMA curves of PLimC-*g*-PDLLA (1 : 2) and PLimC-*g*-PCL (1 : 2) are shown in Fig. S5 (see the ESI†). From the tan δ curves, it can be concluded that the graft copolymers have two separate T_g values. In the case of PLimC-*g*-PDLLA, the first transition was for PDLLA with a T_g of around 53 °C and the second transition was for PLimC with a T_g of around 132 °C, while PLimC-*g*-PCL shows a T_g of around 125 °C for PLimC. The occurrence of two T_g values shows the incompatibility of PLimC and PDLLA or PCL. The microphase separation of both the graft copolymers PLimC-*g*-PCL and PLimC-*g*-PDLLA was further monitored by transmission electron microscopy (TEM). The TEM samples of both graft copolymers were prepared by slowly casting thin films from dichloromethane over 5 days, followed by vacuum drying at room temperature for 2 days. PDLLA was not stained, and only PLimC was particularly stained with ruthenium tetroxide (RuO_4) vapor so that PDLLA appeared bright and PLimC appeared dark in the obtained images. The bright part observed in Fig. 4(a and b) is from PCL or PDLLA and the dark part is from PLimC. The hydrophilicity of films was characterized by the contact angle measurement on a film (thickness 200 ± 10 μm) prepared by solution casting using $CHCl_3$ as a solvent.[31,32] Firstly, the contact angles of pure PLimC (~105°), pure PDLLA (~70°) and pure PCL (~62°) have been measured (Fig. S6, see the ESI†).

There was a decrease in the contact angle and hence the hydrophobicity of homo PLimC on introducing PDLLA or PCL. PLimC-*g*-PDLLA (1 : 10) and PLimC-*g*-PCL (1 : 10) showed contact angles of ~66° and ~79° (Fig. 4(c)), respectively. The polymer films were analyzed by mechanical testing. The results obtained from the tensile testing are represented in

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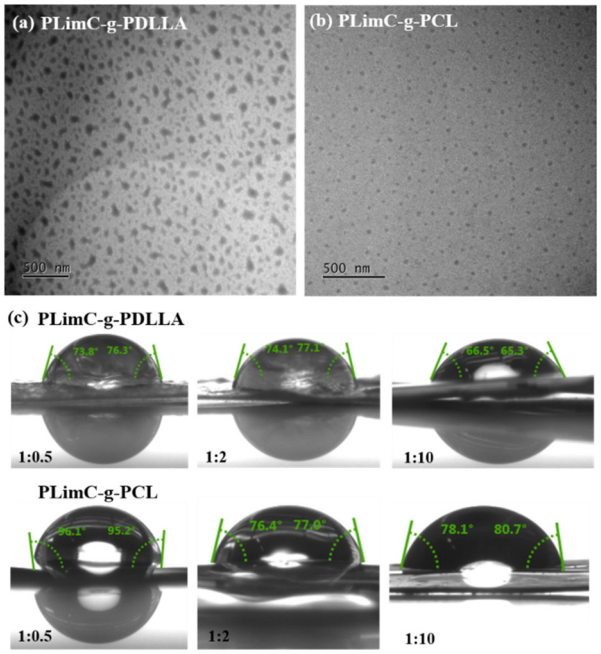

Fig. 4 Morphological study of (a) PLimC-*g*-PDLLA and (b) PLimC-*g*-PCL with a 1 : 2 feed ratio by transmission electron microscopy (TEM). (c) Contact angle measurement of graft copolymers PLimC-*g*-PDLLA and PLimC-*g*-PCL with different feed ratios.

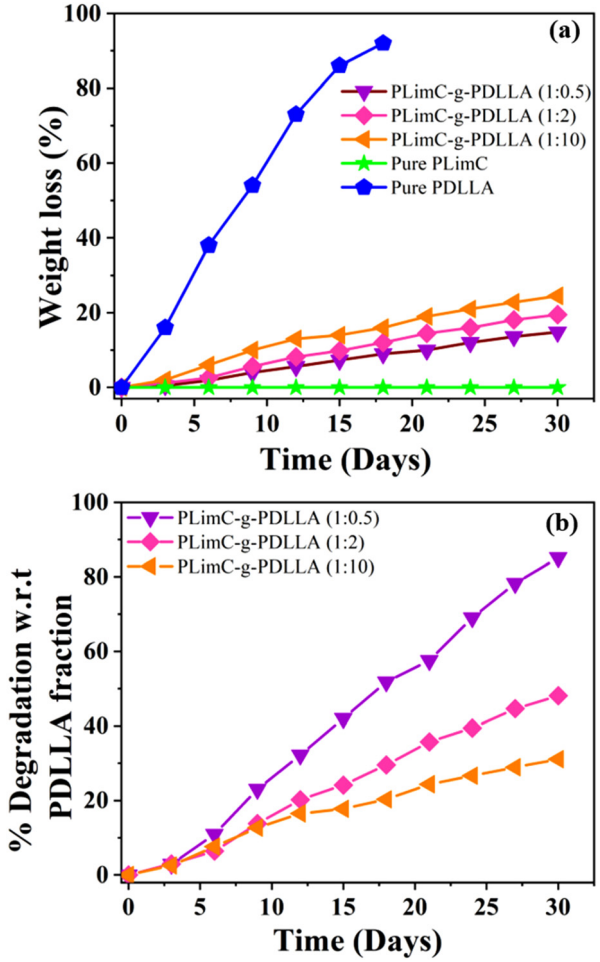

Fig. 5 Enzymatic degradation of graft copolymers: (a) PLimC-*g*-PDLLA films with proteinase K (0.25 mg mL^{-1}) in Tris buffer (0.05 M, pH = 8.6) at 37 °C and (b) percentage degradation with respect to the PDLLA fraction in 30 days.

Table S2,† and the stress–strain curves are shown in Fig. S7 (see the ESI†).

From the curves, no particular trend has been observed for PLimC-*g*-PDLLA polymers. PLimC-*g*-PDLLA (1 : 0.5), PLimC-*g*-PDLLA (1 : 2) and PLimC-*g*-PDLLA (1 : 10) were brittle and showed elongation at break of 2.7 ± 2%, 3.3 ± 1% and 4.6 ± 2%, respectively, whereas pure PDLLA and pure PLimC showed respective elongation at break of 4 ± 1% and 5 ± 2%. In the case of PLimC-*g*-PCL, a trend has been observed; as the amount of PCL increases, the elongation at break increases simultaneously. PLimC-*g*-PCL (1 : 0.5), PLimC-*g*-PCL (1 : 2) and PLimC-*g*-PCL (1 : 10) showed elongation at break of 87 ± 11%, 102 ± 9% and 114 ± 12%, respectively. Interestingly, there was a change in the properties of the material from brittle to elastic on grafting PCL onto PLimC.

The polymer films were tested under controlled conditions for enzymatic hydrolysis. For this test, proteinase-K and lipase were used as the enzymes for PLimC-*g*-PDLLA and PLimC-*g*-PCL, respectively. The enzymatic degradation tests were done at 37 °C in phosphate buffer solution for PLimC-*g*-PCL films at pH 7.0 and tris buffer solution was used for PLimC-*g*-PDLLA films at pH 8.6.[33,34] Sodium azide was added to the solution used for the test to avoid microbial growth. Fig. 5(a) demonstrates the weight loss of the graft copolymers PLimC-*g*-PDLLA with increasing time. Three samples from each graft copolymer have been used to check the mass loss over time. During the enzymatic hydrolysis, the weight loss was confirmed by running blank experiments in which the films were placed in buffer solutions without any enzyme at the same time. No weight losses were observed in the blank experiments. The total weight losses for PLimC-*g*-PDLLA samples were 14%, 19%, and 25% for PLimC-*g*-PDLLA (1 : 0.5), PLimC-*g*-PDLLA (1 : 2), and PLimC-*g*-PDLLA (1 : 10), respectively. Homo PLimC did not show any mass loss. Within 30 days of the degradation experiment, the mass losses were even less than the amount of the corresponding polyesters in the copolymers. Assuming all mass loss was originated from PDLLA grafted chains in copolymers, the percentage of PDLLA degraded with respect to (w.r.t.) its original amount in the copolymers was plotted in Fig. 5(b). In PLimC-*g*-PDLLA (1 : 0.5), around 86% of PDLLA was degraded with respect to the PDLLA fraction in the graft copolymer and in the case of PLimC-*g*-PDLLA (1 : 2) and PLimC-*g*-PDLLA (1 : 10), the degradation percentages are around 48% and 31%, respectively (Fig. 5(b)). Fig. S8 (see the ESI†) reveals the weight loss of the graft copolymers PLimC-*g*-PCL with increasing time. In the case of PLimC-*g*-PCL, the total weight losses of the samples were 23% and 32% for PLimC-*g*-PCL (1 : 2) and PLimC-*g*-PCL (1 : 10), respectively.

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From the normalized mass losses with respect to the amount of PCL in graft copolymers, PLimC-*g*-PCL (1 : 10) and PLimC-*g*-PCL (1 : 2) showed 51% and 80% (Fig. S8(b)†) PCL degradation with respect to the PCL fraction in the graft copolymer. During the enzymatic degradation test, samples at different time intervals were taken out. These samples were analyzed by GPC, ^{1}H NMR spectroscopy, and SEM and the characterization results are summarized in Fig. 6. From the GPC measurements (Fig. 6 (c, d) and Fig. S9†), no change in molecular weight was observed after degradation in the case of both PLimC-*g*-PDLLA and PLimC-*g*-PCL. Since there was a mass loss in the previous experiment but no change in the molecular weight was observed by GPC, a hint at the surface erosion mechanism was obtained. The surface erosion mechanism was also observed in our previous work during the degradation of polyesters made by condensation polymerization.[35] Some prominent changes at the surface with porous structures were obvious from SEM images (Fig. 6(e–h)). All the SEM images of the remaining graft copolymers are given in the ESI (Fig. S10†). The ^{1}H NMR spectra of both graft copolymers before and after degradation are shown in Fig. 6(a and b). Following the copolymer composition calculation (Table 1), the composition of the sample left after degradation was calculated from ^{1}H NMR. It was observed that the area under the peak of the esters has been reduced and no significant change has been detected in the carbonate by using the same representative peaks of PDLLA (5.20 ppm) or PCL (4.10 ppm) and PLimC (5.06 ppm). This change in copolymer composition can be compared with the degradation percentage of the graft copolymers as determined by gravimetry. For PLimC-*g*-PDLLA (1 : 2), a change in the composition from 1 : 1.32 (before degradation) to 1 : 1.06 (after degradation) was observed by NMR. This corresponds to an ~20% change in PDLLA. For the same polymer, 19% degradation by the enzymatic degradation test has been observed. In the case of PLimC-*g*-PCL (1 : 2), the ratio of PLimC : PCL was found to change from 1 : 1 (before degradation) to 1 : 0.8 (after degradation) from NMR, corresponding to a degradation of PCL of about 20% and it showed degradation of around 23% from the enzymatic degradation test. Similarly, the composition of other samples before and after degradation was calculated from ^{1}H NMR (Fig. S11, ESI†) and these values closely matched the degradation values we obtained from the enzymatic degradation study. Despite the generated porosity due to the degradation of polyesters and the enhanced hydrophilicity of copolymers, the overall degradation is still too slow.

A biodegradation test in an aerobic environment was also conducted according to ISO 14851 to see the degradation of the graft copolymer films in wastewater sludge by monitoring

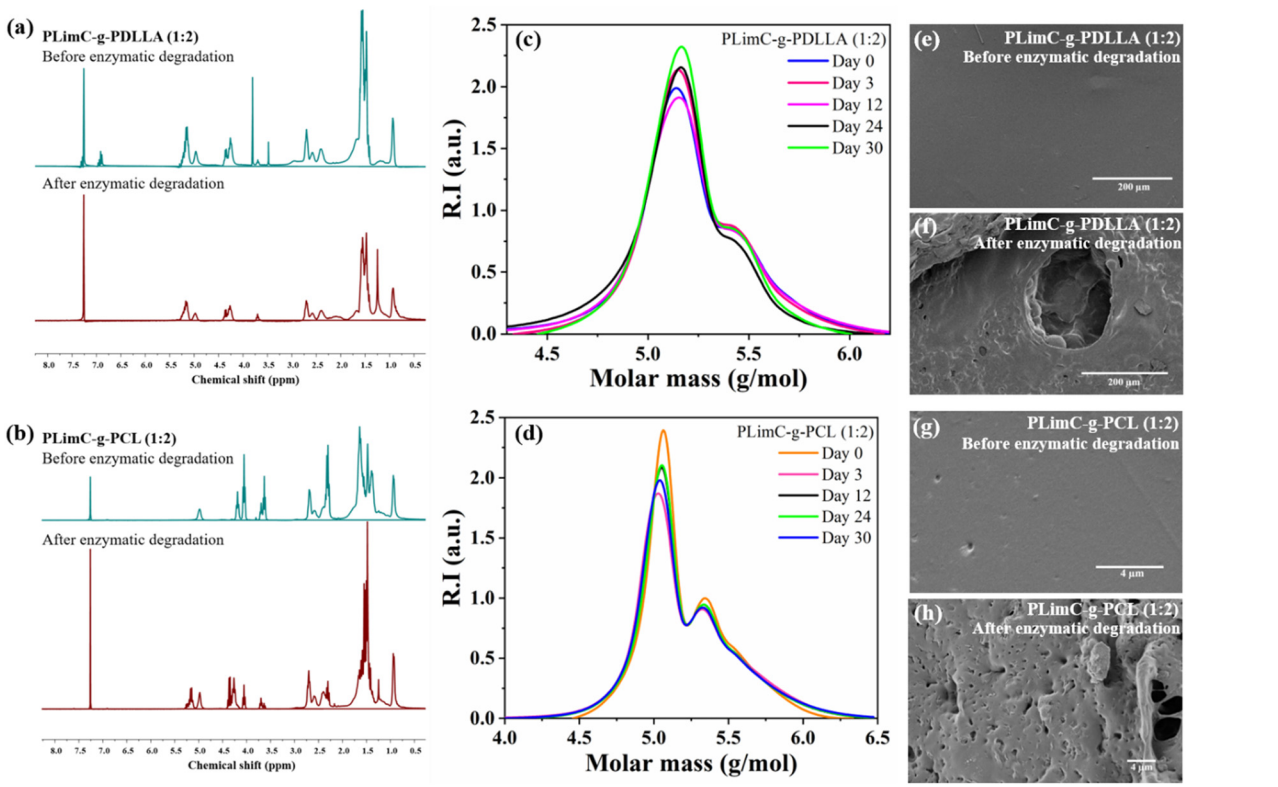

Fig. 6 ^{1}H NMR spectra of the graft copolymers before and after enzymatic degradation: (a) PLimC-*g*-PDLLA with a 1 : 2 feed ratio and (b) PLimC-*g*-PCL with a 1 : 2 feed ratio. THF–GPC curves of graft copolymers: (c) PLimC-*g*-PDLLA with a 1 : 2 feed ratio and (d) PLimC-*g*-PCL with a 1 : 2 feed ratio. SEM images of the graft copolymers: (e) PLimC-*g*-PDLLA with a 1 : 2 feed ratio before enzymatic degradation starts and (f) after the enzymatic degradation of PLimC-*g*-PDLLA with a 1 : 2 feed ratio; (g) PLimC-*g*-PCL with a 1 : 2 feed ratio before enzymatic degradation starts and (h) after the enzymatic degradation of PLimC-*g*-PCL with a 1 : 2 feed ratio.

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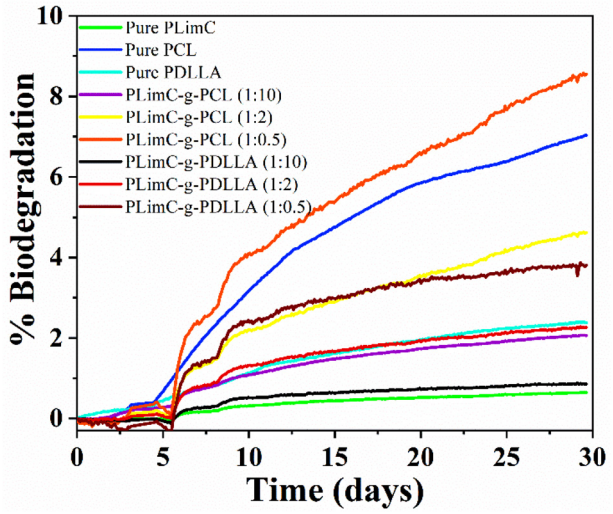

Fig. 7 Wastewater degradation of graft copolymers PLimC-*g*-PCL and PLimC-*g*-PDLLA with different feed ratios in a Micro-Oxymax Respirometer.

conversion into CO_2 for 28 days. Aniline, as a positive sample, was used during the biodegradation test, and the percentage of biodegradation was calculated based on the conversion of cumulative CO_2.

Fig. 7 represents degradation curves. PLimC-*g*-PDLLA (1 : 10) shows degradation of around 1%, whereas the other two PDLLA graft copolymers PLimC-*g*-PDLLA (1 : 2) and PLimC-*g*-PDLLA (1 : 0.5) show 2.3% and 3.7% degradation, respectively. Similarly, in the case of the other graft copolymers, such as PLimC-*g*-PCL (1 : 10), degradation is around 2.1%, and PLimC-*g*-PCL (1 : 2) and PLimC-*g*-PCL (1 : 0.5) show degradation of 4.6% and 8.5%, respectively. Pure PDLLA and pure PCL films were also tested, which showed degradation of 2.5% and 7%, respectively. As all samples showed slow degradation, macrophase separation might help in achieving fast degradation in the future.

Conclusions

Two different types of graft copolymers of PLimC with PDLLA and PCL as hydrolysable side chains and with different feed ratios have been synthesized and structurally characterized. Both graft copolymers are found to be film-forming. The PCL-grafted PLimC was an elastic material with ~13 MPa strength at break. The microphase separation was evident in graft copolymers from TEM and DSC. The enzymatic degradation studies under controlled conditions showed a weight loss pattern matching the copolymer composition, *i.e.*, enhanced weight loss with an increased amount of polyester in the graft copolymers. The SEM study suggests the presence of pores and cracks throughout the surface of the graft copolymer films, which in combination with the weight loss study suggests a slow surface erosion mechanism. A similar but much slower behaviour was also seen in the wastewater degradation test. PLimC-*g*-PCL appears to be an interesting system with elastic properties and should be further explored in the future to make it suitable for packaging applications with a focus on barrier properties and compost degradation.

Author contributions

DG – methodology, experiments, data analysis, and writing – original draft; SA – conceptualization, funding acquisition, supervision, project administration, resources, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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